



**Development of functionalised zeolite and bentonite for  
the recovery of platinum group elements (PGEs) and  
rare earth elements (REEs) from aqueous systems  
impacted by mining activities.**

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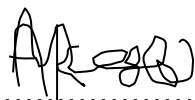
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# DECLARATION

I declare that this thesis is my own, unaided work. It is being submitted for the Degree of Doctor of Philosophy to the University of the Witwatersrand, Johannesburg, South Africa. It has not been submitted before for any degree or examination to any other University.



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# ABSTRACT

The economies of many countries, including South Africa, have been highly dependent on mining activities. Infrastructure including roads, buildings and power supplies has been improved over the years due to mining. As such, minerals such as gold, platinum group elements (PGEs), rare earth elements (REEs) and diamond continue to be mined, and their value increasing as demand outpaces supply due to diminishing resources. This has led to an increase in recycling efforts to salvage these precious elements. However, not much attention has been paid to deriving value from waste streams emanating from processing plants and discharged into the environment.

To this end, the focus of this study was to use functionalised zeolite and bentonite as adsorbents for the recovery of PGEs and REEs from aqueous solutions of the type discharged from mineral processing plants.

The research approach involved functionalising zeolite and bentonite with nitrogen-containing ligands, namely: hydrazine, 3-aminopropyl(diethoxy)methylsilane (APDEMS) and spent yeast. These ligands were used because PGEs have been found to have strong interactions with nitrogen therefore, functional groups containing amine groups were ideal for functionalisation. Moreover, the stability constants between PGEs and nitrogen are very high ( $\log k > 10$ ). The functionalised adsorbents were characterised using: Fourier transform infrared spectroscopy (FTIR) to determine functional groups; X-ray fluorescence (XRF) to determine the elemental composition; powder X-ray diffraction (PXRD) to determine the mineralogy; scanning electron microscope (SEM) to determine surface morphology; and elemental analyser to determine the extent of anchoring of the

ligands. Textural properties (surface area, pore size and pore volume) were determined using Brunauer–Emmett–Teller (BET) for surface area analysis.

The performance of the adsorbents in batch experiments was assessed by studying the effects of: pH; adsorbent dosage; initial concentration; contact time; and competing ions (Fe(III), Ca(II), Mg(II), K(I), Co(II), Ni(II), Hf(IV), Au(I), Zn(II) and other PGEs). Column studies were also conducted to assess the performance of the adsorbents under dynamic conditions. The effects of adsorbent bed height, pH, flow rate and initial concentration were investigated. Experimental results for both batch and column modes were assessed using various models. Adsorption capacity and efficiency models were used to determine the performance of adsorbents. Two-parameter (Langmuir, Freundlich, Dubinin-Radushkevich and Temkin) and three-parameter (Sips, Redlich-Peterson and Toth) isotherm models were used to determine the relationship between adsorbed elements and adsorbents. The adsorption mechanism was investigated using pseudo first-order, pseudo second-order, Elovich and intra-particle diffusion kinetic models. The performance of adsorbents in column mode was determined using column models such as Adams-Bohart, Thomas, Yoon-Nelson, Clark, Wolborska, bed depth service time and modified dose response model. A generalised surface complexation model based on coupling parameter estimation (PEST) and the PHREEQC geochemical modelling code was used to obtain further insight into the adsorption mechanism. The model was calibrated using results from laboratory experiments.

The findings showed that zeolite and bentonite in their natural forms had low adsorption efficiency (<5%) for PGE removal. However, after functionalising the materials with hydrazine, APDEMS or spent yeast, the uptake significantly increased ( $p < 0.05$ ), due to strong interactions between amine groups and the elements. Functionalisation of the

adsorbents was confirmed by FTIR and the elemental analyser. The surface area of bentonite was found to be higher than that of zeolite, resulting in the anchoring of more amine groups onto the former. The recovery of PGEs (Pt(IV), Pd(II) and Ir(III)) was highest at pH 2 and, significantly ( $p < 0.05$ ), decreased at  $pH > 2$ , due to changing speciation and surface charge. However, the recovery of Rh(III) was efficient at  $pH \geq 5$  since, the Rh(III) species become positively charged with increasing pH, making them to be attracted to the negatively charged adsorbent surface. The adsorbents were highly efficient when concentrations of PGEs were low ( $2 \text{ mg L}^{-1}$ ), with an adsorbent dosage of  $10 \text{ g L}^{-1}$ . The results also indicated that 90 min of contact was optimal for maximum adsorption of PGEs. The highest adsorption efficiency was  $>98$ ,  $>98$  and  $>95\%$  for Pt(IV), Pd(II) and Ir(III), respectively, when functionalised bentonite was used and,  $>76$ ,  $>91$  and  $>60\%$  for Pt(IV), Pd(II) and Ir(III), respectively, when functionalised zeolite was used. The uptake of the elements increased in the presence of competing ions, likely due to synergistic effects. The Langmuir isotherm model best fitted the adsorption data, indicating that the elements were only attracted to active sites with similar energies (i.e.  $-NH_2$  groups). The adsorption mechanism was described by the pseudo second-order kinetic model which is associated with adsorption *via* strong chemical interaction.

The recovery of REEs was efficient when both the natural and functionalised adsorbents were used, but the natural adsorbents were used since their adsorption capacities were higher. The uptake of REEs was high ( $>98\%$ ) when bentonite was used at different solution conditions ( $pH > 2$ , concentration ( $0.5 - 10 \text{ mg L}^{-1}$ ) and adsorbent dosage ( $5 - 50 \text{ mg L}^{-1}$ )). However, the maximum uptake of REEs using zeolite was only achieved when the concentration was  $2 \text{ mg L}^{-1}$  or less, at  $pH > 5$  and adsorbent dosage of  $10 \text{ g L}^{-1}$ . The high uptake of REEs by natural zeolite and bentonite was attributed to the negative

structural charge of the adsorbents over a wide range of pH, including acidic pH. Moreover, PHREEQC geochemical modelling code indicated that all REEs are positively charged even in solutions with pH >7. Thus, the adsorbents were always in favourable conditions for the adsorption of REEs. The high surface areas of the adsorbents also played a major role on the uptake of the elements. In contrast, the functionalised zeolite and bentonite had lower surface areas compared to their natural counterparts and the uptake was low at highly acidic pH solutions since the structural surface charges of the adsorbents were positive. The adsorption of most REEs (e.g. Y, Pr) onto bentonite was described by the Langmuir isotherm model and some (e.g. Ce, Gd, Tm) by the Freundlich model. Thus, most of the REEs adsorbed onto active sites with similar energies but some onto different active sites with different energies. The adsorption of all REEs onto zeolite was described by the Langmuir isotherm. Adsorption mechanism of REEs was described by the pseudo second-order kinetic model.

Breakthrough curves from column studies indicated that the uptake of PGEs and REEs increases with increasing bed height due to a higher number of binding sites. Higher flow rates ( $>2 \text{ mL min}^{-1}$ ) do not give the elements enough time (residence time) to interact with the adsorbents therefore, breakthrough times were observed earlier than when lower flow rates were used.

Agreement of experimental and modelled data ( $p > 0.05$ ) indicated that the coupling of PHREEQC to PEST can be used to determine the efficiency of the adsorbents on the recovery of precious elements when necessary conditions such as pH, concentration and surface area are determined and used for the calibration of the PHREEQC model. Also, it was observed that only a few experiments were required for this purpose.

Indicative cost-benefit analyses showed that the efficient uptake of PGEs and REEs by amine-functionalised and natural adsorbents, respectively, implied that these elements could be potentially recovered from wastewaters. For instance, up to 25 ounces of Pt per kg of yeast-functionalised bentonite and 54 ounces of REEs per kg of natural bentonite could be recovered, which are higher recoveries compared to amounts cited for economical mining. This could be important even for low level concentrations in waste streams as companies seek to salvage these metals from sundry sources to make up for increasing costs, declining natural resources and increasing demand.

The successful coupling of PHREEQC and PEST suggests that limited experimental data can potentially be used to do predictions of sorption processes in generalised surfaces such as those studied here. Upon successful calibration, complex reactions and time consuming experiments can be simulated. This procedure can potentially be used by mining companies and other industries as a preliminary step to determine the feasibility of administering adsorbents to recover elements from wastewaters.

The use of PHREEQC coupled to PEST for simultaneous recovery of REEs using a generalised surface could not be done but, would be important for future studies. Such studies should also focus on the recovery of elements in the presence of organic compounds such as low molecular weight humic and fulvic acids.

# DEDICATION

**To my God** whom I am nothing without. I would not have achieved this without Him. It has not been easy but I was able to pull through because I was not alone. You provided knowledge, wisdom, strength and mercy at the right time. Kea leboga.

**To my father** aka Pa. You have played a major role in all that I have become and I will forever be grateful. I was able to overcome many challenges because of your love and presence.

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# **CHAPTER 1:**

# **INTRODUCTION**

**This chapter introduces the research project and includes the background, motivation, problem statement and novelty of the study. Research aim, objectives, research questions and approach are also covered in this chapter.**

# 1. INTRODUCTION

## 1.1. Background and motivation

Mining continues to play a vital role on the development of many countries including South Africa, Zimbabwe, Canada, Russia and the United States (Erasmus et al., 2020; Nyemba et al., 2020). The mining industry has an impact on the overall gross domestic product (GDP) of such countries (Dahl et al., 2020; Lara-Rodríguez, 2020). In South Africa, mining contributes more than 11 USD billion in GDP (Trading Economics, 2020). However, in recent years, the mining industry has been facing many challenges which have forced the reduction of production and as a consequence closing some shafts and many people losing their jobs (Creamer, 2018). Mining Review Africa (2019) has reported that platinum group elements (PGEs) mining has been facing declining productivity and rapidly escalating costs. They have also reported that more than 60% of platinum mining is loss making (Mining Review Africa, 2019). Miningmx higher grade (2018) has reported that platinum mining will find it difficult to recover from the market share loss and that many mining shafts will still close. All these allude to the fact that many countries depending on the mining industry may suffer drastically with time thus, a solution is required.

Large amounts of wastewater is released into the environment during mineral processing, leading to significant environmental issues such as soil, air and water pollution (Maboeta et al., 2006; Erasmus et al., 2020). The mine waste rock impoundments and tailings from processing plants can cause pollution in water bodies due to direct or indirect discharges (Heikkinen et al., 2009). Water bodies namely; rivers, lakes, dams and streams always have to be protected from waste materials due to possible health risks in living organisms. Preventing accumulation of waste materials in water bodies has proven to be very challenging (Kossoff et al., 2014). Therefore, waste materials have been accumulating in

water bodies over the years. Moreover, groundwater pollution has been increasing due to intense mining and other anthropogenic activities (Heikkinen et al., 2009).

Freshwater which is very limited in the whole planet has to be protected from pollution but, it is often affected by mining waste due to heavy use of chemicals during ore processing (Kelly et al., 2012). These chemicals including ore waste are often released into the environment as wastewater. The cost used to clean the affected water is often very expensive. Thus, freshwater as an important natural resource is negatively affected by anthropogenic activities and should this continue, more environmental risks than what we face today will erupt (SDWF, 2017). The waste produced from mining plants is usually in the form of tailings storage facilities and mine leachates which contains elements such as Ca, Na, K, Mg, Fe, Co, Hg, U, Cd, Cu, Cr, Ni, As and traces of mined elements which could be harmful to living organisms when they exceed threshold limits (Hwang et al., 2019; Li et al., 2019). These elements can reach living organisms through ingestion via the food chain and inhalation. However, it is noteworthy that other elements such as Ca, Na, K, Mg and a number of other elements are essential to living organisms when they are in moderate concentrations but, can also become toxic at high concentrations (Abollino et al., 2003). There is therefore a need to remove elements from water bodies which would otherwise accumulate overtime. Research studies have been conducted to come up with methods that can be employed to remove elements accumulated in water bodies. For example, clay linings which constitute bentonite and montmorillonite have been found to effectively remove elements from water bodies and have therefore also been used as barriers in landfills to prevent groundwater pollution (Visentin et al., 2019; Garg et al., 2020). Clay minerals are always used for remediation because they have high specific surface areas and are cost-effective since they are readily available in the environment (Bailey et al., 1999). For example, natural laterite which is a composite of iron, aluminium and silicon was found to be very effective in removing arsenic

from aqueous solutions (Maiti et al., 2008). Conventional methods including coagulation, precipitation, reverse osmosis, ion exchange and evaporation have been used in remediation processes to remove elements from wastewaters; however, they require high energy and cost to operate (Bakatula, 2012). Adsorption on the other hand has been used in remediation processes but, contrary to other methods, it has been found to be more effective and cheap (Bakatula et al., 2015).

The mining of gold, diamond and PGEs has been increasing over the years due to high demand. The processing of these minerals leads to large amount of wastewater which may contain significant amounts of valuable elements such as gold, PGEs and rare earth elements (REEs) (Kumar et al., 2017). In this study, the recovery of PGEs and REEs from aqueous solutions using passive agents was investigated. The adsorption of these elements was done using natural zeolite and bentonite clay materials. Moreover, these materials were functionalised with nitrogen containing ligands since, the adsorption of PGEs was found to be very effective in the presence of N-containing ligands (Chi et al., 2017). The dual efficacy of the adsorbents was tested i.e. the ability to recover precious elements so that mining companies can gain profit and also removing other harmful elements so that the resulting wastewater is safer to be released into the environment or to undergo recycling.

## **1.2. Problem statement**

PGEs and REEs have unique physical and chemical properties that make them very important components in many environmentally-related technologies (Glaister and Mudd, 2010). These technologies are often improved and expanded in order to meet environmental challenges hence a need for their sustainability into the future. Moreover, PGEs are found in few parts of the world including South Africa, Canada, Zimbabwe, Russia and the United States of America (USA) (Erasmus et al., 2020; Nyemba et al., 2020). REEs are found in many parts

of the world but naturally occur in economically viable deposits in few parts of the world including South Africa, Russia, USA, India, Australia and China (Kulczycka et al., 2016). Thus, cheap and efficient ways to recover PGEs and REEs from wastewaters are of high importance in ensuring sustainability of these elements. Currently, research on the recovery of PGEs and REEs from waste has been highly focused on spent catalytic converters or spent automotive catalysts, electronic waste and magnet scraps, not so much on mining wastewater (Ambaye et al., 2020; Morcali, 2020).

Water is used in the processing of PGEs and REEs, as a result, large amount of wastewater is released into the environment. This wastewater has been found to contain large amount of trace elements including valuable PGEs such as platinum (Pt), osmium (Os), rhodium (Rh), iridium (Ir) and ruthenium (Ru) and REEs such as scandium (Sc), dysprosium (Dy), europium (Eu), gadolinium (Gd), holmium (Ho), cerium (Ce), lanthanum (La), neodymium (Nd), samarium (Sm) and erbium (Er) (Kumar et al., 2017; Rankin, 2011). The losses of valuable elements can accumulate and become quite significant overtime, especially in the face of declining commodity prices and weak economic growth. The greatest loss of PGEs occurs during crushing, grinding and flotation stages (Jones, 1999). Many mining companies lose a lot of profit due to the loss of precious elements during processing. Overall losses from platinum mines are between 15 and <22% in underground and opencast mining, respectively.

Research has indicated that chlorination processes, pyrometallurgy and hydrometallurgy are methods that have been used for the recovery of PGEs and REEs from waste. Selective chlorination processes using different vapour pressures of metal chlorides have been used to recover PGEs but this technique uses CO and Cl<sub>2</sub> which are hazardous and therefore not ideal (Kim et al., 2000). Pyrometallurgy uses high temperatures to separate PGEs and REEs in aqueous solutions (Benson et al., 2000; Yun et al., 2020). Hydrometallurgy has been used to leach PGEs and REEs in oxidising solutions but, this technique requires extremely aggressive

conditions (Baghalha et al., 2009; Yun et al., 2020). All these point to the fact that there is a need for cheaper, efficient and safer ways of retrieving precious elements from wastewaters. Most mining companies are exploring cost-effective ways that can be used to recover lost precious elements from waste, so that they can gain profit (Yıldız et al., 2020). Since the current methods used are expensive, energy intensive and non-economic as indicated above, the mining industry is still in search of cost-effective approaches to recover precious elements (He and Kappler, 2017). Thus, elements continue to accumulate in the environment, leading to an increase in water, air and soil pollution. Other recovery techniques such as adsorption and ion exchange have been used to remove elements from aqueous solutions and found to be cost-effective and successful for elements such as Cd, As and Cr (Abollino et al., 2003; Babel and Kurniawan, 2003).

Due to the expense of current remediation techniques, the idea of recovery of precious elements in low concentrations has been ignored. Thus, the accumulation of precious elements has been increasing with time and this can lead to negative health effects in human beings and other living organisms since some of the elements can be carcinogenic or cause defects in morphology. Moreover, other diseases like kidney failure which may be permanent due to persistence and toxicity of elements exceeding threshold limits may result (McLaughlin et al., 2000).

Processes that include the recovery of elements from wastewaters may require many steps including ultrafiltration to deal with ligand-metal complexes which may be costly but, a process to prevent such steps in the recovery of precious elements is needed so that the process is cheaper and efficient (Jin and Ranford, 2000). Moreover, finding appropriate ligands for recovery is often a problem because of the chemical and physical characteristics of the materials and the behaviour of the elements of interest. Different ligands were used to take up precious elements from aqueous solutions and the ability of zeolite and bentonite to

act as support materials or anchors for the ligands was investigated. The supporting materials were chosen for this study because they are readily available, cheap and have high surface areas and an overall negative structural charge which is very important for this study (Peskov, 2020).

In this study the recovery of PGEs and REEs from aqueous solutions with a host of other element was considered and therefore, selectivity was very crucial especially. There is therefore a need for dual efficacy techniques and methods, that is, to recover precious elements whilst removing contaminants.

### **1.3. Multidisciplinary aspects of the study**

This study includes a number of fields in chemistry such as environmental analytical chemistry, organic chemistry, inorganic chemistry and physical chemistry. On the environmental analytical chemistry part, the adsorbents were used to recover elements from aqueous systems at different conditions such as pH, adsorbent dosage, contact time and initial concentration for each adsorbent. The relationship between organic nitrogen-containing ligands and PGEs and REEs was investigated, thus incorporating both organic and inorganic chemistry. The physical chemistry of the ligand-element interactions was determined as this helps in identifying the best working conditions of the adsorbents as well as the feasibility of using the adsorbents at a large scale. Statistics was used to determine the reliability of the results. The engineering application involved column designs and column conditions such as flow rates that are applicable for the dynamic treatment of mining wastewaters. Indicative cost-benefit analyses were conducted to obtain estimates of return on investment.

### **1.4. Novelty and scientific contribution to new knowledge**

The purpose of the study was to come up with engineered materials that can selectively capture platinum group elements (PGEs) and rare earth elements (REEs) from aqueous

solutions such as refining wastewaters as well as rivers and dumps in the vicinity of mining areas. Zeolite and bentonite clay materials were functionalised with some nitrogen containing ligands such as yeast, hydrazine, polyethyleneamine, spermine, amino acids and other N-containing ligands. There is no evidence of the use of zeolite and bentonite functionalised with N-containing ligands (including the ones used in this study) for the recovery of precious elements as in this study. Moreover, the interaction of the ligands with negatively charged surface has not been reported before. These ligands were irreversibly anchored onto the clay materials which act as support structures since, they would be ineffective on their own. The hybrid adsorbents were used to recover PGEs and REEs from aqueous solutions at different conditions so that optimum conditions for wastewater recovery could be determined. The high demand of PGEs and REEs makes every part that can be recovered very valuable. Thus, recovering a milligram of any precious element from wastewaters will be very vital for mining companies (Jones, 1999).

The recovery of gold and other precious elements other than PGEs and REEs was also investigated therefore, the success of this study may bring insight on the recovery of other precious elements which have been lost during mineral processing (Lara-Rodríguez, 2020). Moreover, the adsorbents which were selected for this study can probably be used in municipal and other industrial wastewaters that may contain elements of interest which will add value to the economy when recovered. The process used for the recovery of elements in this study can provide a benchmark that can be used in future potential applications of these adsorbents such as tap filters and columns that can be inserted in drinking water holding containers such as kettles and water jars. This is particularly important in areas that obtain water directly from water bodies such as rivers and lakes.

The functionalised zeolite and bentonite can also be used in remediation processes where unwanted and toxic elements such as cadmium, mercury and arsenic are removed from

aqueous systems accessible to living organisms including humans, livestock and aquatic organisms (Bakatula et al., 2015).

This study has high potential to capture the interest from many mining companies, water purification companies, remediation scientists and environmental scientists in general, as new knowledge especially on the formation of new functionalised materials which are cheap, efficient, less energy-requiring and minimal labour requirement is presented. This research can also spark interest many institutions including universities and environmental research companies which are doing extensive research on the adsorption of elements.

### **1.5. Research aim and objectives**

The main aim of the research was to use cost-effective engineered materials to recover valuable elements that are lost from mining processing plants through waste streams.

This aim was achieved by addressing the following objectives:

1. Functionalising cost-effective adsorbents such as zeolite and bentonite with various ligands (including amine based ligands such as polyethyleneimine, lysine, arginine, histidine and yeast) that can selectively remove the elements of interest from aqueous solutions.
2. Characterising the functionalised adsorbents with Fourier transform infrared (FT-IR) spectroscopy, powder X-ray diffraction (PXRD), X-ray fluorescence (XRF) and elemental analyser.
3. Assessing the capability of the functionalised adsorbents to remove elements of interest (in batch and column/flow through mode) from aqueous solutions under a variety of conditions: adsorbent dosage, pH, initial concentration, contact time and competing ions.
4. Conducting geochemical modeling simulations (using PHREEQC and PEST) to augment experimental work and gain insight into the processes involved.

## **1.6. Research questions**

The following research questions were addressed so as to achieve the aims and objectives:

1. Can zeolite and bentonite be functionalised with nitrogen containing ligands that have high affinity for PGEs and REEs?
2. Will the functionalised materials be efficient on the recovery of PGEs and REEs from aqueous solutions?
3. Will the efficiency increase when the ligands are mixed together or treated separately?
4. Are the functionalised adsorbents selective for the recovery of the elements of interest?
5. Which conditions will make the adsorbents more selective for PGEs and REEs?
6. What is the adsorption mechanism between the elements and the functionalised adsorbents?

## **1.7. Research approach**

Natural zeolite and bentonite were chemically modified with nitrogen containing ligands and the modified adsorbents were characterised to confirm the anchoring of the ligands. The adsorbents were then applied in aqueous solutions containing PGEs and REEs. The efficiency and selectivity of the adsorbents was determined by measuring the concentrations of PGEs and REEs before and after the adsorption process. The selectivity of each of the functionalised zeolite and bentonite as well as their maximum adsorption capacities for PGEs and REEs were determined and the best adsorbents selected use in for subsequent experiments.

The best operating conditions (pH, temperature, concentration, adsorbents dosage, time, bed height and flow rate) for the adsorbents using batch and column experiments were determined.

Various models (kinetic and isotherm) were used to describe the adsorption mechanism and adsorption process between the elements and the adsorbents. The modelling of the adsorption process (surface complexation) was further augmented by treating the adsorbent surfaces as generalised surfaces using parameter estimation (PEST) and the PHREEQC geochemical modelling code.

#### **1.8. The thesis is structured as follows:**

**Chapter 1** is an introductory section discussing the background and motivation of the study. The problem statement and novelty of the study are also outlined.

**Chapter 2** presents the literature and theoretical background of platinum mining, zeolite, bentonite and precious elements applications. The need for the recovery of precious elements and recovery issues with current methods are outlined in this chapter.

**Chapter 3** deals with the research aim and objectives of the study. The research questions and approach are also covered in this chapter.

**Chapter 4** presents the materials and methodologies used in this study. The ligands used for functionalisation, characterisation techniques and operating conditions are presented herein.

**Chapter 5** presents the results and discussion of the study in the form of papers. The papers used are either published or sent to journals for consideration.

The outputs of the study and recommendations are summarised in **Chapter 6**. Optimum conditions for the recovery of precious elements are also summarised.

# **CHAPTER 2:**

# **LITERATURE**

# **REVIEW**

**This chapter focuses on the literature review related to this study including platinum mining, precious elements under study and adsorption techniques.**

## 2. LITERATURE REVIEW

In this chapter the literature review supporting this study was included. Some of the issues associated with mining wastewater and the need to treat it are outlined herein. The need to preserve precious elements (PGEs and REEs) using cheap and efficient methods is clearly outlined. The background in the mining of precious elements and why it is important is also included in this chapter. The current methods and adsorbents used to remove elements from aqueous solutions are described and the reason for choosing zeolite and bentonite over other adsorbents is clearly indicated.

### 2.1. Platinum mining

Significant amount of platinum is produced in South Africa, Zimbabwe, Canada, Russia and United States of America. However, South Africa is the leading supplier of platinum with more than 70% of the world's platinum reserves (Jones, 1999). The Bushveld Igneous complex (BIC) resting on a floor of sedimentary rocks is situated in the northern part of South Africa and contains the country's highest PGEs output (Cousins, 1959). BIC is composed of five distinct regions; which are eastern limb, western limb, northern limb, south eastern limb and the far western limb as shown in Figure 2.1 (McLaren and de Villiers, 1982; Jones, 1999). Most of the mining activities have been taking place in the eastern and western limbs due to large surface crops. There are currently five primary smelting of ore concentrates in South Africa which are; Impala Platinum, Northam Platinum, Anglo Platinum and Lonmin Platinum (Jones, 2005). Impala Platinum and Anglo Platinum and Lonmin Platinum are the three largest producers in the world. The platinum primary producers led to a total of twelve active platinum mines in the BIC (Jones, 1999). In other countries, only small quantities of platinum are produced as by-products or co-products of base metal production especially of nickel. The Platinum around the world is used in jewellery,

autocatalysts, industrial equipment, electrical, dental and investment (Benson et al., 2000; Kim et al., 2000).

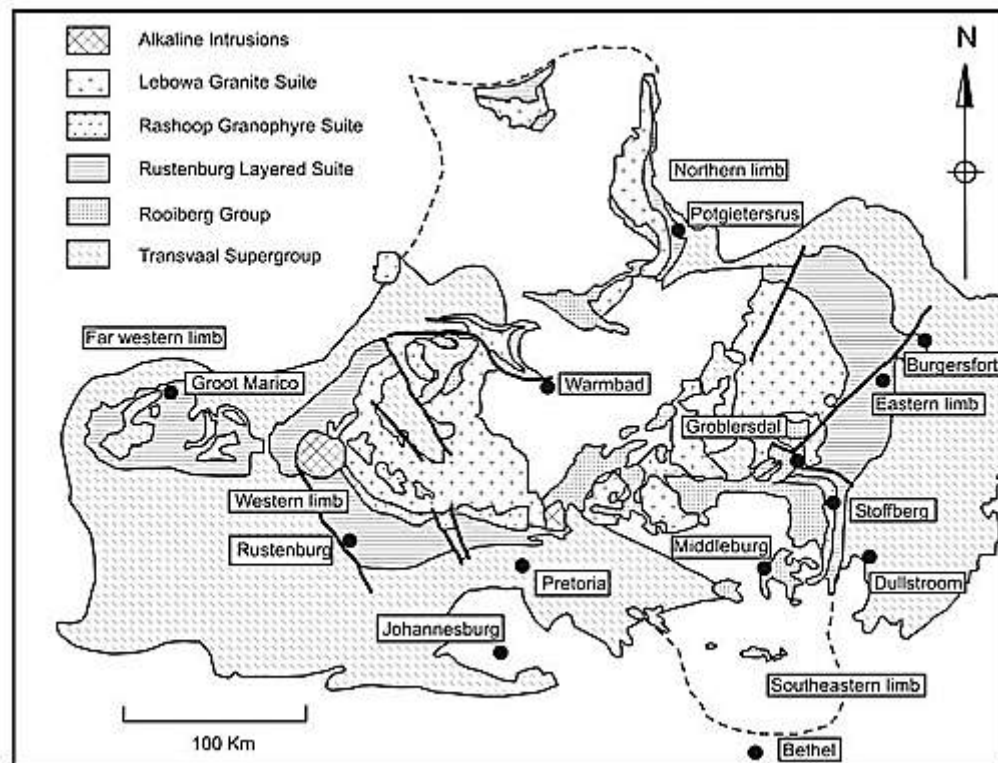


Figure 2.1: The map of the Bushveld Complex showing the location of the various limbs: the eastern, western, far western and northern limbs and the south-eastern limb (Kinnaird et al., 2004).

There are five main lithostratigraphic suites of rocks in the Bushveld complex: the Rustenburg Layered Suite, suite of intrusive mafic sills, the Lebowa Granite Suite, the Rasehoop Granophyre Suite and the Rooiberg lavas (McCall, 2016). The platinum group elements, chromium and vanadium mineralisation occur with the ultramafic rocks of the Rustenburg Layered Suite and the mafic.

The platinum in South Africa occurs primarily in the Merensky Reef. The reef is mined by Anglo American Platinum in Rustenburg which is in the North West Province, South Africa (Jones, 2005). The output of platinum has grown substantially, making Rustenburg the

world's leading platinum metals producer. It is noteworthy that the platinum extracted in nature is not in its pure state but it is a composite of other platinum group metals viz palladium, rhodium, osmium, ruthenium and iridium alongside copper and nickel. Platinum, rhodium and palladium are the most economical PGEs and the rest are produced as co-products (Implats distinctly platinum, 2005). Significant amount of platinum occurs in association or alloyed with iron (ferro-platinum) and the rest occurs as arsenide, sulph-arsenide, sperrylite and cooperite (Jones, 1999). The ore in which the platinum is contained has nickel and copper which add appreciably to the value of the ore (Cousins, 1959).

The northern limb of the Bushveld complex contains another reef known as the Platreef in which a unique type of mineralisation has developed. The reef contains a complex assemblage of pyroxenites, serpentinites and calc-silicates. In this reef, the Bushveld magma is hot and reacts with the lime-rich floor rocks. It is this exchange of heat between the magma and the floor rocks that led to the formation of abundant lime-rich minerals (Penberthy and Merkle, 1999). The PGE concentrations in this reef were found to be irregular in value and distribution. The major platinum minerals consist of PGEs tellurides, platinum arsenides and platinum sulphides (Chapman et al., 2011).

Anglo American Platinum Corporation Ltd. and other mining operations in the reefs utilise froth flotation for the recovery value of PGEs (Ndlovu, 2019). Figure 2.2 shows the simplified illustration of the PGM activity chain. Froth flotation is the widely used method for ore beneficiation in which PGEs are separated from other minerals through induction in or on the surface of a froth layer. During grinding, sufficient amount of water is used which then results in slurry called the pulp. The purpose of smelting is to separate the gangue (oxide and silicate) minerals from the sulphide minerals which are associated with PGEs. The converter matte undergoes milling before the next step which refinery. During refinery, individual precious metals are separated and refined to pure metals. The recovery of PGEs is 85% in the

concentration stage, 98% smelting and 99% in refining. Much of the PGEs are lost during crushing, grinding and flotation (Jones, 1999).

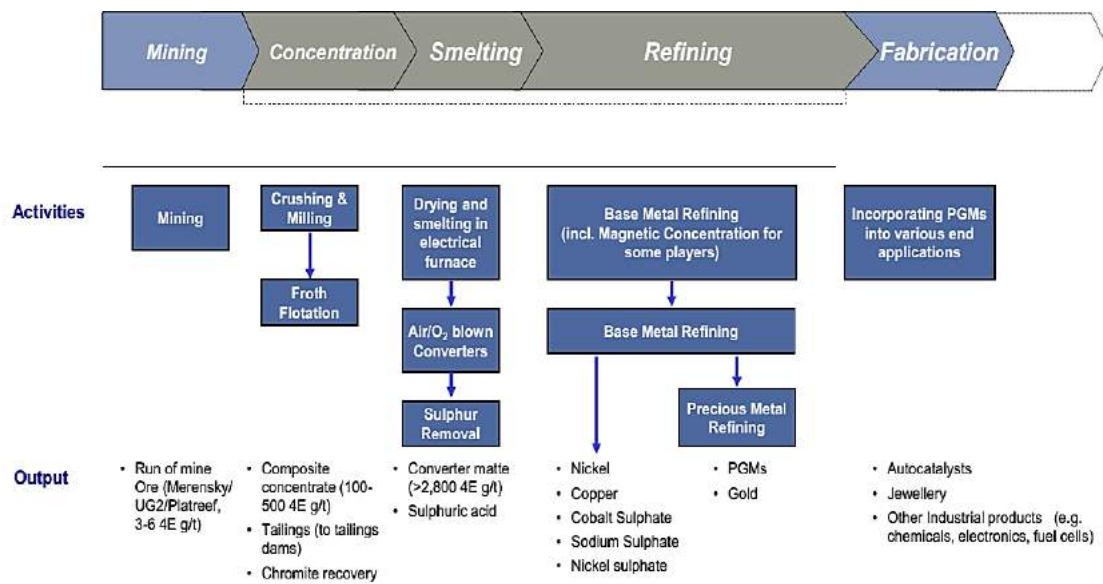


Figure 2.2: Simplified illustration of PGM activity chain (Ndlovu, 2015)

All processes leading to the production of PGEs use large amounts of water. The wastewater produced during the processing contains significant amounts of elements including PGEs and REEs (Ochieng', 2002). Once the wastewater leaves the processing plant, these elements can find their way into the environment and accumulate into soils and natural water systems such as rivers, lakes, dams and in the air (Abollino et al., 2003). Ochieng' (2002) determined the concentrations of elements near and far from platinum plants. He found that the concentrations of the elements were high in soils near mining areas. Burt et al., (2011) found that the concentrations of Cd, Mn, Sr, Cu, Cr, Zn and others were high in water systems and soils due to long-term mining activities in the mountains around Creede, Colorado. Olowo et al (2013) also investigated the concentrations of different elements in soil and plant composition from a mining area and found that elements such as Fe, Cr and Ni were high especially on the topsoil. They concluded that the high concentrations of these elements were high enough to cause diseases to human beings living in the area (Olowoyo et al., 2013). The

concentrations of Cu and Cd were found to be very high in the soil in the northeast part of Jiangxi province, China and this was due to mining activities in the area (Wu et al., 2014). Thus, mining environments add significant amounts of elements into the environment.

The contamination of water systems and soils by anthropogenic sources such as mining activities has been and is of concern worldwide (Abollino et al., 2006). One of the major concerns with the contamination of water bodies and soils is that these elements can reach groundwater through movement within the aquifer (Berg et al., 2001). From the recharge areas, contaminants move in the direction of topography into discharge areas and thus contaminating groundwater which should be kept safe and clean because human beings and other living organisms depend on it for sustainability. Moreover, contaminated groundwater is difficult and expensive to clean (Guérin et al., 2020).

## **2.2. Platinum group elements and applications**

Platinum group elements are precious elements which are also classified as rare elements because they naturally occur in very low concentrations in Earth's crust (Ravindra et al., 2004). They comprise of six elements viz platinum (Pt), iridium (Ir), rhodium (Rh), palladium (Pd), osmium (Os) and ruthenium (Ru) whose maximum concentrations are 0.005, 0.001, 0.0001, 0.015, 0.005 and 0.0001 mg kg<sup>-1</sup>, respectively (Hartley, 1991). These elements are widely used because they have high purity, high melting points and unique physical and chemical properties. They are chemically less reactive therefore, extremely resistant to corrosion (Johnson Matthey, 2020). Due to their excellent catalytic properties, PGEs are widely used in catalytic converters to reduce the amount of gaseous pollutants such carbon monoxide, nitrogen oxides and hydrocarbons (Ravindra et al., 2004). The high melting points and low diffusivities of the elements make them suitable agents in the jewellery industry (Wright, 2002). In medicine, PGEs are used to form complexes with organic ligands in order to improve the bioavailability and bioactivity of the ligands (Yufanyi et al., 2020). PGEs have

also been used in high performance electronic materials such as optoelectronic devices, field-effect transistor, dye-sensitized solar cells, and wearable electronics due to their strong electrical stability in harsh environments because of the excellent catalytic activity which leads to the reduction of the redox couple (Wang et al., 2017). All these indicate that there are other PGEs wastewaters around the world apart from the PGEs mining industrial wastewater.

Kümmerer et al. (1999) indicated that hospitals release large amount of wastewater containing high concentrations of platinum. The automotive industry, which mostly uses platinum, palladium and rhodium, discharges large amount of water containing PGEs in recoverable concentrations (de Oliveira Demarco et al., 2020). The electronic waste (E-waste) containing toxic elements such as Pb, Cr, Hg and Cd as well as precious elements such as PGEs, Au and REEs contributes significantly to the waste produced annually (Islam et al., 2020). These elements have been found to accumulate in soils and find their way to groundwater (Ouabo et al., 2019). E-waste has also been discharged in open wellsprings and thereby accumulating elements in water bodies overtime (Islam et al., 2020). Based on the importance and demand for PGEs, Pt, Pd, Ir and Rh were considered in this study.

### **2.3. Rare earth elements**

There are 17 known rare earth elements viz (Sc), dysprosium (Dy), europium (Eu), gadolinium (Gd), holmium (Ho), cerium (Ce), lanthanum (La), neodymium (Nd), samarium (Sm) and erbium (Er), Yttrium (Y), praseodymium (Pr), Terbium (Tb), lutetium (Lu), thulium (Th), ytterbium (Yb) and promethium (Pm) (Kumar et al., 2017; Rankin, 2011). REEs occur in moderate concentrations in the Earth's crust but are widely dispersed making it difficult to be extractable (Woodward, 2019). They are widely used for the physical and chemical properties. REEs reserves are found in few parts of the world including Canada, South Africa, China, Southern Greenland and the United States of America (USA), with notable large reserves in China, Australia and USA (García et al., 2017). They are very

expensive to mine and therefore their market price is high. They are used in renewable energy technologies, laser technology, superconductors and magnets (Angerer et al., 2009, Du and Graedel, 2013). They cannot be substituted with other elements because of their magnetic, heat resistant and phosphorescent properties which cannot be found in other elements (Woodward, 2019). Since they cannot be substituted in many applications, the European Commission has classified REEs as critical raw materials indicating that there is a need to preserve and recover them from waste (Amato et al., 2019). Moreover, China has increased the export taxes and this made countries like the USA to seek alternative sources of REEs (Mutlu et al., 2018).

REEs waste is normally found in dams and reservoirs near mining processing facilities (Woodward, 2019). Due to the increasing demand, REEs resources have been exploited in large scale and this led to increased soil and water contamination around the mining areas. As such, the European Agency for Safety and Health at Work has listed REEs as “New and Emerging Risks to Occupational Safety and Health” (Zhuang et al., 2017). Thus, there is a need to remove REEs from wastewaters and water bodies for sustainability and health purposes.

#### **2.4. The need to recover PGEs and REEs**

Wastewaters emanating from PGEs and REEs processing plants and from industries such as automotive, contain elements that are toxic to living organisms, which also cause environmental pollution (Sprynskyy et al., 2011; Erasmus et al., 2020; Komendova, 2020). The inability of some of these elements to biodegrade makes them persist in the environment for long periods of time; increasing their accumulation overtime and thus requiring physical removal (Abollino et al., 2006). From the processing plants, these elements can be transported into the air, soil and water bodies. Transport into the soil may occur through dust fallout or precipitation. Once in the soil, they can travel through the soil profile to

groundwater and lead to groundwater pollution (Mosai et al., 2017). These elements can accumulate in other water bodies such as rivers, lakes and dams through direct and in direct discharges. Though wastewaters contain toxic and non-valuable elements, some may contain elements such as PGEs and REEs which are valuable and precious. All these elements have to be physically removed to protect water bodies. Moreover, removing precious elements can improve economies of many countries dependent of mining activities.

The PGEs and REEs markets are expected to grow over the years due to their need in various technologies that govern the modern world. These elements cannot be substituted by other elements owing to their unique physical and chemical properties hence; their sustainability is of high importance. Moreover, the natural resource deposits of PGEs are very limited and the resources are diminishing drastically due to their demand hence the market prices are high (Morcali, 2020). There is therefore a need to recover PGEs from secondary sources such as mining wastewaters. Wealth Daily (2017) indicated that the global growth rate of REEs market is expected to be 13.7% annually. Moreover, even though some of the REEs are widely available, others such as yttrium and terbium (known as heavy REEs) are in low concentrations and facing scarcity (Ganguli and Cook, 2018). Thus, if no plan is made for their sustainability, the world will be in danger of losing some of the important elements that cannot be replaced by others. In addition, there are few regions in the world where REE are concentrated enough to make their extraction valuable due to their ability to be interchangeable with mineral structures such as phosphate and silicate minerals (Royer-Lavallée et al., 2020).

## **2.5. Removal of trace elements from aqueous solutions**

Due to the worldwide concerns of water pollution by trace elements, interventions have been proposed and applied in water systems to reduce pollution in mine impacted water (Li and Thornton, 2001). The methods used to remove trace elements from water are ion exchange,

solvent extraction, precipitation, filtration, phytoremediation, physicochemical remediation, microbial remediation and adsorption (Sternberg and Dom, 2002; Morifi et al., 2020). These methods can be classified into active and passive techniques. Active methods involve the use of biological techniques to eliminate elements from wastewater where; microorganisms, algae, fungi and higher plants are used (Monteiro et al., 2008; Gunatilake, 2015). The techniques used are activated sludge, trickling filters and stabilization ponds. The most common is the activated sludge where, microorganisms are used to break down the organic material with aeration and agitation which then allows for the elements to settle out. Stabilisation ponds are also used since they are cheap. Stabilisation ponds depend on the interaction of sunlight, algae, microorganisms and oxygen (Gunatilake, 2015).

#### **2.5.1. Ion exchange**

Ion exchange is a passive method that is widely used to treat water in the industry. In this method, water (liquid phase) flows through a bed (solid phase) which is the ion exchange material. The ions in the aqueous solution will replace those on the material (usually sodium and hydrogen ions) (Gunatilake, 2015). This method has been proved to be effective in cleaning water especially when the levels of elements are low (Dizge et al., 2009). The exchange material has water-insoluble ion exchangers which are synthetic organic ion exchange resins.

#### **2.5.2. Membrane filtration**

Membrane filtration method is one of the most widely used sorption methods for water treatment. The lower driving force and small space required in membrane filtration are some of the advantages that led to the high usage of this method. Ultrafiltration and reverse osmosis are common membrane filtration methods used depending on the size of the analyte to be retained (Vigneswaran et al., 2004). One of the commonly used ultrafiltration method is

the polymer-supported ultrafiltration technique which uses polymeric ligands which are soluble in water. These ligands can bind metal ions from wastewaters and form macromolecular complexes (Rether and Schuster, 2003). This method requires low energy and it has high selectivity for elements. In reverse osmosis, pressure is used to push water through a semipermeable membrane that will retain the metals and allow clean water to pass through to the collecting vessel. The separation occurs at the dense barrier layer in the polymer matrix of the semipermeable membranes. This method is effective but costly due to the expensive membranes (Crittenden et al., 2008).

### **2.5.3. Solvent extraction**

Solvent extraction technique is one of the commonly used methods in hydrometallurgical processes to remove elements from wastewaters. It consists of three steps viz extraction, scrubbing and the stripping. In the extraction step, the wastewater is contacted with solvent extractant in a mixer-settler where, the elements are transferred to water-immiscible phase which will be moved to another mixer-settler containing the stripping solution (Cole, 2002; Mansur, 2011). The remaining aqueous solution is then submitted for the recovery of other elements, discharged or recycled. The water-immiscible phase will go on to the scrubbing step if the selectivity in the extraction step was low. Other elements or impurities are removed in this step. In the final step, the stripping step, the elements are stripped out of the water-immiscible phase to another aqueous solution and this will result in a concentrated solution of the elements where they are purified to obtain metal oxides or pure metals (Mansur, 2011). This method has disadvantages because it uses a number of chemical and time consuming due to the number of steps involved (Wang and Cheng, 2011).

#### **2.5.4. Chemical precipitation**

Chemical precipitation is another well-known technique whereby dissolved contaminants in wastewater are transformed into insoluble solids. In the treatment of industrial wastewaters, sodium hydroxide or lime are used as coagulants or flocculants to enlarge species of the elements. The results obtained from this technique however, are not satisfying hence; other additional techniques such as ion exchange are normally used for high efficiency (Akpore and Muchie, 2010). Other disadvantages include; high cost of waste disposal, use of corrosive chemicals, non-environmental friendly hydroxides and each of the dissolved elements have their own particular pH for hydroxide precipitation. Above or below the precipitation points the metals become soluble. Thus, even a slight change of pH can turn the precipitated metal back into the solution (EPA, 2000).

#### **2.5.5. Electrochemical treatment**

Electrochemical treatment has been used to remove elements from wastewaters. In this technique, electricity is used to pass current through the wastewater solution which has cathode plate and insoluble anode. As electrons move from element to element, electricity is generated. In electrochemical process, the metals have to be precipitated in a weak acid (Shim et al., 2014). This method requires large amount of chemicals to reduce the elements so that they can be discharged (Gunatilake, 2015).

#### **2.5.6. Phytoremediation**

Phytoremediation uses plants to remediate wastewater, groundwater, surface water, sediment, sludge and contaminated soils (Figure 2.3) (Ali et al., 2013). Phytoremediation focuses on the areas of phytodegradation, phytoextraction, phytostimulation, phytovolatilization phytostabilisation and rhizofiltration (Akpore and Muchie, 2010; Ali et al., 2013). In phytodegradation, plants take up contaminants, store and degrade them within their tissues.

Phytoextraction is a process whereby plants adsorb contaminants from the soil matrix, translocate and store them into their root and shoot tissue (Figure 2.4). This process can occur naturally through plants called hyperaccumulators or can be induced by adding chelators which increase bioavailability (Akpore and Muchie, 2010). Hyperaccumulators can absorb large amounts of metals than other plants (UNEP, 2012).



Figure 2.3: Phytoremediation tests in Montreal (Guidi et al., 2013)

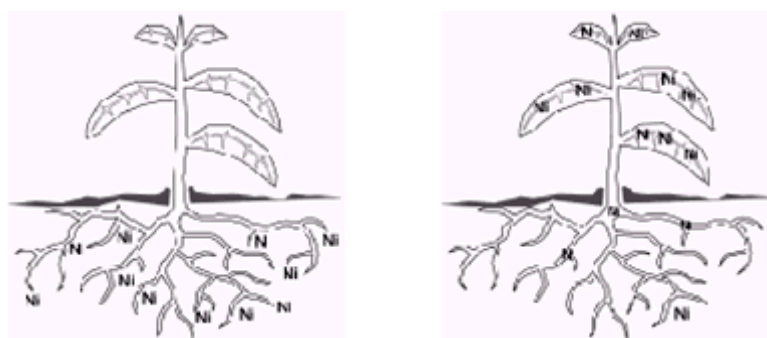


Figure 2.4: Uptake of Metals (Nickel) by Phytoextraction (Etim, 2012)

Phytostimulation uses rhizospheric associations between plants and symbiotic soil microbes to degrade contaminants. Phytovolatilisation is a process whereby plants uptake contaminants and transform them to other forms after which they will be volatilised into the atmosphere.

This process occurs as plants take up water and other organic contaminants. One of such plants is Poplar trees. In phytostabilisation, plant roots are used to reduce the movement of contaminants through adsorption and therefore reducing their bioavailability. These contaminants can also be precipitated in the rhizosphere (UNEP, 2012). The reduction in mobility of contaminants will prevent their migration to groundwater or air. Rhizofiltration is one of the phytoremediation techniques whereby contaminants are adsorbed or precipitated onto plant roots or even absorption into the roots. This process is similar to phytoextraction. Elements such as Cu(II), Cr(VI), Cd(II), Pb(II) and Ni(II) have been removed from wastewaters using rhizofiltration with great success (Dushenkov and Kapulnic, 2000). The process is administered by planting in the contaminated area or by bringing wastewater to the plants. When the roots are saturated with contaminants, they are then harvested (UNEP, 2012). Sunflower is one of the plants used in this process.

#### **2.5.7. Bioremediation**

Bioremediation using microbes to remove contaminants from wastewaters has received much attention lately due to high efficiency and less costs (Radhika et al., 2006; Simate and Ndlovu, 2015). Bioremediation also known as biosorption is a safe and economic physicochemical process which occurs in biological systems. The elements are adsorbed onto the cellular structure of microbes. Some of the advantages of this technique are that no energy is required, cost-effective, less chemical, physical sludge, environmental friendly, no waste generated and self-sustaining (Babarinde et al. 2009; Das et al. 2008). However, it is not easy to obtain suitable microbes, it is time consuming and is not always suitable (Viladi, 2001). In biosorption, the biological material (solid phase) and wastewater (liquid phase) containing elements come into contact and adsorption onto the cell walls of microbes occurs. Carbonyl, hydroxyl, ketone and amino groups in cell walls are responsible for biosorption of the

elements (Babarinde et al. 2009). Bacteria, fungi and algae can also be used in this process (Won et al., 2005).

### 2.5.8. Adsorption

Adsorption has been proven to be the most efficient and economical alternative method from removing elements from wastewaters (Matsumoto et al., 1989; Abollino et al., 2006; Ballay et al., 2018). The adsorption process uses adsorbents such as zeolites (Bakatula et al., 2015), bentonite (Bakatula, 2012), polymers (Saad et al., 2012), chitosan (Liu et al., 2009), fly ash (Hernandez-Ramirez and Holmes, 2007) and clay (Lin and Juang, 2002) to adsorb elements. The adsorption can occur through chemical, physical and ionic processes. Adsorption is a mass transfer process whereby elements (adsorbates) or substance from the liquid phase are transferred to the solid phase surface (adsorbent) and is bound through physical or chemical interactions or sometimes both (Kurniawan et al., 2006). The characteristics of physisorption and chemisorption forces of interaction are described in Table 2.1.

Table 2.1: Characteristics of physisorption and chemisorption (Koopal, 2001)

| <b>Physisorption</b>                                                                            | <b>Chemisorption</b>                                                                                                                       |
|-------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------|
| Physical adsorption occurs in physisorption where the forces involved are van der Waals forces. | Chemical bonds form which are based on chemical specificity.                                                                               |
| There is minimal perturbation of the electronic states of the adsorbent and adsorbate.          | There are significant changes in electronic state which can be detected spectroscopy, electrical conductivity and magnetic susceptibility. |
| The adsorption and desorption of the                                                            | The adsorption may not be reversible thus                                                                                                  |

|                                                                                                        |                                                                                                    |
|--------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------|
| adsorbate does not change the chemical nature of the liquid phase in which the adsorbate is contained. | desorption is impossible.                                                                          |
| Adsorption energy between the adsorbent and adsorbate is the same. Always exothermic.                  | The chemical reactions can be exothermic or endothermic                                            |
| The elementary step does not include activation energy.                                                | The elementary step includes activation energy.                                                    |
| Equilibrium is reached between the adsorbate and the liquid phase.                                     | If the activation energy is large enough, equilibrium may be reached slowly or not reached at all. |
| Multilayer adsorption occurs                                                                           | Monolayer adsorption occurs                                                                        |

In physisorption, the adsorbate can move over the surface since the forces involved are weak and therefore not fixed to a particular site. In chemisorption, the adsorbate is fixed on the surface due to strong forces involved (Sawyer et al., 1994). Electrostatic or covalent bonds exist between the adsorbent and the adsorbate with shorter bond lengths and higher bond energies (Montgomery, 1985).

There are four steps that take place during the adsorption process; the bulk solution transport, film diffusion transport, pore transport and adsorption. In the bulk solution, the adsorbate is transported from the bulk solution to the reaction sites on mineral surfaces through advection and dispersion (Bakatula, 2012). In film diffusion transport, the adsorbate is transported by diffusion through the stagnant liquid film to the surface. The pore transport occurs through the pores on the surface of the adsorbent where the adsorbate travels through the pores by a combination of molecular diffusion and by diffusion along the surface. Lastly, the adsorption

step involves the attachment of the adsorbate to the adsorbent at an available adsorption site (Metcalf and Eddy, 2003; Bakatula, 2012). The adsorption process was used in this study.

## **2.6. Zeolites**

Zeolites are naturally occurring crystalline hydrated aluminosilicate minerals which were discovered about 250 years ago by Axel Cronstedt (Woodford, 2016). They are formed in nature as crystals in basaltic rocks or as volcanic turfs or glass altered by the interaction with saline water. They are formed under natural condition in different geological environments such as lake sediments, alkaline deserts, ash ponds and marine sediments (Jha and Singh, 2016). Natural zeolites have industrial applications such as water treatment, plant growth and soil amendment (Peter et al., 2012; Jha and Singh, 2016; The Mineral Group Zeolite, 2017). The problem with natural zeolites is that they contain other minerals such as iron ( $\text{Fe}^{2+}$ ), quartz and other minerals which make them difficult to use in some crucial commercial applications that require some form of purity and uniformity (Jha and Singh, 2011). Thus, zeolites with purer and uniform states have been synthesized over the years by chemical processes (Simate et al., 2016). The synthesized zeolites have specific lattice structures and pore size in the framework (Mishra and Tiwari, 2006).

Zeolite is made up of interlinked tetrahedra of alumina ( $\text{AlO}_4$ ) and silica ( $\text{SiO}_4$ ) groups. The tetrahedral are linked by common oxygen at their corners (Kozák et al., 2010). Thus, they contain aluminium, silicon and oxygen elements that form an inorganic macromolecule with a structurally distinct 3-dimensional framework. The silicon or aluminium ions are surrounded by four oxygen ions in a tetrahedral configuration (Figure 2.5). The framework contains large open pores in a regular arrangement which contains water molecules and cations such as sodium, calcium, potassium and magnesium. The net formulae of the tetrahedra are  $\text{SiO}_2$  and  $\text{AlO}_2^-$  (Weitkamp, 2000). Thus, the negative charge in zeolites is due

to alumina species in the centre of the tetrahedron. The negative charge on zeolites can simply be attributed to the replacement of silicon atom by aluminium ion. The charge is balanced by the presence of monovalent and divalent cations (Kozák et al., 2010). The common oxygen atom between silica and alumina ions remains orientated in such a way that the pores develop in a form of cages in the framework as shown in Figure 2.6 (Peskov, 2020). The chemical composition of zeolites can be represented by the equation:



where  $\text{Me}^+$  is a monovalent cation (Na, K, Li),  $\text{Me}^{2+}$  is a divalent cation (Ca, Mg, Ba, Sr).



Figure 2.5: The structure of tetrahedral silicate (Kozák et al., 2010)

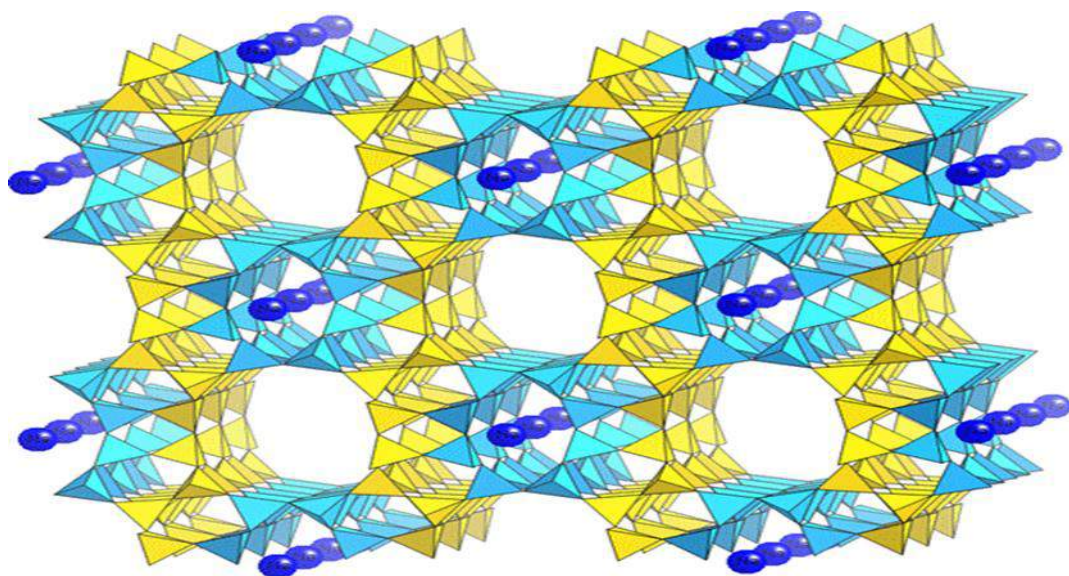


Figure 2.6: Zeolite framework showing cages (Peskov, 2020)

There are about 40 zeolite materials that occur naturally including clinoptilolite, offretite, faujasite, chabazite and mordenite which are the mostly mined (Weitkamp, 2000). About 150 artificial zeolites have been synthesized for specific applications such as catalysts and detergents (Woodford, 2016). Some of the zeolites are shown in Figure 2.7.

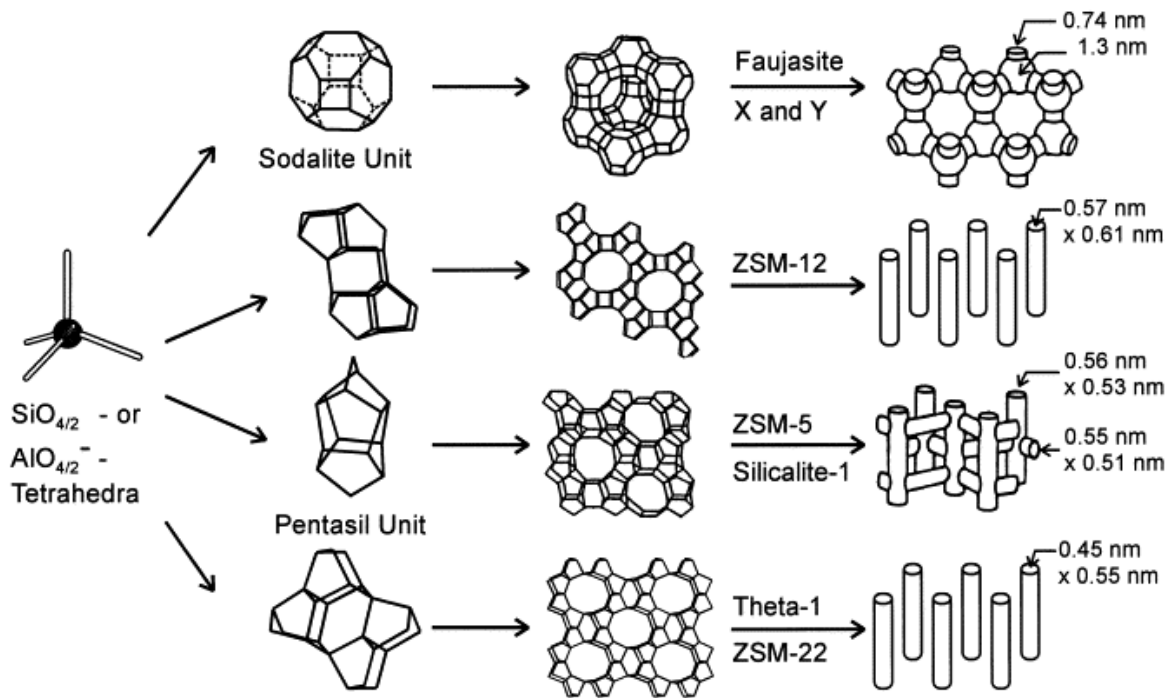


Figure 2.7: Structures of four zeolites (Weitkamp, 2000).

Zeolite materials are very stable and can resist different kinds of environmental condition such as high temperatures, high pressures and oxidation. They are stable at high temperatures since they have high melting points (Peskov, 2020). They are insoluble in organic and inorganic solvents. The negatively charged porous framework and the cations in the pores allow zeolites to be ion exchangers whereby cations in the pores are replaced by other cations (Bakatula et al., 2015). The ions in the pores are loosely bound and therefore can be easily removed or exchanged without destroying the framework. Zeolites are sometimes called molecular sieves because they have fixed-size opening that allows for small molecules to

pass through them and preventing larger ones (Woodford, 2016). The well-known zeolites can be classified in terms of silicon and aluminium contents.

### ***Low silica or aluminium rich zeolites***

These zeolites have molar ratio of  $\text{Si/Al} = 1$  and is considered to have the highest content of aluminium. Thus they have the highest number of cation exchange sites due to  $\text{AlO}_2^-$  leading to high ion exchange capacities. These kinds of zeolites have the highest known heterogeneous surface among porous materials and this is due to high field gradients resulting from exposed cationic charges nested in aluminosilicate framework (Woodford, 2016). The surface of such zeolites is highly selective for water and other polar molecules. Examples of such zeolites are analcime, natrolite and sodalite.

### ***Intermediate silica zeolites***

These zeolites are characterised by the high silica content they contain with molar ratio of  $\text{Si/Al} = 3-5$ . They are highly stable and less likely to be attacked by acid or water vapour that renders zeolites unstable. Thus, these zeolites are thermally, hydrothermally and acid stable. Chabazite, faujasite and mordenite are some of the zeolites which fall into this category (Jha and Singh, 2011).

### ***High silica zeolites***

Zeolites in this category are basically molecular sieve zeolites with molar ratios of  $\text{Si/Al} = 10-100$  or higher. They have different surface characteristics. The surface is homogeneous with an organophilic-hydrophobic selectivity. The less polar organic molecules are strongly adsorbed by these kinds of zeolites. The interaction between the zeolites with water and other polar molecules is weak (Guisnet and Gilson, 2002). The high silica zeolites are ZSM-5(MFI) and zeolite-beta (Jha and Singh, 2011).

Zeolites can be classified into different families which have different minerals and characteristic shapes. The minerals of the zeolites families are summarised in Table 2.2.

Table 2.2: The shapes and minerals of zeolite families

| <b>Family</b> | <b>Minerals</b>                                | <b>Shape</b>            |
|---------------|------------------------------------------------|-------------------------|
| Analcime      | Analcime, pollucite, boggsite                  | Cubic or tetrahedral    |
| Chabazite     | Chabazite, Faujasite, erionite                 | Rhombohedral            |
| Gismondine    | Amicite, gismondine, garronite                 | Monoclinic/ orthogonal  |
| Harmotome     | Harmotome, phillipsite, wellsite               | Monoclinic              |
| Heulandite    | Clinoptilolite, levyne, mazzite, mordenite     | Monoclinic/ orthogonal  |
| Natrolite     | Mesolite, natrolite, offretite, perlialite     | Orthogonal/ tetrahedral |
| Stilbite      | Stilbite, stellerite, thomsonite, yugawaralite | Monoclinic              |

### 2.6.1. Physical properties

Zeolite materials have specific physical properties that define them. Bulk density and specific gravity are some of the important ones since, they can correlate with their size of the pores (porosity) and cation exchange capacity (CEC) as shown in Figure 2.8 (Jha and Singh, 2016). Void volume is also an important physical property of zeolites and can be correlated to the CEC and surface area (Scott et al., 2001 Singh and Kolay, 2002). The pore radius of zeolite

materials is crucial because it helps with understanding the adsorption mechanism (Bakatual et al., 2015). Particle size of zeolites is another physical property that makes them favourable for adsorption. The particle size of zeolites ranges from 2  $\mu\text{m}$  to 800 nm.

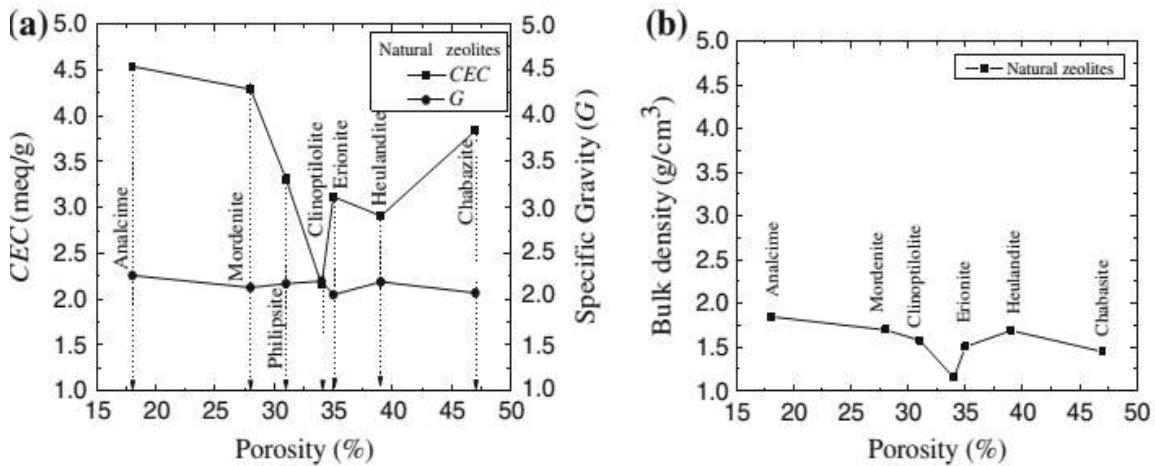


Figure 2.8: The relationship between bulk density and specific gravity with porosity (Jha and Singh, 2016)

## 2.6.2. Chemical properties

Zeolite materials contain metal oxides (aluminium oxide, silicon oxide, magnesium oxide, sodium oxide, calcium oxide, iron oxide and potassium oxide) in the pores of the framework which, are contained with water molecules and other cations (Mishra and Tiwari, 2006). The water in the pores can be lost on ignition, leading to a decrease in the mass of the materials (Ojha et al., 2004). The adsorption properties, CEC and pH are some of the important chemical properties which are dependent on the composition of zeolite materials (Park et al., 2000; Mishra and Tiwari, 2006).

## 2.7. Bentonite

Bentonite is a common clay mineral which is named after a formation called Benton Shale from Fort Benton which is near Rock River in Wyoming (Heathman, 1939). Bentonite consists predominantly of smectite minerals and is formed from volcanic ash that has

weathered and aged in the presence of water (Christidis, 2001). Montmorillonite is one of the major smectite minerals found in bentonite. Nontronite, hectorite, beidelite and saponite are some of the smectite minerals. Smectite group minerals consist of individual crystallites which have a size of  $< 2 \mu\text{m}$  in dimension (Isloor et al., 2014). The crystallites are three-layered minerals consisting of two tetrahedral layers and one octahedral layer. The tetrahedral layers in montmorillonite consist of  $\{\text{SiO}_4\}$ -tetrahedrons which enclose the  $\{\text{M}(\text{O}_5, \text{OH})\}$ -octahedron layer (M is mainly aluminium (Al) and magnesium (Mg) but iron (Fe) is also found) (Figure 2.9) (Isloor et al., 2014). The silicate layers are negatively charged due to the oxygen atoms. This negative charge is compensated by exchangeable ions (calcium, magnesium or sodium ions) which are in the intercrystalline region (Mukasa-Tebandeke et al., 2015). Thus, bentonite has a strong negative electromagnetic charge which can be activated by water to act as a magnet and attract toxins and positively charged elements such as sodium, calcium, cadmium, iron and lead. The presence of water swells (volume increases) bentonite and makes it open like a sponge which can in turn absorb substances up to 40 to 50 times its weight (Manoufali et al., 2016). When bentonite volume increases, a gelatinous and viscous fluid is produced. It is these properties such as swelling, adsorption of water, hydration, viscosity and thixotropy that make bentonite a valuable material for a variety of application such as pelletizing and water purification. Other properties such as exposed surface area, pore structure, exchange cation identity and layer charge influence the adsorption of elements. The non-stoichiometric formula of bentonite is  $[(\text{Al}_{1.67}\text{Mg}_{0.33})(\text{Si}_{3.5}\text{Al}_{0.5})\text{O}_{10}(\text{OH})_2]$ .  $\text{Al}^{3+}$  ions are often substituted by  $\text{Mg}^{2+}$  ions and results in a net negative charge (Mukasa-Tebandeke et al., 2015).

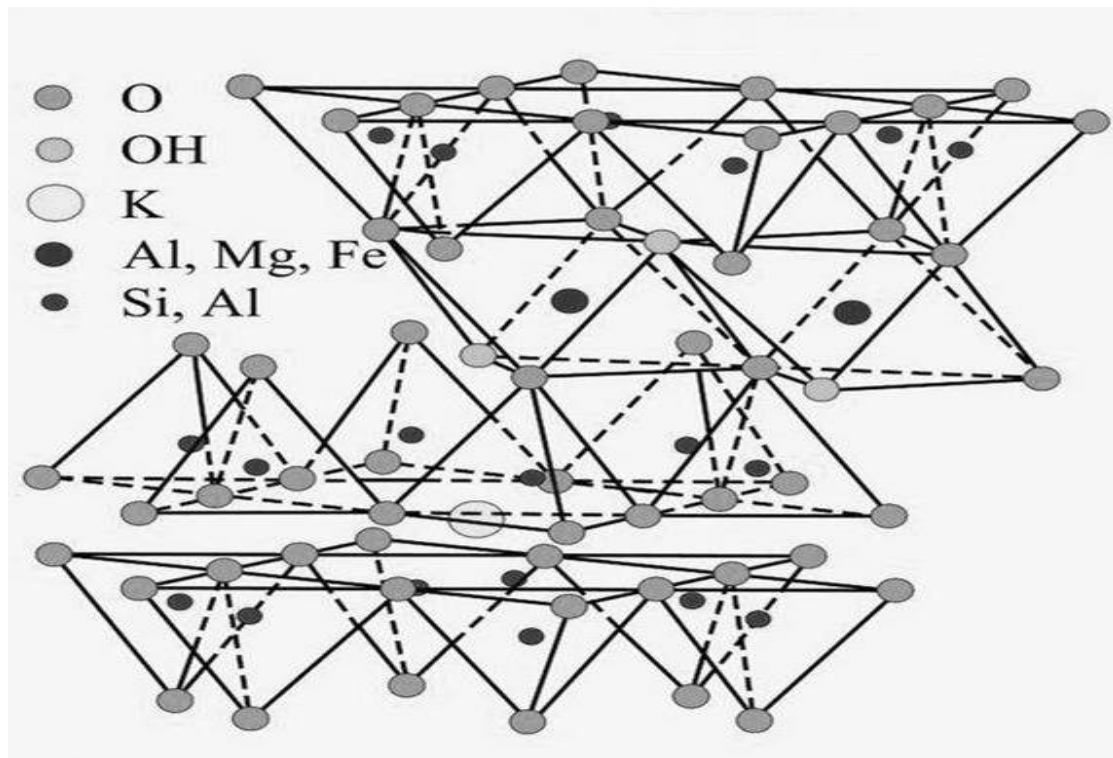


Figure 2.9: Bentonite framework showing the groups and elements attached (Isloor et al., 2014; Mukasa-Tebandeke et al., 2015).

The permeability of liquids through the pores in bentonite increases adsorption of elements (Güven, 2009). Since bentonite surface pores interact strongly with permeable substances, ionic strength, density, surface tension of the substance and the charge of the dissolved ions can affect its performance (Bouazza et al., 2006). In addition to montmorillonite, bentonite has other accessory minerals such as quartz, feldspar, calcite and gypsum. There are different types of bentonite clay and are named after the dominant element they contain viz sodium bentonite, calcium bentonite, aluminium bentonite and potassium bentonite.

### ***Sodium bentonite***

Sodium bentonite has more than 50% of the exchange ions as sodium ions (Na<sup>+</sup>). It is used in barrier applications in the environment as components of liners for containing hazardous wastes. The widely used bentonite for barrier technology has about 70 wt% montmorillonite and swells as water is adsorbed. Sodium bentonite can retain water against high suction and

thus reduce the ability of contaminant migration (Landis and von Maubeuge, 2004). Moreover, the swelling of bentonite is susceptible to exchange by other ions in the water hence hydraulic conductivity increases with time. The exchange is limited by inhibition of physical penetration by cations into the interlayer and the diffusion within. Therefore, the factors that increase swelling enhance cation exchange capacity.

## 2.8. Chitosan

Chitosan is one of the adsorbents that have been widely used for the adsorption of elements. It is a polysaccharide derived from chitin. Chitosan is a cheap biopolymer that is non-toxic and has high bioactivity and biodegradability (Ibrahim and El-Zairy, 2015). It has amine and hydroxyl groups in its backbone which are very reactive hence it is widely used for the removal of elements from wastewaters (Figure 2.10). The chemical structure of chitosan allows for easy modification in order to design polymers for various applications. In an acidic media, the amine groups can be positively charged and capture negatively charged species in wastewaters. Contrary to clay adsorbents such as zeolite and bentonite, the presence of primary amines in chitosan leads to high cationic charge density and the formation of long chains (Nechita, 2017).

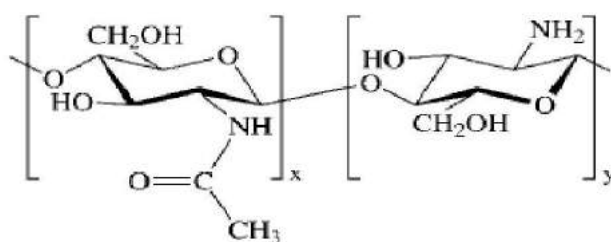


Figure 2.10: Chemical structure of chitosan (Ibrahim and El-Zairy, 2015).

Chitosan can be sourced from the shells of shellfish, prawns, lobster and crab. It can also be obtained from the cell walls of fungi (Ghormade et al., 2017). These organisms are put under harsh conditions in order to obtain chitosan. About  $10^{12}$  kg of chitosan is synthesised per

annum (Ghormade et al., 2017). Though it is one of the most abundant biodegradable materials, chitosan was not considered in this study because it has an overall positive structural charge which would make it difficult to functionalise with the ligands used in this study as they require a negatively charged counterpart. Also, it has low acid stability and the mining wastewaters are normally acidic. The surface areas of chitosan materials are low and they also have resistance to mass transfer (Zhang et al., 2016). There are many steps involved in obtaining chitosan material and would therefore be more costly than the readily available zeolite and bentonite materials (Ghormade et al., 2017).

## **2.9. Activated carbon**

Activated carbon is a carbonaceous adsorbent with a high volume of pores of different sizes which allows for the uptake of different elements from aqueous solutions (Ahmed et al., 2019). Activated carbon has an amorphous structure with a disorganised graphite form. It is widely used for adsorption owing to its high surface area (up to  $1500 \text{ m}^2 \text{ g}^{-1}$ ) (Chen et al., 2002). It is manufactured from materials such as coal, rice husk and peels with high carbon content. It has been found to remove elements from aqueous solutions better than many other techniques due to the ability to treat high volumes of solutions, ease of operation and insensitivity to toxic substances (Danish and Ahmad, 2018). Activated carbon is made by placing the biomass in a tank without oxygen which is then heated to very high temperatures ( $>500^\circ\text{C}$ ). Chemicals such as nitrogen and argon are used to further purify the material under high temperatures (Ahmed et al., 2019). Thus, even though it is very effective, its high cost precludes its application in most cases. This adsorbent was also not considered in this study since the aim was to come up with a cheap material but efficient.

## **2.10. Biochar**

Biochar is a charcoal-like substance with high carbon content (approximately 70%) (Taghizadeh-Toosi et al., 2012). Its chemical composition is highly dependent on the feedstock used and the method of heating. It is produced from the pyrolysis of biomass (dead plants, leaf litter and wood chips) under oxygen-limited environment (Zhu et al., 2016). It has been found to have many benefits in agriculture including improvement of soil fertility, increasing water retention, decreasing acidity and increasing plant yields. Biochar has also been found to be a good adsorbent that can adsorb contaminants from aqueous solutions either by electrostatic interactions or ligand-exchange mechanism. Zhu et al. (2016) found that bismuth impregnated biochar can successfully remove arsenic, phosphorus and chromium from aqueous solutions. However, it was also not considered in this study due to the costs involved in production and its efficiency has been found to be less than that of many adsorbents (Niu et al., 2020).

## **2.11. Adsorption of elements using zeolite and bentonite**

The removal of some toxic elements (including arsenic, lead, uranium, mercury, chromium and cobalt) and other pollutants using zeolite and bentonite has been reported by a number of researchers (Bakatula et al., 2015; Shirzadi and Nezamzadeh-Ejhi, 2017). The use of these materials have gained popularity mainly because of their physical and chemical properties including the ability to adsorb different elements, high surface areas as well as ion-exchange and molecular sieve properties. They are also easily modifiable, which is an attribute that many researchers look for in adsorption materials. Motsi et al. (2009) studied the ability of zeolite to adsorb  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Zn}^{2+}$  from aqueous solutions and found that more than 90% removal percentage of all the elements can be obtained. The authors compared the efficiency of zeolite with activated carbon and found that zeolite will be cheaper to use and efficient. Shirzadi and Nezamzadeh-Ejhi

(2017) compared the ability of the natural and modified zeolite to simultaneously remove mercury and lead from aqueous solutions. They found that modified zeolite can simultaneously remove mercury and lead better than the natural one. They also found that the modified zeolite used both ion-exchange and complexation processes to remove the elements. Thus, modification can provide different ways in which elements can be captured.

Bentonite has been used to adsorb both metallic and non-metallic substance. For example, organic pollutants such as Rhodamine B and Acid red 1 were removed from dye wastewater using organic modified bentonite (Huang et al., 2017). Dye wastewater is one of the major hazardous industrial wastewaters. Huang et al. (2017) found that organo-bentonite can remove highly concentrated dyes from wastewaters. The adsorption of zinc using natural and Na-enriched bentonite was investigated by Kaya and Ören, (2005) who found that the adsorption was affected by pH. However, the modified bentonite performed better than natural bentonite in all physical and chemical changes. The surface area of bentonite was higher after functionalisation with Na hence higher efficiency. They also found that bentonite provide different active sites for the adsorption of zinc. A study by Niu et al. (2020) investigated the adsorption capacities of  $\text{Cr}^{3+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  using natural and sulphate-aluminate-amended-bentonite. There was no significant difference between the natural and the modified bentonite on the adsorption of  $\text{Cr}^{3+}$ , but the modified bentonite was better for the adsorption of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$ . The removal percentage of all elements was >99%. The activity of the modified adsorbent was compared with that of other adsorbents such as biochars, phosphate titanium oxide, surface modified jackfruit peel and amino-magnetite kaolin clay which were all found to be less effective than the modified bentonite. Thus, bentonite which can be easily

modified can take up elements better than other adsorbents even though they are modified. Hence, bentonite was used in this study.

## **2.12. Functionalising zeolite and bentonite**

Metals have been discharged into the environment as industrial waste, leading to soil and water pollution. Many elements such as Pb, Cd, Cr, Fe, As and many others are commonly released. These elements are also common groundwater pollutants especially in industrial areas. Zeolite and bentonite materials have been found to be alternative low-cost materials for the removal of elements from aqueous solutions. These materials are widely available in large quantities and this makes them very relevant adsorbents which can be adopted all over the world including under developed countries.

Although the adsorption of low-cost adsorbents such as zeolite and bentonite has been found to be effective in removing elements from wastewaters, their modified versions can perform better (Chisholm-Brause et al., 2001; Babel and Kurniawan, 2003). One or more functional groups can be used to functionalise adsorbents. The functional groups must have chemical reactions with target elements. For example, PGEs are known to have strong interactions with amine containing ligands, therefore functional groups containing amine groups will be ideal for functionalisation. Thus, the natural adsorbents can just be used as support beds for ligands i.e. they do not take part in adsorption but they hold the ligands that have affinity for target elements (Zhang et al., 2009). Due to the known interaction of specific ligands with elements, different functional groups have been used to functionalise zeolites. Bakatula et al. (2015) modified zeolite with ammonium to remove uranium from aqueous solutions and because the interaction of ammonium and uranium was great, over 90% removal of uranium was achieved. Zeolite was modified with dithizone which contains sulphur and nitrogen groups to adsorb lead and mercury from aqueous solutions and, it was found that the modified zeolite

significantly ( $p < 0.05$ ) removed the elements from the solutions (Shirzadi and Nezamzadeh-Ejhieh, 2017).

Su et al. (2011) functionalised bentonite with octadecyl benzyl dimethyl ammonium to successfully remove As(III) and As(IV) from aqueous solutions. The authors found that the modified bentonite removed As species better than the natural bentonite. Dousov et al. (2009) reported that the modification of bentonite either with Fe, Al, or Mn salts showed significant improvements in adsorption affinity for arsenic and, the removal percentages ranged from 92% to >99% with the corresponding adsorption capacity up to  $4.5 \text{ mg g}^{-1}$ .

The functionalisation will also be made in such a way that even low levels of precious elements (PGEs and REEs) can be salvaged from mine wastewaters to recover value thus, providing a good and effective mining method that is cost-effective.

# **CHAPTER 3:**

# **MATERIALS AND**

# **METHODS**

**This chapter shows which ligands were used for functionalisation. The characterisation techniques, methods and operating conditions used are outlined.**

### 3. MATERIALS AND METHODS

The study sought to develop functionalised zeolite and bentonite for the recovery of platinum group elements (PGEs) and rare earth elements (REEs) from aqueous systems impacted by mining activities. The natural adsorbents were first used on their own to recover PGEs but the adsorption efficiency was not significant ( $p > 0.05$ ) and less than 5% recovery efficiency for most of the elements was obtained. Studies have indicated that the affinity of the adsorbents for elements can be increased by functionalising the adsorbent materials with ligands that have affinity for the elements of interest (Bakatula et al., 2015). This idea was adopted in this study. Nitrogen containing ligands were used to modify zeolite and bentonite to get the best adsorption capacities of the elements, which are known to result in high recoveries.

Natural zeolite and bentonite were sieved using a molecular sieve to get the required particle size ( $\sim 2$  mm). The chemicals used were of analytical grade from Sigma Aldrich, South Africa. The adsorbents were added to 2 M NaCl (1 L) after sieving and shaken for 24 h at  $25^{\circ}\text{C}$  using a bench-top shaker (Figure 3.1) to make the surface homogenous with sodium ions, therefore making it easy to introduce some of the ligands.



Figure 3.1: Bench-top shaker (Labcon, 2021)

The adsorbents were filtered and washed with deionised water and silver nitrate was used to ascertain that chloride ions were removed completely. The mono ionic adsorbents were then dried at 60°C for 24 h and stored for future use.

### **3.1. Introduction of ligands on zeolite and bentonite**

The cost-effective zeolite and bentonite materials were functionalised with various ligands (including amine based ligands such as polyethyleneimine, lysine, arginine, histidine and yeast) and their ability to selectively remove the elements of interest from aqueous solutions was tested. Sodium mono ionic zeolite and bentonite were functionalised with the ligands as follows:

#### **3.1.1. Functionalisation with ammonium ion**

1 L of 2 M  $\text{NH}_4\text{Cl}$  was prepared and mixed with 100 g of mono ionic adsorbents and shaken for 24 h using an elliptical bench-top shaker. The adsorbents were filtered and washed with deionised water until all chloride ions were removed.

#### **3.1.2. Functionalisation with polyethyleneimine**

1 L of 2 M polyethyleneimine was also prepared by dissolving an appropriate amount in deionised water. The prepared solution was mixed with 100 g of mono ionic adsorbents and the contents were reacted using a microwave reactor at 60°C for 2 hours. The microwave reactor was used because functionalisation using just a shaker failed. Thus, higher temperatures may assist with functionalisation. The adsorbents were filtered, washed with deionised water and dried.

#### **3.1.3. Functionalisation with Yeast**

The bakers' and brewers' yeasts were used to modify the adsorbent surfaces. Five grams of instant baker's yeast was dissolved in deionised water and contacted with the adsorbents for 24 h at room temperature (about 23°C) using a shaker. The solution of the spent brewers'

yeast was collected from a microbrewery at the University of the Witwatersrand, South Africa. The spent yeast was added to the adsorbents and reacted using a shaker. The functionalised zeolite and bentonite were filtered and washed with deionised water to remove unbound yeast. The adsorbents were dried at 25°C for 24 h. The yeast was used in this study since it contains different amino acids as shown in Figure 3.2.

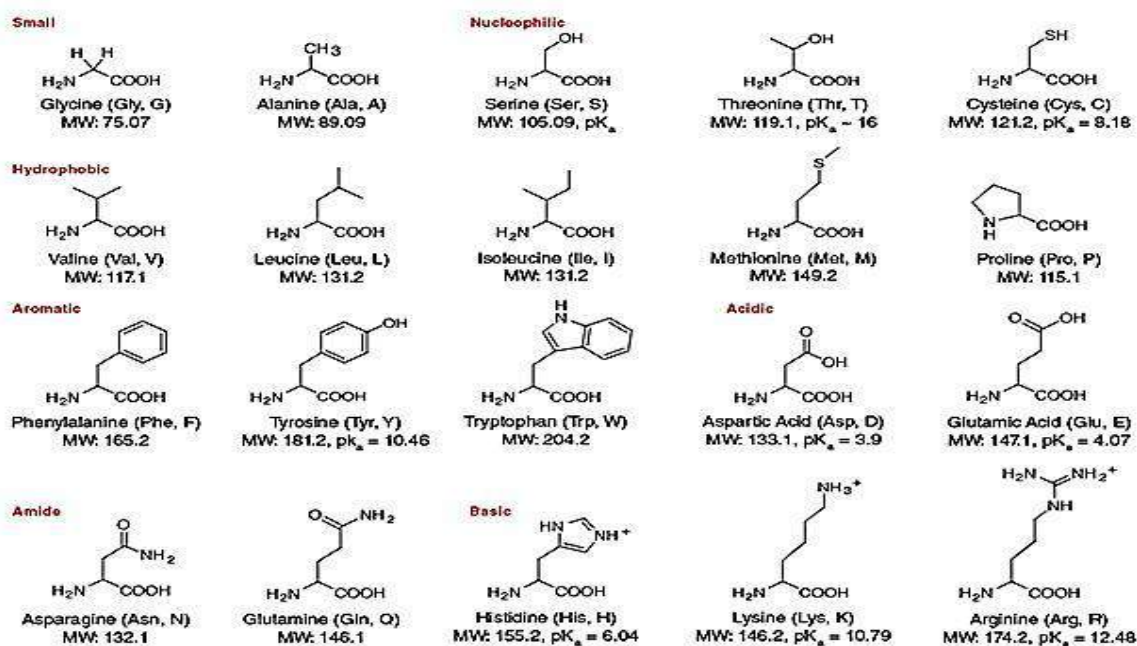


Figure 3.2: Amino acids found in yeast (Sturm, 2020)

### 3.1.4. Functionalisation with L-Lysine

18.3 g L-Lysine was dissolved in deionised water and 100 g adsorbent was added. The contents were reacted at 60°C for 48 h. The functionalised adsorbents were filtered and washed with deionised water to remove the unreacted ligand. The suspension was dried at 60°C for 24 h. In order to determine the amount of the adsorbed ligand, the amount of L-Histidine was measured before and after equilibration time.

### **3.1.5. Functionalisation with 3-aminopropyl(diethoxy)methylsilane (APDEMS)**

A solution of 3-aminopropyl(diethoxy)methylsilane ( $C_8H_{21}NO_2Si$ ) (mp: 85 - 88°C, MW: 191.34 g mol<sup>-1</sup>) was added to zeolite and bentonite so that the amine group could be introduced on the surface of the materials. An automated Microwave-assisted Extraction monowave 450 was used for this purpose. The resulting adsorbents were filtered using suction and dried at 100°C for 24 h.

### **3.1.6. Functionalisation with hydrazine**

Hydrazine monohydrochloride ( $NH_2NH_2 \cdot HCl$ ) (1.36 g) was dissolved in 20 mL deionised water and added to 5 g the zeolite and bentonite. The contents were reacted in an automated Microwave-assisted Extraction monowave 450 for 30 minutes. The solution was cooled to room temperature and filtered using suction. Deionised water was used to remove excess hydrazine and chlorine. Silver nitrate was used to determine the removal of chlorine. The modified zeolite was then dried at 25°C for 24 h and stored for further usage.

### **3.1.7. Functionalisation with L-Histidine**

15.5 g L-Histidine was dissolved in deionised water and 100 g adsorbent was added. The contents were interacted using a microwave reactor for 2 h. The functionalised adsorbents were filtered and washed with deionised water to remove unreacted ligand. The suspension was dried at 60°C for 24 h. The amount of L-Histidine was measured before and after the reaction time.

### **3.1.8. Functionalisation with L-Arginine**

17.42 g L-Arginine was dissolved in deionised water and 100 g adsorbent was added. The contents were reacted at 60°C for 48 h. The functionalised adsorbents was filtered and

washed with deionised water to remove unreacted ligand. The suspension was dried at 60°C for 24 h.

#### **3.1.9. Functionalisation with ammonium ion and polyethyleneimine**

A mixture of ammonium ion and polyethyleneimine was used to modify the adsorbents using a microwave reactor for 2 h and their adsorption efficiencies were compared to those of the individual substances.

#### **3.1.10. Functionalisation with ammonium ion and Yeast**

A mixture of ammonium ion and instant bakers' yeast was also used to modify the adsorbents. The ligands were dissolved in deionised water and the mixture was added to 100 g of zeolite and bentonite. The contents were shaken for 24 h at room temperature so that the ligands can attach onto the adsorbents. The modified adsorbents were filtered, washed and dried at 25°C for 24 h.

#### **3.1.11. Functionalisation with polyethyleneimine and Yeast**

Polyethyleneimine was mixed with yeast and used to functionalise zeolite and bentonite materials using a microwave reactor and, the resulting adsorbents were compared with the individual substances to determine if they are more effective than the individual ligands.

#### **3.1.12. Functionalisation with polyethyleneimine and hydrazine mixture**

Polyethyleneimine and hydrazine monohydrochloride were mixed together (50:50) and interacted with zeolite and bentonite materials for 30 min using a microwave reactor. The efficiency of the resulting adsorbents was compared with the individual ligand functionalised adsorbents.

### **3.1.13. Functionalisation with yeast and hydrazine mixture**

Zeolite and bentonite materials were contacted with a mixture of yeast and hydrazine monohydrochloride for 30 min using a microwave reactor. The contents were filtered using suction after the reaction time and dried.

### **3.1.14. Functionalisation with APDEMS and hydrazine**

A 20 mL solution of APDEMS was mixed with dissolved hydrazine monohydrochloride and 5 g of zeolite or bentonite was added to the mixture and reacted using an automated Microwave-assisted Extraction monowave 450. The resulting adsorbents were filtered using suction and dried.

### **3.1.15. Functionalisation with L-Arginine and hydrazine**

17.42 g L-Arginine and 27.20 g hydrazine monohydrochloride were dissolved in deionised water and 100 g of either zeolite or bentonite was added. The contents were reacted at 60°C for 48 h using a shaker. The functionalised adsorbents was filtered and washed with deionised water to remove unreacted ligand. The suspension was dried at 60°C for 24 h.

## **3.2. Operating conditions**

The capability of the functionalised adsorbents to remove elements of interest (in batch and column/flow through mode) from aqueous solutions under various conditions was assessed. The best working conditions (pH, initial concentration, mass of adsorbents and contact time) for the adsorbents were determined from these modes. This is very important because wastewaters can be in different conditions of which, some may not be ideal for the adsorbents. For example, a study by Abollino et al. (2003) indicated that efficient recovery of some elements only occurs at highly acidic pH solutions and thus applying the adsorbents in wastewaters that have undesirable pH values may render the adsorbents very useless and non-

economical. Thus, some wastewaters conditions might have to be adjusted to suit the best working conditions of the adsorbents.

The selectivity of each of the functionalized zeolite and bentonite as well as their maximum adsorption capacities for PGEs and REEs were determined.

### **3.3. Batch studies**

Batch adsorption studies were conducted using acid-cleaned and rinsed polypropylene containers. The chemicals used were of analytical grade. Stock solutions of PGEs, REEs and other elements (e.g. Zn) were prepared and the working solutions were prepared daily. A known amount of the adsorbent (after optimising for the appropriate dosage) was added to a particular volume of the solutions containing elements with known concentrations and pH. The contents were shaken using an elliptical bench-top shaker to allow the adsorption process to take place. The contents were filtered using a filter paper and the equilibrium concentrations of elements were determined using inductively coupled plasma optical emission spectroscopy (ICP-OES).

### **3.4. Column studies**

Column studies were conducted using glass columns with a porous bed to support the adsorbent materials. The solutions containing the elements of interest were added in a continuous flow mode so that they may be in contact with the adsorbents. Vials were used to collect the solutions that have passed through the column at regular intervals, as determined by the pore volume of the respective adsorbents (Figure 3.3). The collected samples were analysed using ICP-OES. Breakthrough curves and breakthrough times were determined from these studies.

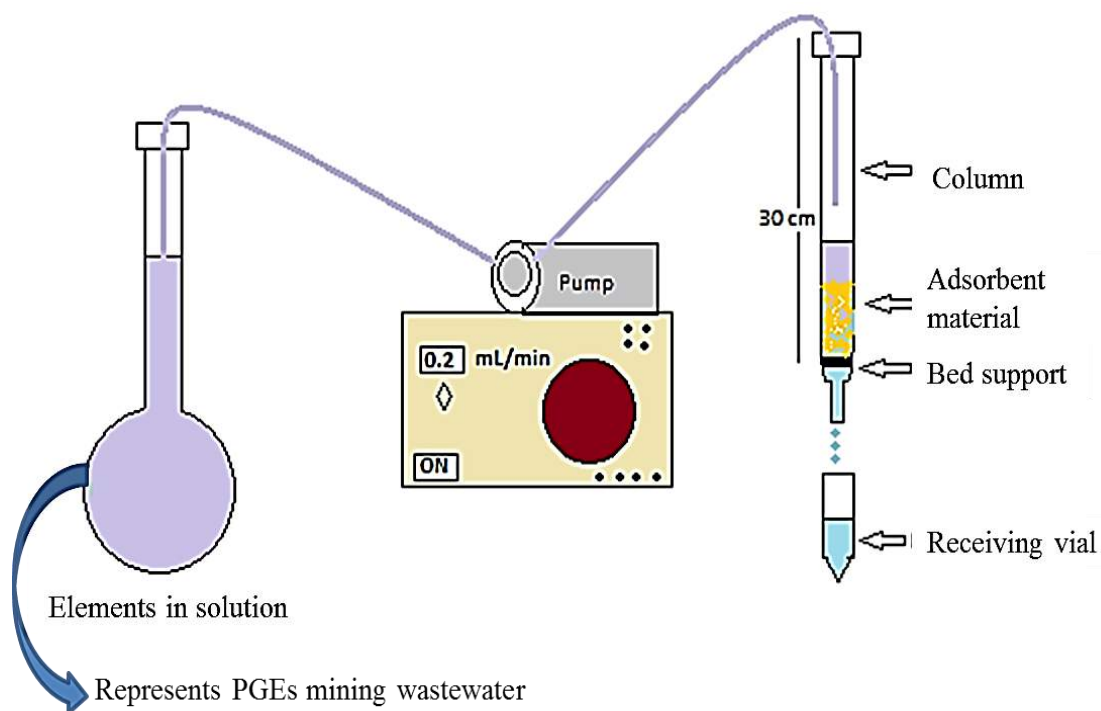


Figure 3.3: Schematic representation of the column studies setup

### 3.5. Models to describe the experimental data

#### 3.5.1. Adsorption isotherms

There are empirical models used to describe the adsorption of elements in different adsorbents. These models are based on mathematical relationships known as isotherms between the concentrations of elements in the liquid and solid phase at equilibrium (Toth, 2002; Bradl, 2004). In other words, adsorption isotherms describe the retention or the mobility of elements from aqueous media to a solid phase. The equilibrium can be reached when the liquid and the solid phases have been contacted for sufficient amount of time. The physicochemical parameters obtained in the models can provide information about the affinity of the elements to the surface of the adsorbents, surface properties and adsorption mechanisms (Bulut *et al.*, 2008).

The adsorption of elements onto surfaces can be through monolayer or multilayer adsorption. In 1916, Langmuir mathematically explained the monolayer adsorption of gases onto homogenous planar surfaces. In his theory, at equilibrium, the numbers of adsorbed and desorbed molecules on the surface per unit time are equal (Langmuir, 1916; Vermeulen et al., 1966). However, this model did not take into consideration, the lateral interactions and the horizontal mobility of the adsorbed molecules. It was concluded that adsorption occur onto finite number of definite localized sites which are identical and equivalent. Statistical thermodynamics were incorporated later and new models were developed for homogenous surface (Volmer, 1925). Brunauer et al. (1938) came up with a model that describes the multilayer adsorption.

The commonly used isotherm models which were also used in this study are; Langmuir (Langmuir, 1916; Vermeulen et al., 1966), Freundlich (Adamson and Gast, 1997; Hutson and Yang, 2000; Zeldowitsch, 1934), Dubinin-Radushkevich (Gunay et al., 2007; Dubinin, 1906) and Temkin isotherms (Temkin and Pyozhev, 1940). These are two-parameter isotherm models. There are also three-parameter isotherm models which are more complicated because they have 3 unknowns which have to be determined (Choudhary et al., 2018). When such models are used, excel solver must be used to determine some of the unknowns. Three-parameter isotherm models were considered in this study since, they can describe the experimental data better than the two-parameter isotherms. The Sips, Redlich-Peterson and Toth models are the three-parameter isotherm models that were used in this study (Choudhary et al., 2018).

### **3.5.2. Kinetic models**

In addition to adsorption isotherms, kinetic models have been widely used in adsorption studies to assess the controlling mechanism of adsorption processes between elements and

adsorbents (Bakatula et al., 2015). The intraparticle diffusion, Elovich, pseudo first- and second-order kinetic models are commonly used models and were applied in this study.

### **3.5.3. Thermodynamics**

When determining the adsorption process between elements and adsorbents, it is crucial to consider thermodynamics analyses in order to determine the spontaneity, type of reaction (endothermic or exothermic) and feasibility of adsorption. The thermodynamic parameters, namely, the standard Gibbs free energy ( $\Delta G^0$ ), change in enthalpy ( $\Delta H^0$ ), and entropy change ( $\Delta S^0$ ) were determined in this study (Diban et al., 2008).

## **3.6. Characterisation**

The adsorbents used in this study were characterised using powder X-ray diffraction (PXRD) for the mineralogy of the materials, X-ray fluorescence (XRF) for chemical composition, Fourier transform infrared spectroscopy (FT-IR) for functional groups and scanning electron microscope (SEM) for structural morphology.

### **3.6.1. PXRD**

During the PXRD process, there is a constructive interference of monochromatic X-rays and a crystalline sample (Dutrow and Clark, 2017). The monochromatic X-rays are generated by a cathode ray tube which is filtered to produce monochromatic radiation which is directed toward the sample. When the conditions satisfy Brag's law, the incident rays can interact with the sample and produce constructive interference. This can only happen when the sample is bombarded with X-rays of a fixed wavelength and specific incident angles (Henry et al., 2016). This constructive interference will lead to a diffracted beam of X-rays that leaves the crystal at an angle equal to that of the incident beam as shown in Figure 3.4.

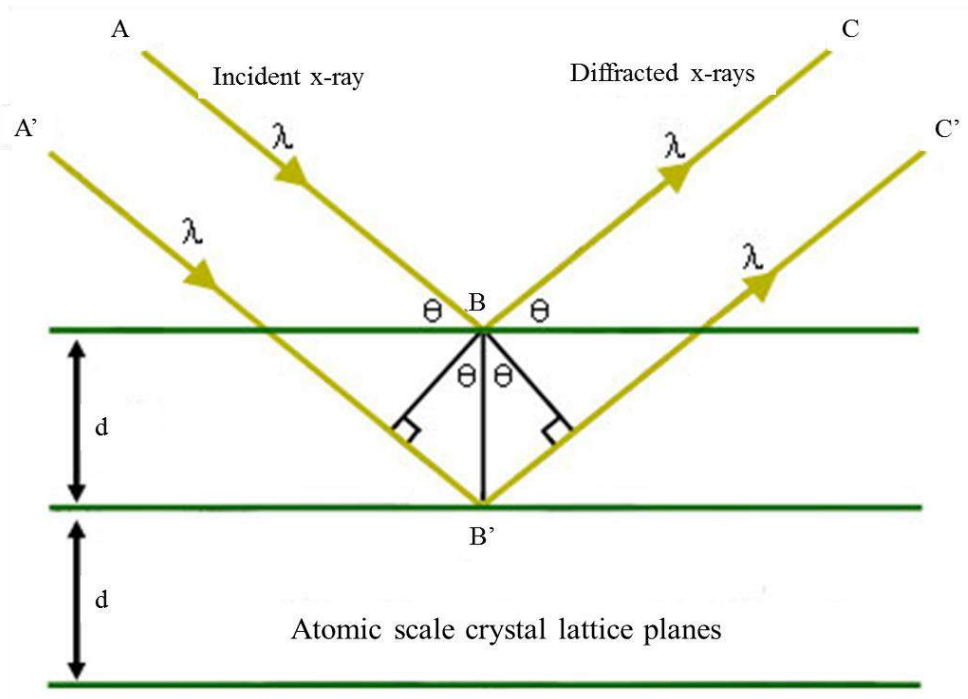


Figure 3.4: Bragg's Law reflection. The diffracted X-rays exhibit constructive interference when the distance between paths ABC and A'B'C' differs by an integer number of wavelengths ( $\lambda$ ) (Henry et al., 2016).

The powder X-ray diffractometer consist of three elements which are; an X-ray tube, sample holder and X-ray detector. The cathode ray tube produces X-rays when the filament is heated to produce electrons. The electrons are accelerated to the target by applying voltage, thus, bombarding the target material with electrons. The X-ray spectra are produced when the electrons have sufficient energy to dislodge inner shell electrons of the target material (Dutrow and Clark, 2017).

### 3.6.2. XRF

XRF spectrometry is used as an elemental analysis technique. When the spectrometer is run, individual atoms will emit X-rays photons with characteristic energy and wavelength when excited by an external source. The present elements such as chromium, copper and cadmium may be identified and quantified by counting the number of photon in each energy emitted

from the sample. One of the advantages of this spectrometer is that, both major and trace components of the sample can be identified (Guthrie, 2012).

### 3.6.3. FT-IR

Infrared (IR) spectroscopy is an analytical method that monitors the vibrations of functional groups that characterise the molecular structure and also determine the course of chemical reactions. Infrared is an electro-magnetic radiation which falls in the region around  $0.7\ \mu\text{m}$  –  $1000\ \mu\text{m}$ . But, the region around  $2.5\ \mu\text{m}$  –  $25\ \mu\text{m}$  is the most important for chemical analysis because it corresponds to fundamental vibrations of functional groups of organic molecules (Petit and Puskar, 2018). In this region, narrow and distinct spectral lines are produced, which correspond to specific structural features (Harris, 2010). All FT-IR spectrometers have an amplitude division interferometer which contains a beamsplitter, a compensating plate and a pair of mirrors as shown in Figure 3.5.

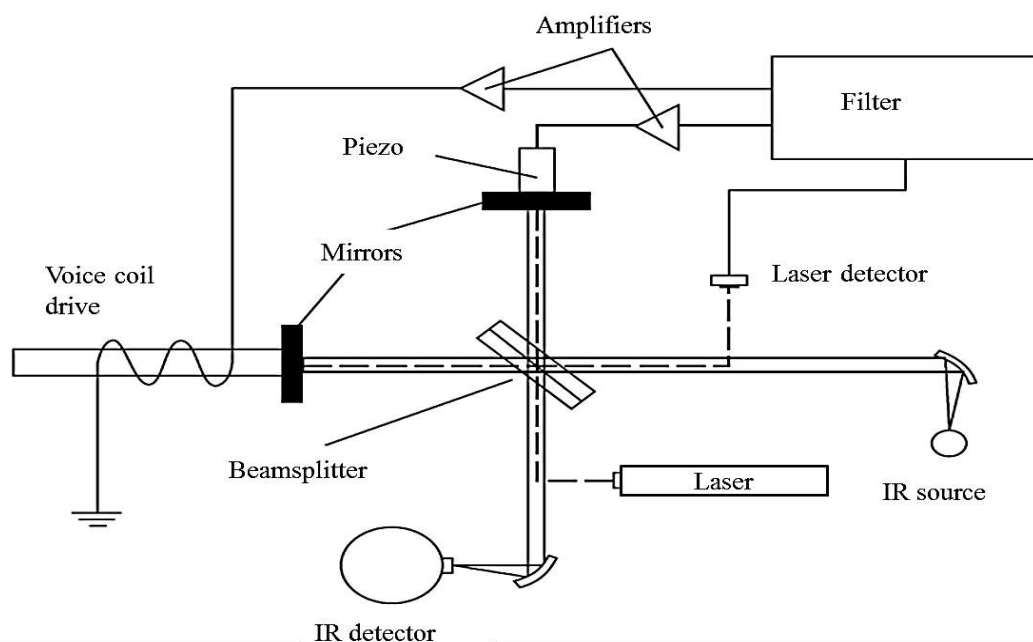


Figure 3.5: Schematics of a Michelson interferometer (Griffiths and Chalmers, 2006).

When the position of one of the mirrors is mechanically scanned, there is a difference in path length that results between the two arms. This difference gives rise to a time dependent

variation in transmitted optical intensity which is called interferogram. The electrical signal is obtained from the IR detector, the intensity of a given spectral point could be determined. The complete spectrum of a sample can be determined varying the filter frequency (Harris, 2010).

#### 3.6.4. SEM

SEM (Figure 3.6) allows for the observance of the structural morphology of surfaces of particles. SEM has an effective resolution around 1 nm. The design of SEM is similar to that of light microscope, but in electron microscope, electrons are used instead of light and electromagnetic or electrostatic lenses are used instead of glass lenses. SEM is a high vacuum system. When SEM is activated, an electron beam is formed at the tip of the heated filament and the electrons are accelerated with voltage between 0.2 – 30 kV. These electrons will be guided through the SEM column by the electromagnetic lenses. The electron beam formed is focused in the objective lens and a small beam is scanned over the material surface and interacts with the material. This is done using deflector coils. The electrons which are emitted will be detected by the detector (Kaech, 2013).

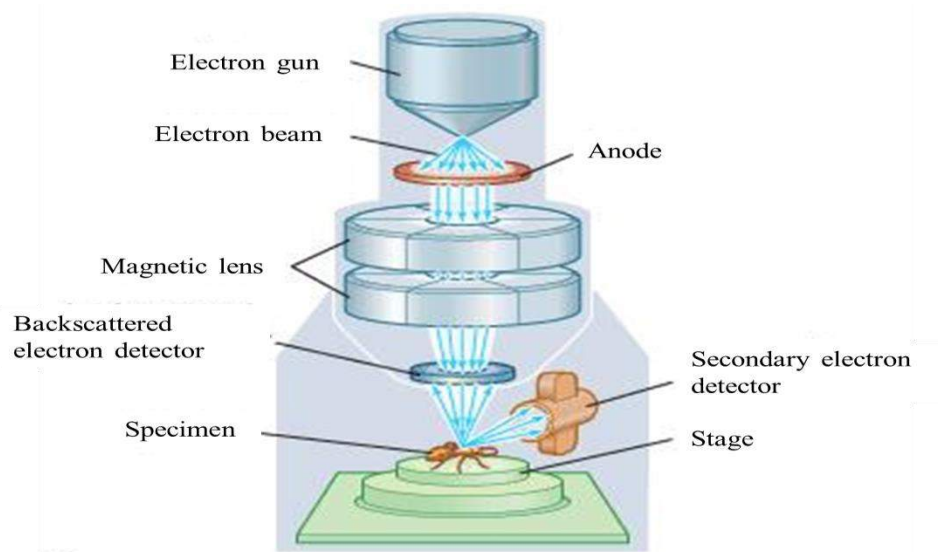


Figure 3.6: Scanning electron microscope (Joy et al., 2017).

# **CHAPTER 4:**

# **RESULTS AND**

# **DISCUSSION**

**This chapter reports the results  
obtained from this study in a form of  
either published or submitted  
manuscripts.**

### **The following sections include publications as part of the results and discussion**

Preliminary studies were conducted with all the synthesised adsorbents but, some did not work while some poorly recovered the elements. FTIR spectra indicated success on the functionalisation of zeolite and bentonite with ammonium ion but, the uptake was poor because the ammonium ions were not strongly attached to the materials. A study by Bakatula et al. (2015) indicated that the ammonium ions on the zeolite were replaced by the uranium ions due to the exchange process. Thus, amine modified adsorbents are suitable as cation exchangers. The functionalisation of the clay materials with polyethyleneimine, L-Lysine, L-Histidine and L-Arginine was not successful because the materials could not hold on to them. The mixing of ligands involving the ones mentioned above was also not successful.

The following chapters involve ligands which were able to attach onto the materials however, there was no significant difference ( $p > 0.05$ ) between the mixed and individual ligands on the materials therefore, only the materials functionalised with individual ligands were considered.

Section 5.1 includes papers focusing on the recovery of platinum by engineered materials, using batch studies.

Section 5.2 includes papers dealing with the recovery of palladium, iridium and rhodium using batch studies.

Section 5.3 reports on the recovery of rare earth elements using batch studies

Section 5.4 includes papers where column adsorption studies were used to determine the efficiency of the adsorbents on the recovery of precious elements.

Section 5.5 deals with the modelling of the recovery of palladium using PHREEQC geochemical model coupled to parameter estimation (PEST) thus, indicating that the recovery of other elements is possible when databases containing elements of interest are available.

# **SECTION 4.1:**

# **RECOVERY OF**

# **PLATINUM USING**

# **ENGINEERED**

# **MATERIALS**

# PAPER I

**This paper investigated the recovery of Platinum (IV) from aqueous solutions using hydrazine-functionalised zeolite.**

**The paper is published in Minerals Engineering. Impact Factor: 3.795.**

**Contribution:** lead author, conducted experimental work and data modelling, conceptualization, methodology, software validation, formal analysis, investigation, writing - original draft and visualization.



# The recovery of Platinum (IV) from aqueous solutions by hydrazine-functionalised zeolite

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## ARTICLE INFO

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## ABSTRACT

The recovery of platinum group elements (PGEs) which are normally lost during processing, can add value especially in times of declining commodities prices, high operational costs and weak economic growth. The recovery of platinum (Pt(IV)) from aqueous solutions with zeolite functionalised with hydrazine monohydrochloride ( $\text{NH}_2\text{NH}_2\cdot\text{HCl}$ ) was studied. The zeolite was characterised with powder X-ray diffraction (PXRD), X-ray fluorescence (XRF) and Fourier transform infrared (FTIR) spectroscopy. The effect of pH (2–9), concentration ( $0.5\text{--}10\text{ mg L}^{-1}$ ), contact time (0–540 min), adsorbent dosage (50–500 mg), competing ions ( $\text{Fe}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Hf}^{4+}$ ,  $\text{Zn}^{2+}$  and PGEs) on the recovery of Pt(IV) was studied. The recovery of Pt(IV) was found to be more effective in acidic pH (2–5). The adsorption capacity increased with concentration from  $0.5\text{ mg L}^{-1}$  to  $5\text{ mg L}^{-1}$  and remained constant beyond  $5\text{ mg L}^{-1}$ . A slight increase (9%) in the adsorption capacity of Pt(IV) was observed in the presence of competing ions which could be due to the synergistic Pt-Fe interaction. The experimental data was best described by Langmuir isotherm model ( $R^2 > 0.99$ ), indicating a monolayer adsorption. The adsorption behaviour was best described by pseudo second-order kinetic model ( $R^2 > 0.99$ ), implying a chemisorption process through Pt-N interaction. A cost-benefit analysis was done and indicated that  $\sim 120\text{ g Pt}$  can be recovered per kg adsorbent and this would amount to around \$3355 profit under the optimum conditions. These findings demonstrate the potential of this adsorbent for use in recovering low level concentrations of Pt and other PGEs.

## 1. Introduction

The development of many countries has been highly dependent on mining industries (Dubiński, 2013). However, during the processing of minerals such as gold, platinum and diamond, large amounts of waste is discharged into the environment, leading to significant environmental issues such as soil, air and water pollution (Fashola et al., 2016; Habashi, 2012; Jenkin et al., 2016; Falagán et al., 2017; Zhou et al., 2018; Han et al., 2018). Fresh water is affected by mining due to heavy use of water during ore processing. The mine waste rock impoundments and tailings from processing plants can cause pollution in water bodies due to direct or indirect discharges (Byrne et al., 2018). Water bodies, namely rivers, lakes, dams and streams always have to be protected from waste materials due to possible health risks to living organisms which are dependent on them (Hobbs et al., 2008).

The waste produced from mining plants is usually in the form of tailings and mine leachates which contain elements such as  $\text{Hg}^+$ ,  $\text{U}^{6+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cr}^{6+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{As}^{3+}$  which could be harmful to living organisms when they exceed threshold limits (Abollino et al., 2003;

Zhang et al., 2012; Cox et al., 2017; Arcos-Casarrubias et al., 2018). These elements can reach living organisms through ingestion via the food chain and inhalation (Ahmad et al., 2018). Notwithstanding the toxic nature of some of the elements that may be discharged, the waste may also contain significant amounts of valuable elements such as gold, platinum group elements (PGEs) such as platinum (Pt), osmium (Os), rhodium (Rh), palladium (Pd), iridium (Ir) and ruthenium (Ru), depending on the type of mineral ores that are processed. The losses of these elements into the environment can accumulate and become quite significant for PGE processing companies, especially in times of declining commodity prices, high operational costs and weak economic growth (Kumar et al., 2017).

Studies have been conducted to design methods that can be employed to remove elements accumulated in water bodies. For example, conventional methods such as coagulation, reverse osmosis, ion exchange and evaporation have been utilised in some instances. However they usually require high energy to operate and are rather generic and less selective for targeted elements (Bakatula, 2012; Fu and Wang, 2011; Fujiwara et al., 2007). Cost effective clay linings such as zeolite

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and bentonite have been found to be useful in adsorbing elements from water bodies and have therefore been applied in landfills to act as barriers that reduce groundwater pollution (Kaya and Durukan, 2004). Clay minerals have high specific surface areas and are cheap since they are readily available in the environment (Bailey et al., 1999; Allard et al., 2018).

In this study, zeolite functionalised with hydrazine was developed for selective recovery of Pt(IV) from aqueous solutions that closely resemble those found in PGE processing. The co-removal of other elements that are usually found alongside Pt in such solutions was also studied so as to establish the potential dual efficacy of the developed adsorbent.

## 2. Methodology

The precursor natural zeolite used in this study was supplied by Sigma-Aldrich (Pty) Ltd, South Africa. The precursor was crushed to a fine powder in order to get a homogeneous median (D50) grain size between 0.25 and 0.83  $\mu\text{m}$ .

### 2.1. Functionalisation of zeolite

The natural zeolite was functionalised with hydrazine monohydrochloride ( $\text{NH}_2\text{NH}_2\cdot\text{HCl}$ ) which was purchased from Sigma-Aldrich (Pty) Ltd, South Africa. A mass of 1.36 g of hydrazine was dissolved in 20 mL deionised water in a polypropylene container and 5 g zeolite was added. The contents were reacted in an automated Microwave-assisted Extraction monowave 450 (Anton Paar, South Africa) at 180 °C with a retention time of 30 min. The solution was cooled to room temperature and filtered using suction. Deionised water was used to remove excess hydrazine and chlorine. Silver nitrate was used to determine the removal of chlorine. The modified zeolite was then dried at 25 °C for 24 h and stored for further usage.

### 2.2. Characterisation

The natural and functionalised zeolite were characterised using Fourier transform infrared (FTIR) spectroscopy (Tensor 27, Bruker, Germany) to identify the functional groups on the zeolite, thus determining the success of functionalisation with hydrazine. Powder X-ray diffraction (PXRD) (Bruker D2 Phaser, Germany) using Ni-filtered Cu K $\alpha$  radiation was used to determine the mineralogy of the zeolite whilst X-ray fluorescence (XRF) (PANalytical, Netherlands) was used to determine the chemical composition. Thermogravimetric analysis (TGA) of the zeolite was done to investigate the thermal stability of the adsorbent at various temperatures (33–870 °C) using TGA 4000 Thermogravimetric Analyzer (Perkin Elmer, USA). The surface area of the natural and the functionalised zeolite was determined using the Micromeritics Flow Prep 060 instrument (Aachen, Germany). The point of zero charge ( $\text{pH}_{\text{PZC}}$ ) was determined using a method described by Fiol and Villacusa (2009). To determine  $\text{pH}_{\text{PZC}}$ , suspensions of 25 g L $^{-1}$  of adsorbent mass were mixed with 0.01 mol L $^{-1}$   $\text{KNO}_3$  and different pH's were adjusted with 0.01 mol L $^{-1}$  HCl and NaOH. The contents were then shaken for 24 h to reach equilibrium. The  $\text{pH}_{\text{PZC}}$  was then determined from the plot of  $\Delta\text{pH}$  and initial pH.

### 2.3. Reagents and standards

The chemicals used were purchased from Sigma Aldrich, South Africa and, there was no further purification done on the chemicals used as they were of analytical grade. Stock solutions of 10 mg L $^{-1}$  of platinum and other PGEs were prepared by diluting appropriate volumes in deionised water. The platinum was in the chloride form ( $\text{PtCl}_6^{2-}$ ) to simulate the form in which it is in at the deposition sites due to the use of acids such as HCl during their processing (Mowafy and Aly, 2007; Pan, 2009). The chloride aqueous medium of PGEs is widely

used in the industry to concentrate PGEs into solution (Bernardis et al., 2005). Other metal ion stock solutions ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{K}^+$ ,  $\text{Ni}^{2+}$ ,  $\text{Hf}^{4+}$  and  $\text{Zn}^{2+}$ ) were prepared from metal nitrate salts and deionised water. Nitric acid was added to the solutions for preservation and stored in a refrigerator at 4 °C. Working solutions were prepared on the day of experiments by making serial dilutions of the stock solutions.

### 2.4. Adsorption experiments

Batch experiments were carried out by adding 200 mg of adsorbent and 10 mL (which were obtained from optimisation) of platinum solutions i.e. dosage of 20 g L $^{-1}$  in plastic bottles using varying conditions. The contents were shaken using an automated shaker (Labcon, USA) at a speed of 150 rpm and were filtered using a 0.45  $\mu\text{m}$  cellulose nitrate Filtech filter paper. The metal content in the filtrates was determined using inductively coupled plasma-optical emission spectroscopy (ICP-OES) (Spectro Genesis, Spectro, Germany).

#### 2.4.1. Effect of adsorbent dosage

Different masses of the functionalised zeolite (50 – 500 mg) were added to 10 mL of Pt solutions (2 mg L $^{-1}$ ) at pH 2 and shaken for 6 h at 25 °C to determine the effect of adsorbent dosage. The pH of 2 is the pH of the solutions as they are discharged from the refining process. Thus, the chosen pH was meant to simulate these solutions. The  $\text{pH}_{\text{PZC}}$  was 5.6. This means that the adsorbent surface at pH 2 is positively charged and thus the negatively charged Pt chloride species would be adsorbed. After the equilibration time, the contents were filtered and the remaining filtrate was analysed with ICP-OES to determine the amount of Pt remaining.

#### 2.4.2. Effect of concentration

The effect of concentration (0.5–10 mg L $^{-1}$ ) on the adsorption of platinum was determined as this is an important parameter in determining the efficiency of the adsorbent on recovery. The amount of the adsorbent was kept constant at 200 mg with a constant volume of 10 mL. Varying concentrations of Pt(IV) at pH 2 were shaken at 25 °C with a speed of 150 rpm for 6 h (determined from optimisation). After the equilibration time the contents were filtered and analysed with ICP-OES to determine equilibrium concentrations. Adsorption isotherms were evaluated at different initial concentrations of Pt(IV) solutions. The modelling of the data from this part of the study was conducted using isotherm models, according to the description given in the data treatment section.

#### 2.4.3. Effect of contact time

The study of the effect of contact time on the adsorption of Pt(IV) was done to determine the equilibration time between Pt(IV) and the adsorbent. Constant mass (200 mg) was added to 10 mL Pt(IV) solutions (2 mg L $^{-1}$ ) at pH 2 and shaken with a speed of 150 rpm at room temperature at different times (0–540 min). The contents were filtered immediately after shaking at specific times and analysed with ICP-OES. The modelling of the data from this part of the study was conducted using kinetic models, according to the description given in the data treatment section.

#### 2.4.4. Effect of pH

The performance of adsorbents can be affected by solution pH and since the mining leachates can have different pH values (as a result of changes following discharge), it is important to determine the effect of varying pH on the adsorption of Pt(IV). 2 mg L $^{-1}$  of 10 mL Pt(IV) solutions were added to plastic containers after adjusting pH (2–9) with NaOH and HCl. An adsorbent mass of 200 mg was then added and shaken at 25 °C for 6 h. The contents were then filtered and the concentration of Pt(IV) was analysed with ICP-OES.

#### 2.4.5. Effect of competing ions

Discharges from mining plants do not contain elements in isolation, but usually in a mixture containing other elements. Thus, the effect of competing ions ( $\text{Fe}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Hf}^{4+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Rh}^{3+}$ ,  $\text{Ir}^{3+}$ ,  $\text{Os}^{3+}$ ,  $\text{Ru}^{3+}$  and  $\text{Pd}^{2+}$ ) on the adsorption of Pt(IV) was determined. In order to determine their effect, a mixed solution of Pt (IV) and competing ions (of  $2 \text{ mg L}^{-1}$ ) was prepared at pH 2. The adsorption of the competing ions was also determined to assess their extent of adsorption by the adsorbent. Thus, the ability of the adsorbent to adsorb multi-element was determined. An adsorbent mass of 200 mg was added to 10 mL of the mixed solution and shaken for 6 h at  $25^\circ\text{C}$ . The solution was filtered and analysed with ICP-OES.

#### 2.4.6. Data analysis

**2.4.6.1. Adsorption capacity and efficiency.** The amount of adsorbed Pt (IV) at equilibrium i.e.  $q_e$  ( $\mu\text{g g}^{-1}$ ) and adsorption efficiency were calculated using Eqs. (1) and (2), respectively:

$$q_e = \frac{(C_0 - C_e)V}{M} \times 1000 \quad (1)$$

$$\% \text{ adsorption} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

where  $C_0$  and  $C_e$  are initial and equilibrium liquid-phase concentrations of Pt(IV), respectively and  $V$  is the volume of the solution in litres (L) whilst  $M$  is the mass of the adsorbent used in grams (g).

**2.4.6.2. Adsorption isotherm models.** The Langmuir, Freundlich and Dubunin-Radushkevich (D-R) adsorption isotherm models were used to determine the type of adsorption occurring between functionalised zeolite and Pt(IV). The physicochemical parameters obtained from the models can provide information about the affinity of an element to the surface of adsorbents, surface properties and adsorption mechanisms (Bulut et al., 2008). The Langmuir isotherm mathematically explains the monolayer adsorption between adsorbates and adsorbents, and how the adsorption energy decreases as the distance between the adsorbate and surface of the adsorbent increases (Langmuir, 1916 (as cited by El Massaoudi et al., 2017); Putro et al., 2017). The linearized form can be expressed as:

$$\frac{C_e}{q_e} = \left( \frac{1}{q_m} \right) C_e + \left( \frac{1}{K_L q_m} \right) \quad (3)$$

where  $q_e$  is the quantity of the adsorbate adsorbed per gram of adsorbent at equilibrium ( $\text{mg g}^{-1}$ ),  $C_e$  is the concentration of adsorbate at equilibrium ( $\text{mg L}^{-1}$ ),  $q_m$  is the maximum monolayer coverage capacity ( $\text{mg g}^{-1}$ ) and  $K_L$  is the Langmuir isotherm constant ( $\text{L mol}^{-1}$ ) which can be described as the measure of the elements affinity for the surface (Langmuir, 1916). The constants  $q_m$  and  $K_L$  were obtained from the slope and intercept (respectively) of the plot of ( $C_e/q_e$ ) versus  $C_e$ .

The Langmuir isotherm has an important characteristic which can be expressed in terms of a dimensionless constant separation factor,  $R_L$  which indicates the affinity of the adsorbate to the adsorbent and can be defined as (Gupta et al., 1998):

$$R_L = \frac{1}{1 + C_0 K_L} \quad (4)$$

where  $C_0$  ( $\text{mg L}^{-1}$ ) is the initial metal ion concentration. The  $R_L$  values can be used to describe the adsorption type as follows:

$R_L > 1$  (unfavourable),  $R_L = 1$  (linear),  $R_L = 0$  (irreversible), and  $0 < R_L < 1$  (favourable).

The Freundlich isotherm is based on the non-ideal and reversible adsorption of elements onto the heterogeneous surface (Hutson and Yang, 2000). There is no uniform distribution of adsorption heat and affinities over the heterogeneous surface (Aljeboree et al., 2017). Moreover, the adsorption of elements onto the surface of adsorbents is

the summation of adsorption on all adsorption sites with specific bond energy. The isotherm assumes that stronger binding sites of the adsorbents are occupied first until adsorption energy is exponentially decreased upon the completion of adsorption process (Zeldowitsch, 1934 (as cited by Foo and Hameed, 2010)). The Freundlich isotherm can be expressed as follows:

$$q_e = K_f C_e^{\frac{1}{n}} \quad (5)$$

where  $K_f$  ( $(\text{mg g}^{-1})/(\text{mol L}^{-1})^{1/n}$ ) is the Freundlich isotherm constant and  $n$  is the adsorption intensity or surface heterogeneity (Bradil, 2004).

The Dubinin-Radushkevich (D-R) isotherm expresses the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface. It is usually applied to distinguish between the physical and chemical adsorption of elements onto surfaces using the mean free energy ( $E_s$ ) (Eq. (8)). This isotherm model is different from other models since it is temperature-dependent (Liu et al. 2018). The equation used for this model is as follows:

$$\ln q_e = \ln X_m - K_{ad} \varepsilon^2 \quad (6)$$

where

$$\varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \quad (7)$$

The parameters are:  $K_{ad}$  is the Dubinin-Radushkevich isotherm constant ( $\text{mol}^2 (\text{kJ}^2)^{-1}$ ),  $X_m$  is theoretical isotherm saturation capacity ( $\text{mg g}^{-1}$ ),  $\varepsilon$  is the Polanyi constant,  $R$  is the universal gas constant ( $\text{J (mol} \cdot \text{K)}^{-1}$ ),  $T$  is temperature (K).

The free energy change,  $E_s$  ( $\text{kJ mol}^{-1}$ ) required to transfer one mole of ion from infinity in the solution to the solid surface can be obtained from the equation:

$$E_s = \frac{1}{\sqrt{2K_{ad}}} \quad (8)$$

**2.4.6.3. Kinetic models.** In addition to adsorption isotherms, kinetic models have been widely used in adsorption studies to assess the controlling mechanism of the adsorption process between elements and adsorbents (Bakatula et al., 2015). The  $R^2$  statistical value was used to determine the applicability of the kinetic model equation to describe the adsorption as well as the closeness of the experimental adsorption capacity,  $q_m$  to the calculated one,  $q_{cal}$ . The pseudo first-, second-order kinetic and Elovich kinetic models were used and the equations are shown below, respectively.

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (9)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (10)$$

$$\frac{dq_t}{dt} = a \cdot \exp(-b \cdot q_t) \quad (11)$$

where  $q_t$  and  $q_e$  are the adsorption capacities ( $\text{mg g}^{-1}$ ) at time  $t$  (experimentally obtained) and at equilibrium,  $k_1$ ,  $k_2$  are the rate constants,  $a$  is the initial adsorption rate ( $\text{mg g}^{-1} \text{ min}^{-1}$ ) and  $b$  is a constant ( $\text{mg g}^{-1} \text{ min}^{-1}$ ) (Cui et al., 2012; Abdehagh et al., 2013; Mohanta and Ahmaruzzaman, 2018).

### 3. Results and discussion

#### 3.1. Characterisation

The constituents of the natural zeolite as determined by XRF are reported in Table 1. Silica ( $\text{SiO}_2$ ) was the main component of the adsorbent and was mainly responsible for the attachment of hydrazine. Studies have shown that nitrogen can interact with silica through  $\text{SiO}_2\text{—NH}_2$  hydrogen bonding and this is likely the reaction that

**Table 1**

The chemical composition of natural zeolite.

| Compound                       | Percentage composition (wt. %) |
|--------------------------------|--------------------------------|
| SiO <sub>2</sub>               | 68.49                          |
| Al <sub>2</sub> O <sub>3</sub> | 11.58                          |
| Fe <sub>2</sub> O <sub>3</sub> | 1.09                           |
| MnO                            | 0.02                           |
| MgO                            | 0.77                           |
| CaO                            | 1.22                           |
| Na <sub>2</sub> O              | 1.47                           |
| K <sub>2</sub> O               | 3.79                           |
| TiO <sub>2</sub>               | 0.12                           |
| P <sub>2</sub> O <sub>5</sub>  | 0.03                           |
| Cr <sub>2</sub> O <sub>3</sub> | 0.01                           |
| Loss on ignition (LOI)         | 11.3                           |

occurred between zeolite and hydrazine (Nonella and Seeger, 2008). Other major chemical components of the zeolite were Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, CaO, Na<sub>2</sub>O and K<sub>2</sub>O with a loss on ignition of 11.3%. The Si/Al ratio was calculated from the data and found to be 5.91, which indicated that the zeolite had high negative charges (Camacho et al., 2010). The results for PXRD are shown in Fig. 1 and the high counts observed were mostly due to clinoptilolite and thus the natural adsorbent used was clinoptilolite zeolite. Quartz (SiO<sub>2</sub>) was also observed at higher counts and this, along with other observations, substantiated the results obtained from XRF. Camacho et al. (2010) and Tahervand and Jalali (2017) also reported on clinoptilolite zeolite with similar results. The mineral sanidine (K(AlSi<sub>3</sub>O<sub>8</sub>)) was also observed from the PXRD pattern. No change in mineralisation was observed on the zeolite after functionalisation with hydrazine. The results from FTIR (Fig. 2) confirmed that the attachment of hydrazine onto zeolite was successful since the N-H broad band due to NH<sub>2</sub> and Si-N stretch were observed at 3340 cm<sup>-1</sup> and 1500 cm<sup>-1</sup>, respectively. The surface area (m<sup>2</sup> g<sup>-1</sup>), pore volume (cm<sup>3</sup> g<sup>-1</sup>) and pore size (nm) were found to be 16.28, 0.0516 and 12.97, respectively.

The surface area, pore size and pore volume of the natural and the modified zeolite are summarised in Table 2. The pore volume and the surface area of the natural zeolite slightly increased from 0.052 to 0.053 cm<sup>3</sup> g<sup>-1</sup> and 16.28 to 18.47 m<sup>2</sup> g<sup>-1</sup>, respectively after functionalisation. This slight increase means that the micropore was only minimally altered by functionalisation with hydrazine (Li et al., 2006).

The thermal stabilities of the natural and the functionalised zeolite were determined and the results are reported in Fig. 3. There was a

significant weight loss that was observed at temperatures > 60 °C for both zeolites and this can be attributed to the loss of free and physically adsorbed water onto the zeolite pores (Musyoka et al., 2015). Usachev et al. (2003) studied the thermal stability of zeolites and concluded that the weight loss of the zeolite beyond 200 °C can be attributed to the loss of water from the hydration complexes which were formed with exchangeable ions. The notable decrease of weight loss in the functionalised zeolite beyond 300 °C can be attributed to the dehydroxylation (Musyoka et al., 2015). Around 845 °C for the natural zeolite and 855 °C for the functionalised zeolite, there was a notable decrease in the derivative curves which can be attributed to the changing zeolite structural framework due to the liberation of surface energy caused by decreasing surface area (Musyoka et al., 2015). The natural and the functionalised zeolite were stable at temperatures less than 850 °C. It can be concluded from the graphs that the weight loss of the hydrazine-functionalised zeolite will be reached at slightly lower temperatures than the natural zeolite but, the stability of the functionalised zeolite was approximately 10 °C more than the natural zeolite.

### 3.2. Effect of adsorbent dosage

The effect of dosage on the adsorption of Pt(IV) was determined and the results indicated that the adsorption efficiency increases with increasing dosage (Fig. 4). This can be attributed to the availability of more binding sites for Pt. However, beyond 200 mg, the adsorption efficiency increases only slightly and finally reaches a plateau which can be attributed to the shortage of Pt(IV) in the solution. In fact, the adsorption capacity decreases beyond 200 mg due to the existence of more adsorption sites with no Pt(IV) to adsorb. This is because the adsorption capacity is expressed as adsorbed amount per unit mass of adsorbent. As such, the latter is increasing while the former is constant. The maximum adsorption capacity (0.12 mg g<sup>-1</sup>) of Pt(IV) was reached at 20 g L<sup>-1</sup> dosage at a concentration of 2 mg L<sup>-1</sup>.

### 3.3. Effect of pH

The effect of pH on the adsorption of Pt(IV) is presented in Fig. 5. The adsorption capacity was found to be strongly affected by pH. A decrease in adsorption was observed with increasing pH and this trend might be caused by the speciation of Pt at different pH levels. A high adsorption capacity was observed in more acidic conditions (pH 2–5) with maximum adsorption achieved at pH 2, which is an important outcome as most discharges from PGE processing are around this pH or

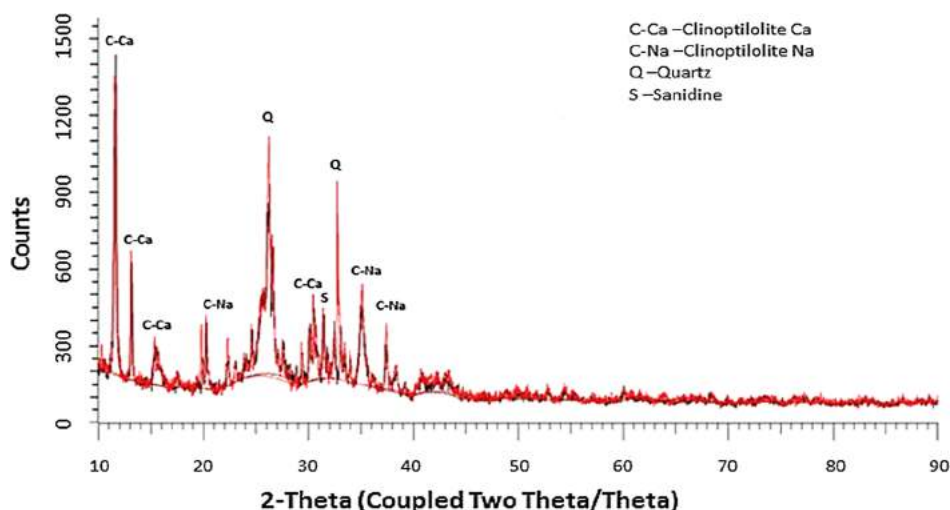


Fig. 1. PXRD pattern of the natural zeolite (black) and hydrazine-functionalised zeolite (red). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

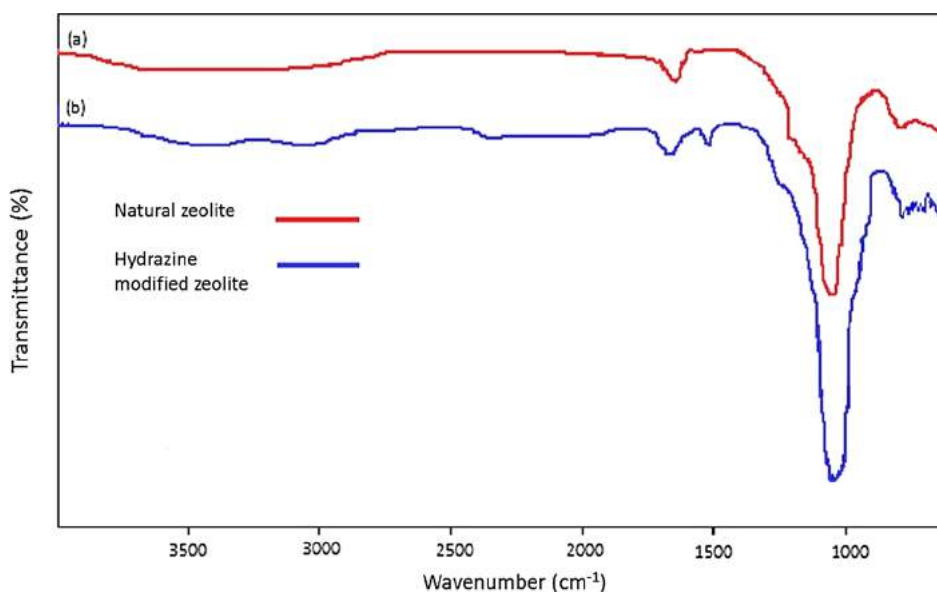


Fig. 2. FTIR spectra of (a) natural zeolite and (b) hydrazine-functionalised zeolite.

**Table 2**

The physical properties of the natural and the hydrazine-functionalised zeolite.

| Sample                           | Pore size (nm) | Pore volume (cm <sup>3</sup> g <sup>-1</sup> ) | Surface area (m <sup>2</sup> g <sup>-1</sup> ) |
|----------------------------------|----------------|------------------------------------------------|------------------------------------------------|
| Natural zeolite                  | 12.97          | 0.052                                          | 16.28                                          |
| Hydrazine functionalised zeolite | 11.63          | 0.053                                          | 18.47                                          |

lower. Platinum exists in the form  $\text{PtCl}_6^{2-}$  around the mining areas due to the process used in the refining steps known as chloride hydrometallurgy (Milbourne et al., 2003; Tagirov et al., 2017). Thus, the chloride ions interact with the PGE elements to form their chloride species. The anionic form of platinum was favourable for adsorption onto the positively charged surface. At acidic pH regions (2–5), there are more chloride ions due to HCl that interact with platinum to form chloro-ion-complexes of platinum. The negative character of the functionalised zeolite decreased above pH 5 as the  $\text{pH}_{\text{pzc}}$  was found to be 5.6. Hence, the adsorption of  $\text{PtCl}_6^{2-}$  was observed to decrease drastically. Thus, beyond pH 5, the anionic species were unfavourable for adsorption onto the negatively charged adsorbent surface, most likely due to repulsion. The negative character of the adsorbent was likely influenced by increasing hydroxide ions as pH increased. Similar results were reported by Ramesh et al. (2008) who used a glycine modified crosslinked chitosan resin to adsorb platinum. Zhou et al. (2010) used magnetic cross-linking chitosan nanoparticles modified with ethylenediamine to recover platinum and found that maximum adsorption was achieved at pH 2. Thus, the optimum pH for this study was chosen to be pH 2. The ability of the adsorbent to behave well even in highly acidic conditions makes it a suitable material for the recovery in the natural environment since the deposition site solutions are very acidic ( $\sim$  pH 2) due to the acids used during the processing of PGEs.

### 3.4. Effect of concentration

The effect of initial concentration of Pt(IV) was studied and the results are shown in Fig. 6. The adsorption capacity increased quite significantly from 0.5 to 2 mg L<sup>-1</sup> followed by a low increase to 5 mg L<sup>-1</sup>. The increase in the adsorption capacity can be attributed to the availability of adsorption sites and the increasing driving force of concentration gradient rather than increasing concentration. Thus, the

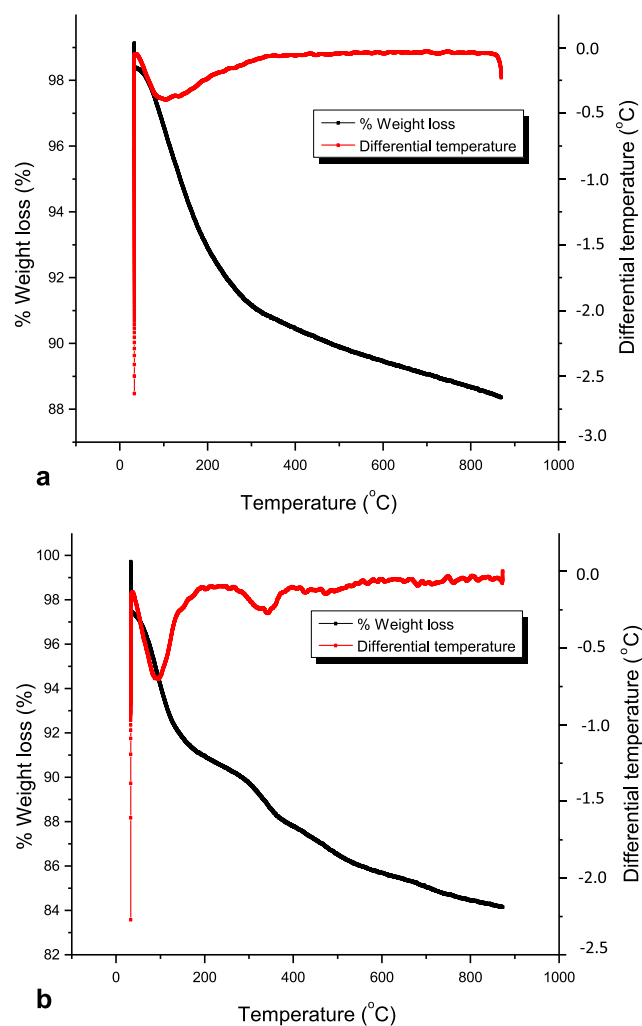


Fig. 3. Thermogravimetric and differential thermogravimetric analysis curves of the (a) natural and (b) hydrazine-functionalised zeolite.

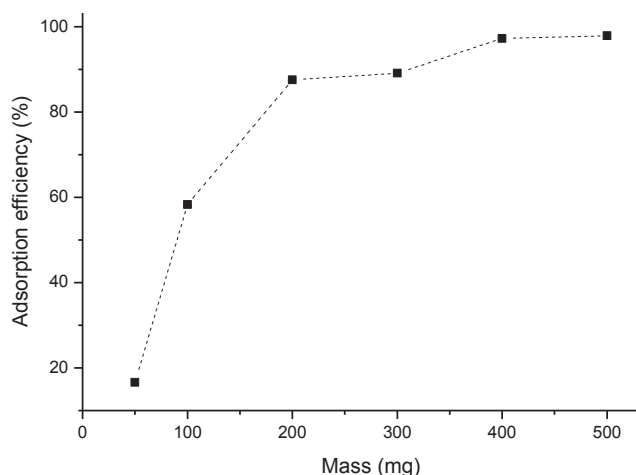


Fig. 4. Effect of dosage on the adsorption of Pt on hydrazine-functionalised zeolite (Conc =  $2 \text{ mg L}^{-1}$ , Temp =  $25^\circ\text{C}$ , volume = 10 mL, time = 6 hrs, pH 2,  $n = 3$ , RSD < 10%).

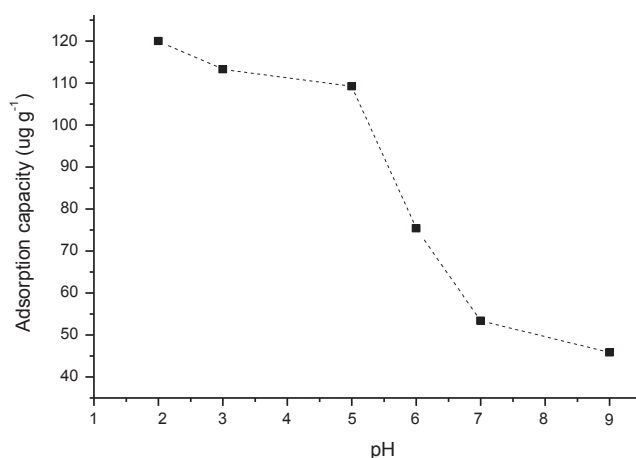


Fig. 5. Effect of pH on the adsorption of Pt on hydrazine-functionalised zeolite (Conc =  $2 \text{ mg L}^{-1}$ , Temp =  $25^\circ\text{C}$ , volume = 10 mL, time = 6 h, mass = 200 mg,  $n = 3$ , RSD < 10%).

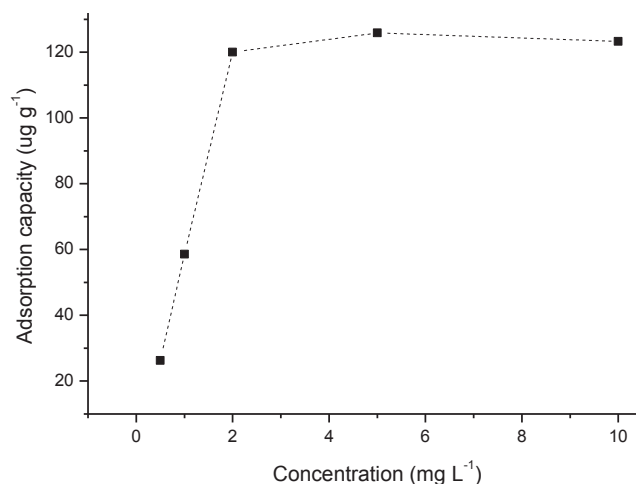


Fig. 6. Effect of concentration on the adsorption of Pt on hydrazine-functionalised zeolite (Temp =  $25^\circ\text{C}$ , volume = 10 mL, time = 6 h, mass = 200 mg, pH 2,  $n = 3$ , RSD < 10%).

more the Pt(IV) species available, the greater the adsorbent-adsorbate affinity hence, high adsorption observed. The adsorption of Pt(IV) occurred due to the presence of N on the surface of the zeolite since, the adsorption capacity of Pt(IV) on the natural zeolite was found to be  $< 10 \mu\text{g g}^{-1}$ . Platinum has strong interactions with N since, studies have shown that the stability constants between Pt and N are high ( $\log K > 10$ ) at  $25^\circ\text{C}$  (Wood et al., 1989; Fujiwara et al., 2007). The adsorption efficiencies were found to be 82, 91, 93, 39 and 58% at 0.5, 1, 2, 5 and  $10 \text{ mg L}^{-1}$ , respectively. A small reduction in adsorption capacity was observed at  $10 \text{ mg L}^{-1}$  which can be attributed to the full occupation of the N binding sites in the adsorbent. Thus, the available sites for adsorption at a given dosage could adsorb up to a certain concentration of Pt(IV) until the binding sites are fully occupied. Hence, a decrease in adsorption capacity owing to high Pt(IV) concentration was observed. Thus, for the optimised conditions used, the maximum efficiency of hydrazine-functionalised zeolite will be achieved at concentrations  $< 5 \text{ mg L}^{-1}$ .

#### 3.4.1. Adsorption isotherms

The results for adsorption isotherms are presented in Table 3. To recap, the Langmuir isotherm is based on monolayer adsorption of species on active sites of the adsorbents whilst the Freundlich isotherm is based on adsorption onto a heterogeneous surface. The D-R isotherm expresses the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface. The results indicated that the adsorption of Pt(IV) was through monolayer adsorption since Langmuir isotherm described the data way better than other isotherms ( $R^2 > 0.998$ ). The failing of other isotherms to describe the experimental data can be attributed to the fact that Pt(IV) reacts only with N-groups from hydrazine and no other functional groups on the zeolite.

The separation factor for Pt(IV) onto the adsorbent was found to be between 0 and 1, indicating that hydrazine-functionalised zeolite had strong affinity for Pt(IV) and thus favourable adsorption.

Although the Freundlich and D-R isotherms did not fit the data as the Langmuir isotherm, some of their parameters remain informative about the adsorption process. For instance, the adsorption intensity obtained from the Freundlich isotherm was high ( $n > 4$ ), indicating that the adsorption was favourable under the studied conditions. The adsorption energy ( $E_a$ ) from the D-R isotherm was found to be  $17.24 \text{ kJ mol}^{-1}$ , indicating that the reaction between Pt(IV) and the functionalised zeolite was chemisorptive in nature. This describes a strong chemical interaction.

#### 3.5. Effect of contact time

The time it takes for Pt(IV) adsorption to reach equilibrium was determined in order to get an indication of the kinetic efficiency of the adsorbent. The adsorption was observed to increase with time (Fig. 7). There was rapid initial uptake which was followed by slow uptake. The results showed that 300 min was the sufficient time for maximum ( $> 90\%$ ) adsorption of Pt since the adsorption was constant beyond 300 min, indicating that equilibrium had been reached and thus, was now controlled by diffusion.

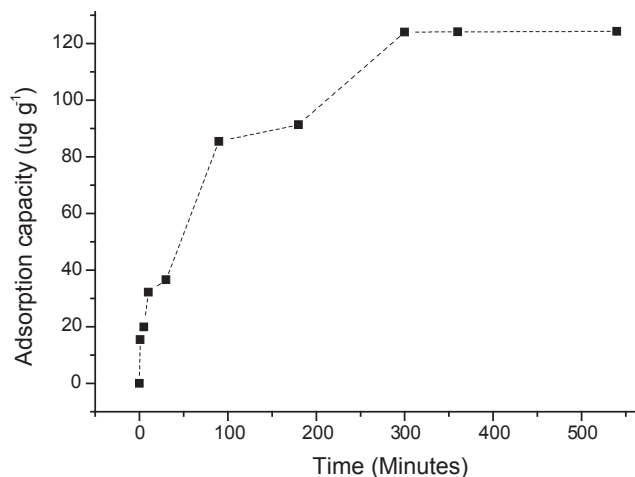
#### 3.6. Kinetic models

The kinetic models were used to fit the experimental data and the results are presented in Table 4. The pseudo second-order model was found to give the best fit ( $R^2 > 0.99$ ) for the data, indicating that the chemisorptive process was the rate controlling mechanism (Bakatula, 2012). The adsorbed amounts obtained experimentally were close to those determined by the model which indicated that the nature of adsorption was concentration dependent and thus the controlling step was a chemisorptive process. The calculated amount in the pseudo first-order model was very small compared to the experimentally determined amount, further affirming that the pseudo second-order was

**Table 3**

Langmuir, Freundlich and Dubinin Radushkevich isotherm constants for Pt(IV) adsorption onto hydrazine-functionalised zeolite at 25 °C (298 K).

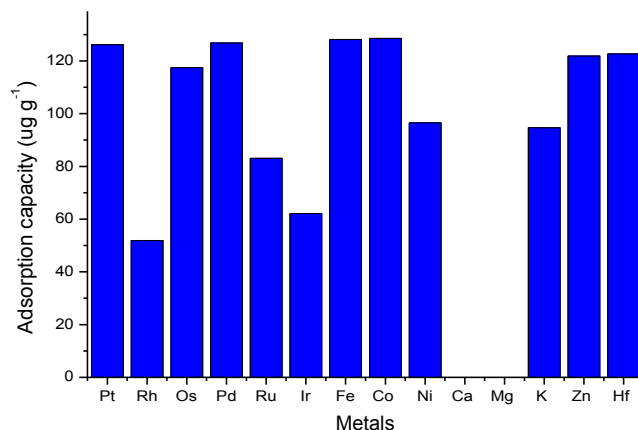
| Langmuir                    |                              |       | Freundlich                                                           |       |       | Dubinin-Radushkevich        |                               |       |
|-----------------------------|------------------------------|-------|----------------------------------------------------------------------|-------|-------|-----------------------------|-------------------------------|-------|
| $q_m$ (mg g <sup>-1</sup> ) | $K_L$ (L mol <sup>-1</sup> ) | $R^2$ | $K_f$ ((mg g <sup>-1</sup> )/(mol L <sup>-1</sup> ) <sup>1/n</sup> ) | $n$   | $R^2$ | $X_m$ (mg g <sup>-1</sup> ) | $E_s$ (kJ mol <sup>-1</sup> ) | $R^2$ |
| 0.117                       | $1.6 \times 10^6$            | 0.998 | 1.68                                                                 | 4.059 | 0.567 | 0.41                        | 17.24                         | 0.59  |

**Fig. 7.** Effect of contact time on the adsorption of Pt on hydrazine-functionalised zeolite (Conc = 2 mg L<sup>-1</sup>, Temp = 25 °C, volume = 10 mL, mass = 200 mg, pH 2, n = 3, RSD < 10%).

the rate controlling step.

### 3.7. Effect of competing ions

Since Pt(IV) occurs with a host of other elements in waste aqueous solutions, it was important to assess the effect that other elements would have on the adsorption of Pt(IV) (Anderson et al., 2003). In this study, the concentration of Pt(IV) and the competing elements (mixture) was kept at 2 mg L<sup>-1</sup>. 10 mL of this solution at pH 2 was contacted with 200 mg of the adsorbent for 300 min was used. The results are shown in Fig. 8 which shows the adsorption capacities of Pt(IV) and all the elements in a mixture with Pt(IV). The results indicated that the adsorption of Pt(IV) was not negatively affected by the presence of other elements which include PGEs (Pd<sup>2+</sup>, Rh<sup>3+</sup>, Ir<sup>3+</sup>, Ru<sup>3+</sup> and Os<sup>3+</sup>) and contaminants (Fe<sup>3+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Hf<sup>4+</sup> and Zn<sup>2+</sup>). Instead, the adsorption capacity of Pt(IV) increased by approximately 9% and this could be attributed to the presence of Fe<sup>3+</sup> which has been found to form complexes with other elements. Duchesne et al. (2014) studied the reaction between platinum and iron oxide and found that there is electrochemical stability between platinum and iron oxide nanoparticles. Baak and Hornyak (1961) found that it was impossible to reach equilibrium for Fe<sup>2+</sup>/Fe<sup>3+</sup> owing to the reaction between platinum and iron. The adsorption of iron onto the functionalised zeolite was also high, further affirming strong interactions with the adsorbent hence, the activated adsorbent had affinity for Pt(IV) even in the presence of other elements (Rosenberg, 1997). The results also show that the adsorption of other elements in the mixture

**Fig. 8.** The adsorption capacities of Pt(IV) and other elements removed from the same aqueous solution by hydrazine-functionalised zeolite (Conc = 2 mg L<sup>-1</sup>, Temp = 25 °C, volume = 10 mL, time = 6 hrs, pH 2, mass = 200 mg, n = 3, RSD < 10%).

(PGEs and contaminants) was significant since, their adsorption capacities were high. Thus, the adsorbent has dual efficacy i.e. recovery of precious elements and the removal of contaminants from water. The concentrations of Ca and Mg after the equilibration time were higher than the initial concentration used and this can be attributed to the detachment of these elements from the zeolite and thus, adding to the initial concentration used. This might have occurred because of the ion exchange with other elements such as Zn, Co and Ni.

### 3.8. Indicative cost-benefit analysis

An indicative cost-benefit analysis was done to determine if the application of the adsorbent will be economically viable for the recovery of Pt(IV) and other PGEs from mine leachates. In order to determine this, the costs used for the functionalisation of zeolite were included, viz: zeolite, hydrazine monohydrochloride and energy. Zeolite is cost effective as it is found naturally and is available in many parts of the world (Misaelides, 2011). Eq. (12) was used to determine the cost-benefit analysis. Using the optimised conditions and parameters, 120 g of Pt(IV) can be recovered using 1 kg of the functionalised zeolite. The prices were in USD.

#### Recovery of Pt only:

$$1 \text{ g Pt} = \$30 \text{ (Markets insider, 2018)}$$

$$120 \text{ g Pt} = 120 \times \$30 = \$3600$$

**Table 4**

Kinetic parameters of Pt(IV) adsorption onto hydrazine-functionalised zeolite at 25 °C (298 K).

| Pseudo first-order                |                                             |                             |       | Pseudo-second order                           |                             |       | Elovich                                                    |                                           |       |
|-----------------------------------|---------------------------------------------|-----------------------------|-------|-----------------------------------------------|-----------------------------|-------|------------------------------------------------------------|-------------------------------------------|-------|
| $q_e$ (exp)<br>mg g <sup>-1</sup> | $k_1$<br>min <sup>-1</sup> 10 <sup>-3</sup> | $q_e$<br>mg g <sup>-1</sup> | $R^2$ | $k_2$<br>g mg <sup>-1</sup> min <sup>-1</sup> | $q_e$<br>mg g <sup>-1</sup> | $R^2$ | A<br>g mg <sup>-1</sup> min <sup>-1</sup> 10 <sup>-7</sup> | b<br>g mg <sup>-1</sup> min <sup>-1</sup> | $R^2$ |
| 0.10                              | 17.7                                        | 0.03                        | 0.95  | 0.26                                          | 0.13                        | 0.99  | 4.95                                                       | 48.7                                      | 0.95  |

**Table 5**  
Maximum adsorption efficiencies for the adsorption of Pt(IV) and other elements on different adsorbents.

| Adsorbent                                                                   | Element | pH  | Contact time (h) | Adsorption efficiency (%) | Reference               |
|-----------------------------------------------------------------------------|---------|-----|------------------|---------------------------|-------------------------|
| Biochar Sd350                                                               | Nd      | 3   | 24               | 78.6                      | Komnitsas et al. (2017) |
| Activated carbon                                                            | Sc      | 3   | 24               | 76.8                      | Komnitsas et al. (2017) |
| poly( <i>N</i> -(hydroxymethyl)methacrylamide-1-allyl-2-thiourea) hydrogels | Pt(IV)  | 0.5 | 48               | 92.6                      | Döker et al. (2005)     |
| Hydrazine-functionalised zeolite                                            | Pt(IV)  | 2   | 6                | 93                        | This study              |

$$\begin{aligned}
 \text{Net profit} &= \$3600 - \text{functionalisation cost} \\
 &= \$3600 - (\text{cost of zeolite} + \text{cost of hydrazine monohydrochloride} \\
 &\quad + \text{energy}) \text{ kg}^{-1}\text{zeolite} \\
 &= \$3600 - (\$6 + \$227 + \$12) \\
 &= \$3600 - \$245 = \$3355
 \end{aligned}
 \tag{12}$$

#### Recovery of Pt, Rh, Pd and Ir:

Based on the findings from the effect of competing ions, a combined cost-benefit analysis can be conducted to assess the implication of recovering Pt together with the other most expensive PGEs, namely Rh, Pd and Ir. The prices of 1 g Rh, Pd and Ir are \$39, \$30 and \$36, respectively (InfoMine, 2018). Moreover, 1 kg hydrazine-functionalised zeolite will recover 47.61 g (\$1858), 121.9 g (\$3657) and 58.1 g (\$2092) of Rh, Pd and Ir, respectively. The following steps show how the cost-benefit analysis of combined Pt, Rh, Pd and Ir was calculated using 1 kg hydrazine-functionalised zeolite.

$$\begin{aligned}
 \text{Net profit}_{\text{Pt,Rh,Pd,Ir}} &= (\$3600 + \$1858 + \$3657 + \$2092) \\
 &\quad - \text{functionalisation cost} \\
 &= \$11,207 - \$245 = \$10,962
 \end{aligned}$$

Therefore, the net profit that can be made with 1 kg hydrazine-functionalised zeolite is \$10,962.

The two recoveries show that the proposed adsorbent can be used for the recovery of Pt(IV) and other PGEs from leachates. The typical application can be sprinkling the adsorbent into vessels containing highly acidic wastewater discharged from processing. As more solutions are discharged into the vessels, more adsorbent can be applied, with occasional agitation of the vessels. The sludge in the vessels can be dredged and taken to the process feed points after three days, where the adsorbed elements can be extracted alongside fresh ore. For this reason, there were no desorption studies conducted as there was no intention of reusing the adsorbent. Generally, the adsorption efficiencies observed in the study are higher than what has been observed using commercial and other functionalised adsorbents at temperatures less than 35 °C of which most had recovery efficiencies around 70% (Parajuli et al., 2007; Xiong et al., 2009; Aktas and Morcali, 2011).

It should be noted here that the value recovery provided is simplistic and not exhaustive as other costs such as labour and other overheads have not been included. However, it shows that it is possible to recover value that PGE companies could be losing through solution discharges.

The adsorption efficiency of Pt(IV) on hydrazine-functionalised zeolite was compared with the adsorption efficiencies of different adsorbents (Table 5). The adsorption efficiency of hydrazine-functionalised zeolite was relatively competitive to that of other adsorbents and cheaper due to low energy used and shorter time of maximum recovery.

#### 4. Conclusion

In this study, the recovery of Pt(IV) from aqueous solutions was investigated. The zeolite functionalised with hydrazine was successfully synthesized and was used as the adsorbent for Pt(IV). The batch adsorption studies carried out under the optimised conditions (20 g L<sup>-1</sup>

dosage, pH 2, 2 mg L<sup>-1</sup> and 6 h) showed that up to 112 µg g<sup>-1</sup> of Pt was removed by the adsorbent and this value increased slightly (by more than 9%) in the presence of competing ions due to synergistic effects, most likely with Fe. The optimum adsorption capacity corresponded to an adsorption efficiency of 93%, which is higher than for most commercial adsorbents. The adsorbent was found to perform exceptionally well at pH 2, which is the pH at which most solutions from PGE processing are discharged at and as such making it an ideal adsorbent for such solutions. Strong Pt-adsorbent interactions were deduced from the pseudo second-order model fit and the isothermic models, notably the Langmuir isotherm and the energy of adsorption obtained from the D-R isotherm which all pointed to a chemisorptive adsorption mechanism. The potential value recovered by the adsorbent was assessed based on the recovery of Pt only and that for Pt, Rh, Pd and Ir. The benefit of recovery was found to far outweigh (by over 15 times) the costs related to the synthesis of the adsorbents. As such, the materials can be used once off without the need for desorption and reuse. The adsorbent can be used in retaining ponds into which processing solutions are discharged and then dredged after a few days and fed back to the processing units together with fresh ore.

#### Acknowledgements

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# PAPER II

**This paper investigated the removal of platinum (IV) from aqueous solutions with yeast-functionalised bentonite.**

**The paper is published in Chemosphere.**

**Impact Factor: 5.778.**

**Contribution:** lead author, conducted experimental work and data modelling, conceptualization, methodology, software validation, formal analysis, investigation, writing - original draft and visualization.


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## GRAPHICAL ABSTRACT

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- Figure 10 consists of two bar charts. The left chart, titled 'Adsorption capacity of Pb(IV) - 95.5% efficiency (0.01M  $\text{CaCl}_2$ )', shows the adsorption capacity of Pb(IV) on Zn, Cu, Ni, and Cd. The y-axis is 'Adsorption capacity (mg/g)' ranging from 0 to 250. The x-axis lists the ions. The right chart, titled 'Adsorption of Pb(IV) in the presence of competing ions at pH 2', shows the adsorption capacity of Pb(IV) in the presence of various competing ions. The y-axis is 'Adsorption capacity (mg/g)' ranging from 0 to 250. The x-axis lists the ions: Ba, Sr, Li, Na, K, Mg, Ca, Mn, Fe, Zn, Cu, Ni, Cd, and Pb.
- | Ion | Adsorption capacity (mg/g) |
|-----|----------------------------|
| Zn  | ~250                       |
| Cu  | ~250                       |
| Ni  | ~250                       |
| Cd  | ~250                       |
- | Ion | Adsorption capacity (mg/g) |
|-----|----------------------------|
| Ba  | ~250                       |
| Sr  | ~120                       |
| Li  | ~250                       |
| Na  | ~250                       |
| K   | ~120                       |
| Mg  | ~250                       |
| Ca  | ~250                       |
| Mn  | ~250                       |
| Fe  | ~250                       |
| Zn  | ~250                       |
| Cu  | ~250                       |
| Ni  | ~250                       |
| Cd  | ~250                       |
| Pb  | ~250                       |

## ABSTRACT

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**Keywords:**  
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Cost-benefit analysis

There is a need for cheap but, efficient methods for the removal of precious metals from wastewaters, which are normally lost during mineral processing. Moreover, the disposal of yeast waste from brewing has been a problem in many parts of the world. In this study, the removal of Pt(IV) from aqueous solutions using the readily available bentonite clay functionalised with spent yeast from brewing was investigated. The maximum adsorption capacity of Pt(IV) with 100 mg yeast-functionalised bentonite at pH 2 within 90 min was  $255 \mu\text{g g}^{-1}$  (98.5% efficiency) but, decreased as pH increased. The adsorption capacity of Pt(IV) was insignificantly ( $p > 0.05$ ) affected by the presence of competing ions (Fe(III), Ca(II), Mg(II), K(I), Co(II)-Ni(II), Hf(IV), Zn(II) and other platinum group metals (PGMs)). Moreover, most of these metals were significantly adsorbed along with Pt(IV). The indicative cost-benefit analysis showed that 1 kg of the yeast-functionalised bentonite can remove  $\sim 700 \text{ g Pt(IV)}$  in which a profit of more than USD20000 can be made. The bentonite functionalised with spent yeast from brewing has a potential to recover lost PGMs in wastewater. Since, this is a cheap process, the mining and other industries can make much profit from such recoveries.

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The waste produced from mineral processing can contain significant amount of minerals including valuable or precious metals such as platinum, gold and palladium (Rankin, 2011). Moreover, the amount of waste produced has been increasing over the years due

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to intense mining caused by increasing standards of living in developing and developed countries (Rankin, 2011). Thus, the accumulation of valuable metals has been increasing in mine waste disposal sites and there is a need for their recovery especially, since many countries have been faced with declining commodity prices and weak economic growth. The waste also contains other metals such as Hg, Cd, U, Ca, Cu, Co, Mg, Ni and As of which some are non-essential and toxic even at low concentrations (Hajeb et al., 2014; Keil et al., 2011). Therefore, the removal of both precious and non-valuable metals from aqueous solutions is of high importance.

Some methods such as phytoremediation (LeDuc and Terry, 2005), ion exchange (Vaaramaa and Lehto, 2003), adsorption (Katsyiannis and Zouboulis, 2002), membrane filtration, precipitation (Deng et al., 2010) and bioremediation (Igiri et al., 2018) have been used to remove metals from wastewaters. Among these, adsorption has been found to be cost effective and simple (Katsyiannis and Zouboulis, 2002; Deng et al., 2010). Many studies have reported on the use of adsorption method using different adsorbents such as chitosan (Ngha et al., 2005), montmorillonite (de Pablo et al., 2011), bentonite (Manohar et al., 2006) and Kaolin (Fathima et al., 2012) due to their high surface area, abundance in nature and ability to be functionalised or modified.

Bentonite is an abundant, naturally occurring clay material known as aluminium phyllosilicate (Manohar et al., 2006). It is highly composed of montmorillonite and has a 2:1 layer structure which exhibit greater fixing of elements (Bradl, 2004). This structure is made up of sheets of silicon ions which are tetrahedrally coordinated and surrounds the sandwiched sheets of aluminium ions which are octahedrally coordinated. Studies have shown that bentonite functionalised with ligands such as surfactants, lanthanum, humic acids and manganese oxide can increase the adsorbate affinity and selectivity of bentonite (Anirudhan and Suchithra, 2010).

In the current study, a new and promising cheap way of functionalising bentonite so that it is suitable for the removal of Pt(IV) and possibly other metals was introduced. The spent yeast waste from brewing was used to modify bentonite surface which acts as a bed support. Yeast is of the species *Saccharomyces cerevisiae* and, is found in both the baker's and brewer's yeasts but, with different strains (Cauvain and Young, 2007; Moyad, 2007). The yeast is known to have a number of amino acids such as leucine, lysine, threonine, glycine, serine, alanine, phenylalanine, valine, tyrosine and proline which are sources of nitrogen (Csonka, 1935; Winkler et al., 2011; Nassary and Nasolwa, 2019). Gunes et al., (2019) reported that the brewing industry in Europe produces about 3.4 million tonnes of solid waste annually, which includes spent yeast. Alcohol is in fact the fifth most consumable beverage in the world (Fillaudeau et al., 2006). A study by Albanese et al. (2018) indicated that about 200 billion litres of beer is consumed per year worldwide. A litre of alcohol produced can lead to about 40 g of yeast as by-product therefore; about 8 million tonnes of yeast is released from beer alone each year (Brown, 1941). The yeast waste is mostly used in the animal feed industry (Nassary and Nasolwa, 2019). The yeast waste was used because it contains N-ligands from amino acids since, nitrogen has been found to form strong interactions with platinum (Citra et al., 2001). Moreover, baker's yeast factories and other food industries release significant amount of spent yeast; which can also possibly be used to modify adsorbents that can remove precious metals from wastewaters (Kobyas and Delipinar, 2008). Thus, this study seeks to utilise waste material (spent yeast) for the removal of Pt(IV) from aqueous solutions and, in the process, removing other polluting metals. Therefore, the functionalised bentonite will have dual efficacy.

## 2. Materials and methods

### 2.1. Reagents and standards

The 1000 mg L<sup>-1</sup> standards of Pt(IV) and a mixture of platinum group metals (PGMs) namely; Rh(III), Ir(III), Os(III), Pd(II) and Ru(III) in 5% w/w c(HCl) were mixed with deionised water to prepare 10 mg L<sup>-1</sup> stock solutions. The stock solution of other ions (Fe(III), Ca(II), Zn(II), etc.) was prepared by dissolving a known mass of metal nitrate salts in deionised water and preserved with 5% HCl. The standards and chemicals used were of analytical reagent grade and purchased from Sigma Aldrich, South Africa. All the solutions were stored in the refrigerator at 4 °C and serial dilutions were done daily from the stock solutions to make the working solutions.

The spent yeast waste used in this study was collected from a microbrewery at the University of the Witwatersrand, South Africa. It was collected using polypropylene containers and stored in the fridge at 4 °C until required. The yeast from brewing was compared with baker's yeast (obtained commercially) to determine if there is a significance difference with regards to the adsorption of Pt(IV).

### 2.2. Synthesis of yeast-functionalised bentonite

The bentonite used was purchased from Sigma Aldrich, South Africa. The functionalised bentonite was synthesised by mixing 40 mL of yeast waste liquid with 5 g bentonite in polypropylene plastic containers and shaken using a precise shaking incubator (Wise Cube, South Korea) with a speed of 100 rpm at 25 °C for 24 h. The contents were left to reach room temperature and settle before filtering using suction. Deionised water was then added to the yeast-functionalised bentonite and shaken for 5 min to remove unbound or excess yeast. The yeast-functionalised bentonite was dried at room temperature (25–27 °C) for 24 h before characterisation and usage.

### 2.3. Characterisation

The mineral composition of bentonite was determined with powder X-ray diffraction (PXRD) D2 Phaser (Bruker, Germany) which uses Ni-filtered Cu K $\alpha$  radiation at 10–90 2 $\theta$  range. X-ray fluorescence (XRF) (PAAnalytical, Netherlands) was used to determine the chemical composition of bentonite and Fourier transform infrared (FTIR) spectroscopy (Tensor 27, Bruker, Germany) with mid-IR source (4000–400 cm<sup>-1</sup>) and KBr beam splitter was used to determine the functional groups of the natural and functionalised bentonite as well as those of brewer's and baker's yeasts. The CHNS analysis using varioELcube V4.0.13 (Elementar, Germany) was done on the yeast, natural bentonite and functionalised bentonite to determine the percentage of C, H, N and S. The textural properties (Brunauer-Emmett-Teller (BET) surface area, pore size and pore volume) were also determined using TriStar 3000 V6.05 A (Micrometrics, USA). Thermogravimetric analysis (TGA) and differential temperature analysis (DTA) using PerkinElmer Pyris 1 TGA (Massachusetts, USA) were used to determine the thermal stability of the natural and functionalised bentonite. The point of zero charge (PZC) was determined using a method by Fiol and Villares (2009). The 0.01 M KNO<sub>3</sub> with different pH values (2–12) was added to yeast-functionalised bentonite to make final suspensions of 25 g L<sup>-1</sup>. To adjust the pH, 0.01 M HCl and NaOH were used. The suspensions were shaken for 24 h after which the final pH was determined.

### 2.4. Adsorption experiments

The efficiency of yeast-functionalised bentonite in adsorbing

Pt(IV) was assessed using batch adsorption experiments which were performed in triplicates ( $n = 3$ ) (Bakatula et al., 2015). The average of the triplicates was then used to represent the results. The effect of time (0–540 min), concentration (0.5–10 mg L<sup>-1</sup>), pH (2–9) and competing ions (Rh(III), Ir(III), Os(III), Ru(III), Pd(II), Fe(III), Ca(II), Mg(II), K(I), Co(II), Ni(II), Hf(IV), Zn(II)) on the adsorption of Pt(IV) was studied. The yeast-functionalised bentonite was added into 10 mL solutions of Pt(IV) solutions in different conditions as stated above and shaken for 3 h using automated elliptical bench-top shaker at 150 rpm. The relative standard deviation (RSD) was used for statistical analysis of the results. Post shaking, the contents were filtered with a 0.45 µm cellulose nitrate Filtech filter paper. The filtrate was then analysed with inductively coupled plasma optical emission spectroscopy (ICP-OES) (Spectro Genesis, Germany) to determine the concentration of Pt(IV). HCl and NaOH were used to adjust the pH which was measured using a pH meter (Mettler Toledo, South Africa).

### 2.5. Amount of Pt(IV) removed and adsorption efficiency

The equilibrium amount ( $q_e$  (µg g<sup>-1</sup>)) of Pt(IV) removed by yeast-functionalised bentonite was determined using Eq. (1) and the adsorption efficiency was calculated using Eq. (2):

$$q_e = \frac{(C_0 - C_e)V}{M} \times 1000 \quad (1)$$

$$\% \text{ adsorption} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

where  $C_0$  is the initial concentration,  $C_e$  is the equilibrium liquid-phase concentration,  $V$  is the volume of the solution in litres (L) and  $M$  is the mass of the yeast-functionalised bentonite in grams (g).

## 3. Results and discussion

### 3.1. Characterisation

The chemical composition of bentonite was determined using XRF and the results indicated that silica (SiO<sub>2</sub>) (51.5%) and alumina (Al<sub>2</sub>O<sub>3</sub>) (16.7%) were the most abundant minerals of bentonite. The oxides of iron (5.0%), magnesium (3.6%), calcium (2.0%) and potassium (1.4%) were also in significant amounts. The results obtained were similar to those reported by other researchers (Abdullahi and Audu, 2017). The minerals that were found in bentonite using PXRD were; montmorillonite (Na,Ca)<sub>0.3</sub>(Al,Mg)<sub>2</sub>(Si<sub>4</sub>O<sub>10</sub>)(OH)<sub>2</sub> · nH<sub>2</sub>O, quartz (SiO<sub>2</sub>), gibbsite (Al(OH)<sub>3</sub>) and enstatite (MgSiO<sub>3</sub>) which are highly composed of Al, Si and O. Thus, the functionalisation of bentonite could have taken place through these elements. The Pt(IV) solution was contacted with the natural bentonite to determine if the adsorbent has affinity for Pt(IV) but, the adsorption efficiency was less than 0.05%. Thus, bentonite serves only as a support for yeast functional groups and does not take part on the adsorption of Pt(IV).

The FTIR spectra of the natural and functionalised bentonite are shown in Fig. 1a. The strong bands at ~999 cm<sup>-1</sup> on both spectra; were due to the Si–O and Al–O bonds. The broad bands at ~3385 cm<sup>-1</sup> observed can be attributed to the O–H stretching bonds of the water molecules (Alabarse et al., 2011). The bands at ~3620 cm<sup>-1</sup> were due to the dioctahedral montmorillonite. There was a distinct peak on the yeast-functionalised bentonite at ~1532 cm<sup>-1</sup> which was attributed to N–H bend, indicative of the presence of amine groups due to amino acids such as leucine, lysine, threonine, glycine, histidine and serine among others.

Moreover, studies have shown that the N–H bands of amino acids such as histidine and leucine can be found between 1510 and 1570 cm<sup>-1</sup> (Baskaran et al., 2016; Li et al., 2016). The CHNS elemental analysis indicated that there was significant amount of N after functionalisation, which was not detected in the non-functionalised bentonite (Table 1). The peak at 1638 cm<sup>-1</sup> was due to C–N stretch and this can be attributed to the C–N bonds of the different amino acids. The peak at ~1070 cm<sup>-1</sup> is due to the Si–O bond signifying the interaction of bentonite and oxygen from the amino acids of the yeast (Al-Oweini and El-Rassy, 2009). The distinct peak at around 2924 cm<sup>-1</sup> was due to the C–H stretching (Song et al., 2015). The CHNS analysis also indicated that there was high percentage of C in the functionalised bentonite probably due to the C-long chain of amino acids of the yeast since; the C content was high in the collected yeast. Thus, the interaction of the yeast and bentonite was through the amino acid chains of yeast and oxides of the adsorbent such as silica. The functional groups of the brewer's and baker's yeasts were also determined and compared. There was no significant difference between the two yeasts (Fig. 1b). This could be because the yeasts have the same compositions and fungal species known as *Saccharomyces cerevisiae* (Márquez et al., 2018; Mihajlovski et al., 2018). The baker's yeast used was obtained commercially and the fact that the FTIR spectrum was similar to that of the brewer's yeast obtained after the brewing process then the yeast species did not change during the brewing process. Thus, either of the yeasts can be used to functionalise the bentonite adsorbent. From the characterisation results, it can be concluded that yeast waste from brewing and baking industries can be used to functionalise the readily available and cheap adsorbent, bentonite for the removal of Pt(IV). This will then help reduce waste released into the environment by brewing and food industries worldwide. Moreover, mining companies can benefit a lot as there will be low costs used to remove precious metals.

Thermogravimetric analysis and differential temperature analysis of the natural and yeast-functionalised bentonite were determined to confirm the thermal stability of the materials. Moisture loss due to dissociated and adsorbed water molecules started at ~41 °C for both the natural and functionalised bentonite which; continued until 150 °C and 272 °C, respectively (Alabarse et al., 2011; Musyoka et al., 2015). The weight loss beyond 150 °C for natural bentonite and 272 °C for the functionalised bentonite can be attributed to the loss of water from hydration complexes such as Ca(OH<sub>2</sub>)<sub>6</sub><sup>2+</sup> and Mg(OH<sub>2</sub>)<sub>6</sub><sup>2+</sup> (Akbar et al., 2005). The percentage weight loss beyond 250 °C and 378 °C for natural and functionalised bentonite, respectively; was due to dehydroxylation (Musyoka et al., 2015). The percentage weight loss of the functionalised bentonite was generally lower than that of the natural. The change of the molecular framework was observed at ~850 °C as indicated by the differential temperature curves. Thus, the yeast-functionalised bentonite can be used even in high temperature processes.

Textural properties of the natural and functionalised bentonite indicated that the surface area of bentonite significantly decreased on functionalisation with yeast. The reduction from 21.29 to 0.39 m<sup>2</sup> g<sup>-1</sup> can be attributed to the smothering of the pores by the yeast and this also indicates the success in functionalisation of the bentonite. The reduction in BET surface area was also indicated by the increasing pore size from 10.38 to 57.46 nm and decreasing pore volume.

### 3.2. Effect of adsorbent dosage

The effect of adsorbent dosage (50–400 mg) of yeast-functionalised bentonite on the removal of Pt(IV) was determined

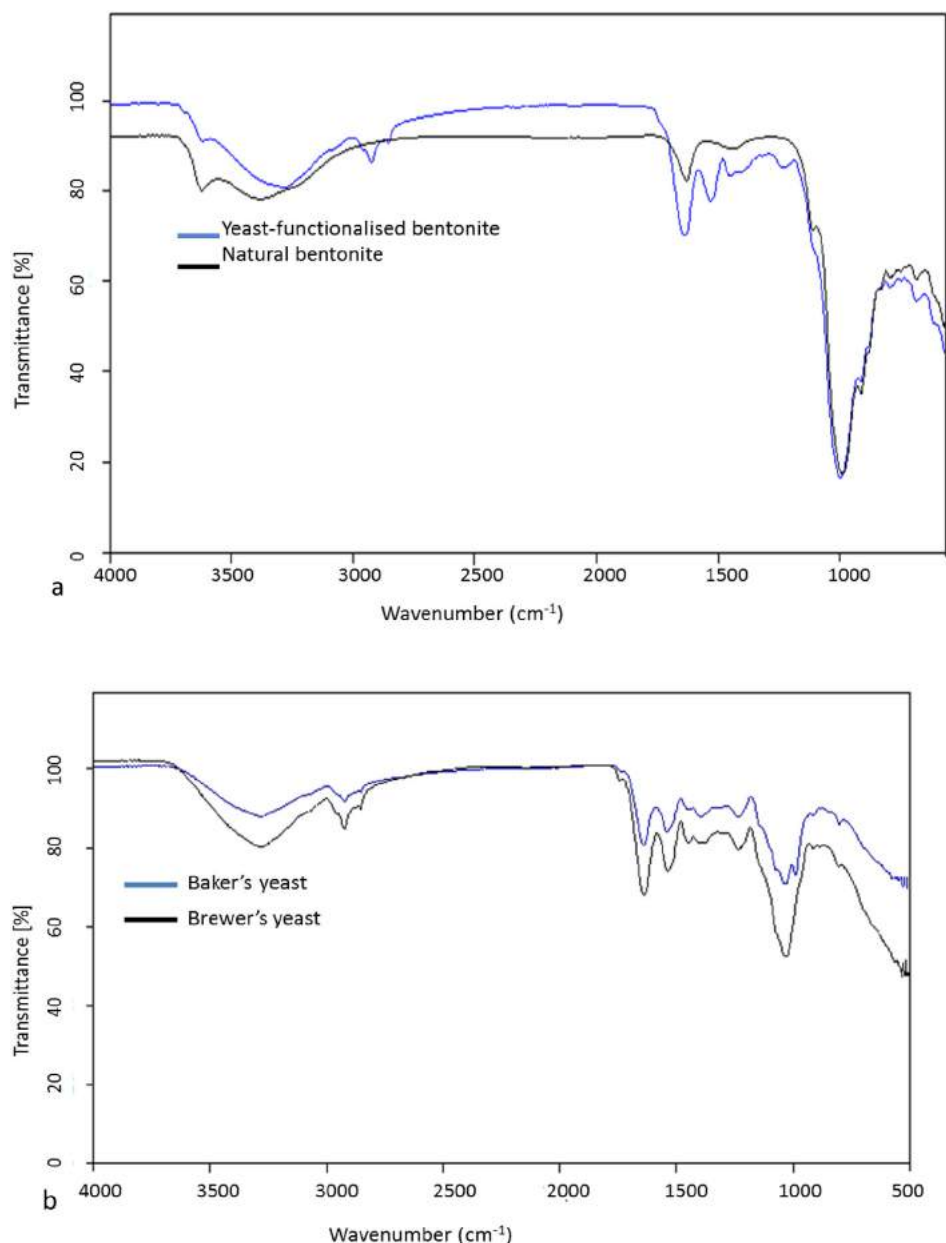


Fig. 1. FTIR spectra of (a) natural and yeast-functionalised bentonite and (b) the comparison of the baker's and brewer's yeasts.

**Table 1**  
Elemental analysis of the natural and yeast-functionalised bentonite.

| Sample                         | C (%) | H (%) | N (%) |
|--------------------------------|-------|-------|-------|
| Natural bentonite              | 0.65  | 3.43  | 0.06  |
| Yeast-functionalised bentonite | 18.24 | 1.72  | 0.00  |

and the results are shown in Fig. 2a. The adsorption efficiency was observed to increase with increasing dosage from 50 to 100 mg due to increasing number of vacant N adsorption sites (Si-RNH<sub>2</sub>). Studies have shown that there is strong interaction between N and Pt and thus, the interaction of Pt(IV) and the yeast-functionalised bentonite was through Si-RNH<sub>2</sub>—Pt interaction (Citra et al., 2001; Chi et al., 2017). The adsorption was constant beyond 100 mg and a slight decrease in adsorption was observed beyond 300 mg. The adsorption capacity was observed to decrease with increasing mass

and the maximum capacity was achieved with 50 mg, meaning that even low amounts of yeast-functionalised bentonite will remove significant amount ( $p < 0.05$ ) of Pt(IV). However, 100 mg was used for subsequent experiments in order to obtain the maximum amount of Pt(IV) (>98.5%). A study by Mansoorian et al. (2014) indicated that 92–97.2% of Pb(II) and Zn(II) were removed from wastewater using electrocoagulation which is more expensive than the method under study which does not require any form of external energy to occur. The adsorbent can simply be sprinkled in wastewater and removed after some time of exposure.

### 3.3. Effect of pH

The effect of pH on the adsorption of metals is very important to consider since, some adsorbents can be efficient for the adsorption at particular pH regions (Xiao et al., 2016; Da'na, 2017). The results obtained indicated that the adsorption of Pt(IV) onto yeast-

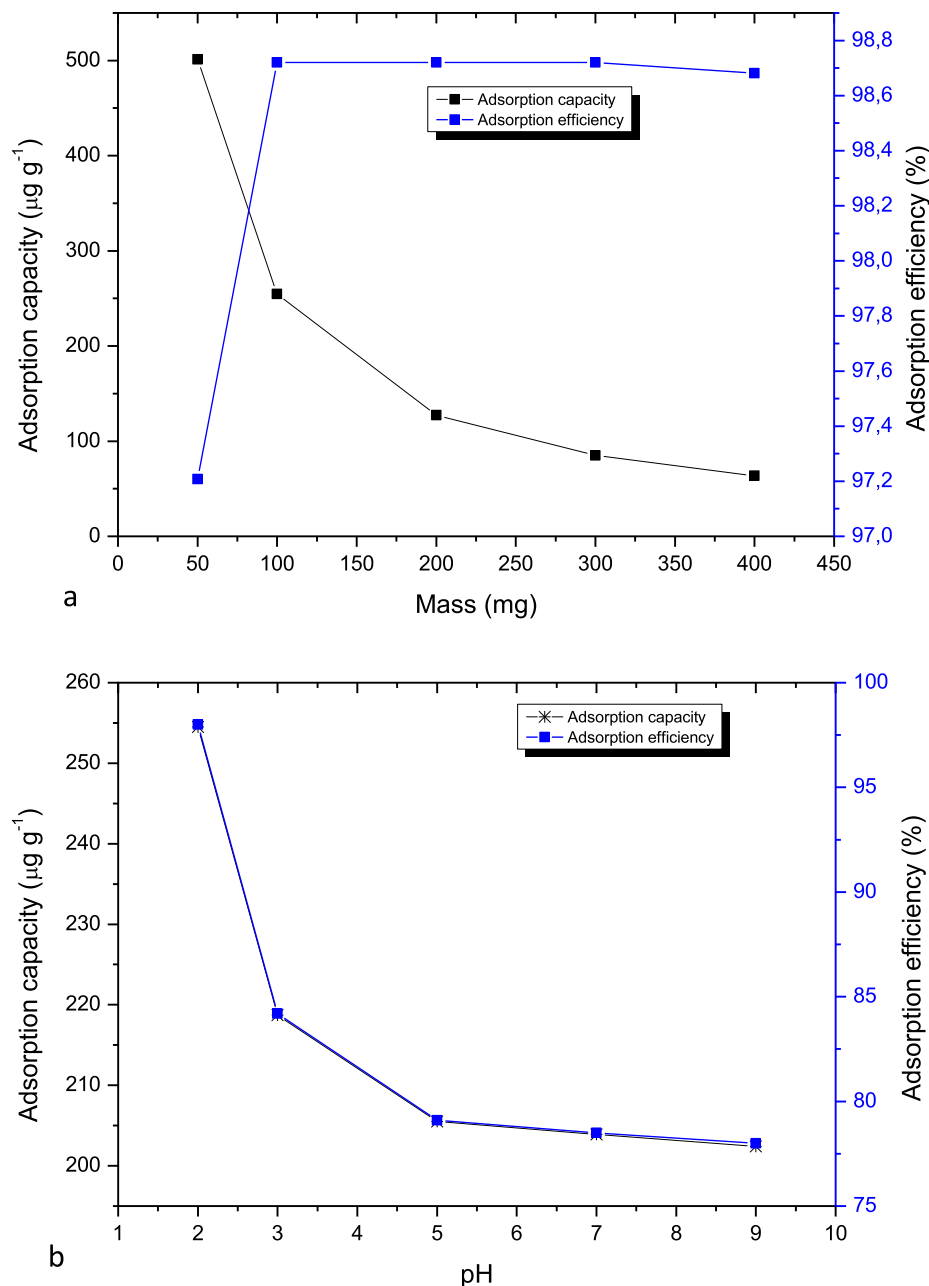


**Fig. 2.** Effect of (a) dosage and (b) pH on the recovery of Pt(IV) by yeast-functionalised bentonite (conc =  $2 \text{ mg L}^{-1}$ , time = 180 min, temp =  $25^\circ\text{C}$ , V = 10 mL, n = 3, RSD < 10%).

functionalised bentonite decreased with increasing pH (Fig. 2b). At lower pH, there were more hydronium ions ( $\text{H}^+$ ) which protonated the amine groups to form  $-\text{NH}_3^+$  thus, making the surface of the yeast-functionalised bentonite positive. The Pt(IV) species at lower pH was in the chloride form ( $\text{PtCl}_6^{2-}$ ) due to high concentration of chloride ions. Thus, at highly acidic conditions, the anionic Pt(IV) formed an electrostatic interaction with the positively charged amine ( $\text{NH}_3^+$ ) to form  $(\text{R}-\text{NH}_3^+)_2\text{PtCl}_6^{2-}$  hence, high amount of Pt(IV) was removed. Acids such as hydrochloric acid are always used to separate PGMs from each other before the final refinement, leading to chloride forms of many metals and thus, Pt(IV) which forms strong interactions with Cl, is highly likely to be found in the hexavalent form ( $\text{PtCl}_6^{2-}$ ) in mining wastewater (Gouldsmith and Wilson, 1963). The maximum adsorption of Pt(IV) was achieved at pH 2 ( $254.5 \mu\text{g g}^{-1}$ ). Though pH 3–5 was still in the acidic region,

the reduction of protonated amines drastically decreased the removal of Pt(IV). At  $\text{pH} > 5$  the amines were not protonated desirably and Pt(IV) was not in the favourable form for adsorption. This indicates that yeast-functionalised bentonite will work more effectively at very low pH. Thus, pH is an important factor that should be taken into consideration when applying the adsorbent. The  $\text{pH}_{\text{PZC}}$  was found to be 5.6 and below 5.6 the surface of the adsorbent was positively charged, hence the adsorption of the negatively charged Pt-complex occurs in acidic conditions. The pH of 2 was chosen for the subsequent experiments as this is the pH solutions are released from the refineries. Other studies have reported that some adsorbents attract metals poorly at acidic regions, therefore they cannot be taken into consideration for the adsorption of Pt(IV) (Maleki et al., 2011).

### 3.4. Effect of contact time

Effect of contact time (0–540 min) on the removal of Pt(IV) was studied and the results are presented in Fig. 3a. Two phases were observed. The first one was the fast adsorption of Pt(IV) by yeast-functionalised bentonite between 0 and 90 min which can be attributed to the availability of binding sites and concentration gradient being the driving force. Thus, the maximum adsorption ( $\sim 250 \mu\text{g g}^{-1}$ ) was achieved within 90 min of contact. The second phase was observed beyond 90 min whereby no change in adsorption was seen due to equilibrium between the analyte and the adsorbent. In this study, 3 h was chosen as the shaking time.

### 3.5. Kinetic models

Kinetic models were used to determine the controlling mechanism of adsorption between Pt(IV) and yeast-functionalised bentonite. Kinetic studies were also used to determine the rate of adsorption. Pseudo first- and second-order as well as Elovich models were used to fit the experimental data and the results are presented in Table 2.

Pseudo first-order model expresses a reaction in which one reactant is very high in concentration and the other is very low such that it can be neglected. The reaction that follows first-order kinetics indicates that the adsorption is highly likely to be through

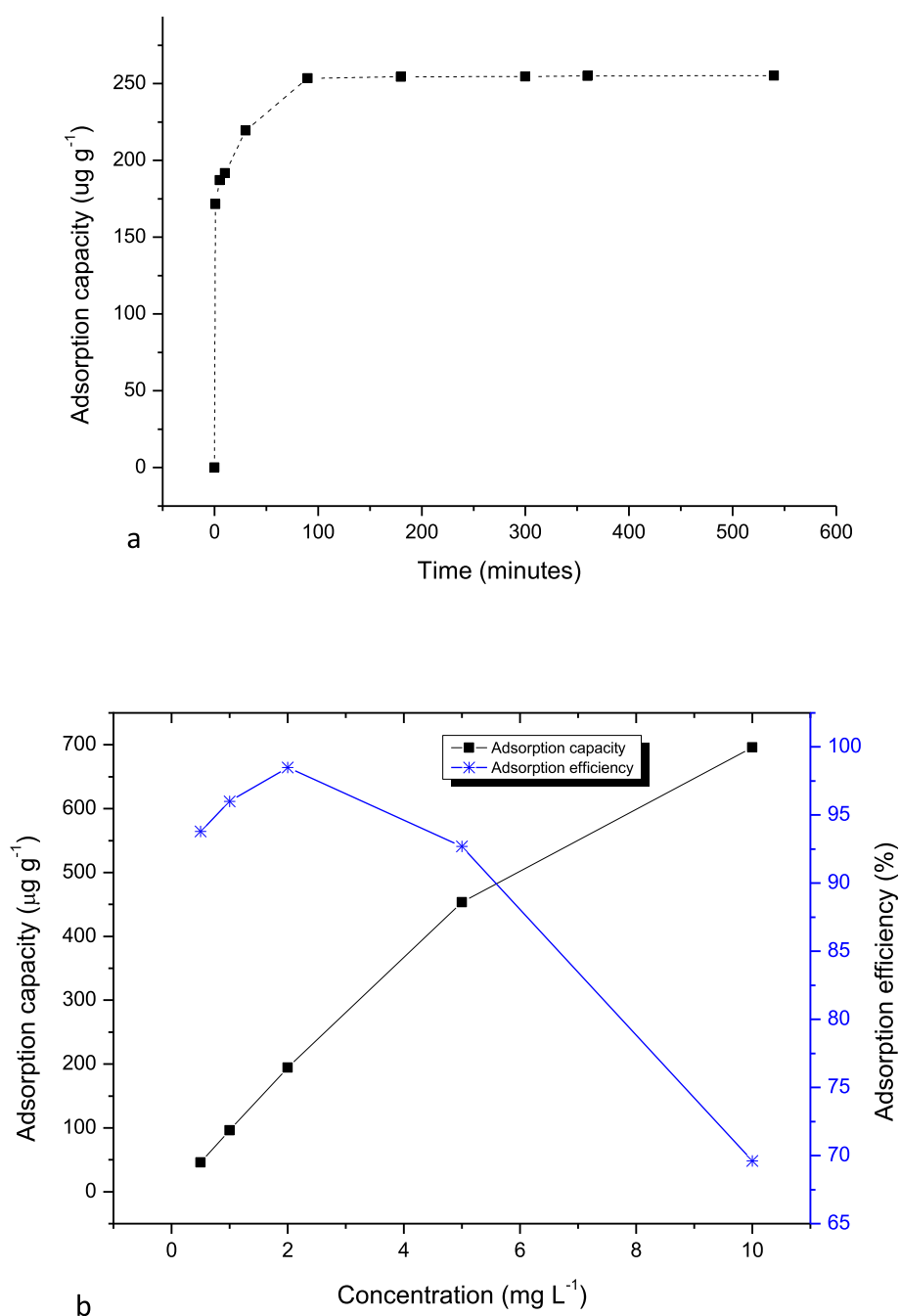


**Fig. 3.** Effect of (a) time (at  $2 \text{ mg L}^{-1}$ ) and (b) concentration on the recovery of Pt(IV) onto yeast-functionalised bentonite (mass = 100 mg, pH 2, temp =  $25^\circ\text{C}$ , V = 10 mL, n = 3, RSD < 10%).

**Table 2**  
Kinetic parameters of the recovery Pt(IV) onto yeast-functionalised bentonite.

| Pseudo first order             |                        |                         |       | Pseudo second order                      |                         |       |                                       | Elovich                               |       |  |
|--------------------------------|------------------------|-------------------------|-------|------------------------------------------|-------------------------|-------|---------------------------------------|---------------------------------------|-------|--|
| $q_e, (exp) \text{ mg g}^{-1}$ | $k_1 \text{ min}^{-1}$ | $q_e \text{ mg g}^{-1}$ | $R^2$ | $k_2 \text{ g mg}^{-1} \text{ min}^{-1}$ | $q_e \text{ mg g}^{-1}$ | $R^2$ | A $\text{g mg}^{-1} \text{ min}^{-1}$ | B $\text{g mg}^{-1} \text{ min}^{-1}$ | $R^2$ |  |
| 0.102                          | 0.011                  | 0.032                   | 0.73  | 3.30                                     | 0.13                    | 0.99  | 0.0055                                | 123                                   | 0.94  |  |

physisorption (Sicilio and Peterson, 1961; Yuh-Shan, 2004).

The rate controlling step of the reaction that follows pseudo second-order is chemical adsorption or chemisorption which involves valency forces through the sharing of electrons between metals and adsorbents (Ho and McKay, 1999).

The Elovich model that describes the chemical adsorption mechanism which applies to chemisorption kinetics was also used. This model has been found to be valid in adsorption involving heterogeneous surfaces of adsorbents (Cheung et al., 2000).

The coefficient of determination ( $R^2$ ) and the closeness of the experimental  $q_e (exp)$  to the calculated  $q_e$  were used to determine the kinetic model that best describes the adsorption process. The experimental  $q_e$  of pseudo first-order was very different from the calculated  $q_e$  thus, the model could not express the adsorption process between Pt(IV) and yeast-functionalised bentonite hence, the  $R^2$  value was low. The results as presented in Table 2 indicated that the experimental data was better described by Pseudo second-order kinetic model whose  $R^2$  was very close to 1. Moreover, the pseudo second-order experimental and calculated  $q_e$  were close, indicating that the model can be used to explain the sorption process between Pt(IV) and yeast-functionalised bentonite. This also meant that there is strong chemical reaction between Pt(IV) and the adsorbent which involves the strong electrostatic interaction. Other studies have shown that the experimental data for the adsorption of Pt onto other adsorbents modified with N ligands was through pseudo second-order (Ramesh et al., 2008; Zhou et al., 2009).

### 3.6. Effect of Pt(IV) concentration

The effect of concentration on the removal of Pt(IV) was also studied and the results are presented in Fig. 3b. The adsorption capacity increased with increasing concentration from 0.5 to 10  $\text{mg L}^{-1}$  at pH 2. The maximum adsorption capacity was found to be 695.8  $\mu\text{g g}^{-1}$  with the initial concentration of 10  $\text{mg L}^{-1}$ . The observed results can be attributed to the availability of binding sites and concentration gradient driving force rather than the increasing initial concentration. The adsorption efficiencies at 0.5, 1, 2, 5 and 10  $\text{mg L}^{-1}$  were found to be 93.8, 96, 98.5, 92.7 and 69.6%, respectively. More adsorption sites on the surface of bentonite were occupied by more species of Pt(IV) as concentration increased which then increased the adsorption capacity. Thus, 100 mg yeast-functionalised bentonite had enough binding sites for Pt(IV). Moreover, there is strong interaction between yeast-functionalised bentonite and Pt(IV).

### 3.7. Adsorption isotherms

Adsorption isotherm models were plotted using the concentration data to determine how Pt(IV) was distributed on the surface of the adsorbent. The Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherms were used. The Langmuir isotherm which was developed by Irving Langmuir describes the monolayer adsorption of metals onto homogeneous surface of adsorbents. The Langmuir equation depicts the relationship between pressure and the number of active sites that will undergo adsorption. One of the assumptions of this model is that there is a fixed number of active

sites which have the same shape and size on the surface of the adsorbent. These active sites can hold one adsorbate which will be in equilibrium with free adsorbates in the solution (Langmuir, 1918).

The separation factor ( $R_L$ ) which can be determined from the Langmuir constant ( $K_L$ ) expresses the affinity of metals to adsorbents (Wang et al., 2012). The affinity can be expressed as favourable ( $0 < R_L < 1$ ), unfavourable ( $R_L > 1$ ), linear adsorption ( $R_L = 1$ ) and irreversible ( $R_L = 0$ ). The  $R_L$  is expressed as:

$$R_L = \frac{1}{1 + C_0 K_L} \quad (3)$$

The  $R_L$  value in this study was found to be ~0.0248 at all initial concentrations used, implying that the adsorption of Pt(IV) onto yeast-functionalised bentonite was favourable.

Freundlich isotherm is an empirical model that describes the adsorption of metals onto a heterogeneous surface. The active sites on the surface are assumed to have different energies (Ng et al., 2002; Nekhunguni et al., 2017).

The Dubinin-Radushkevich (D-R) equation is used to express the adsorption between solutes and adsorbents onto a heterogeneous surface with Gaussian energy distribution (Wang et al., 2012). The linear form of the D-R is as follows:

$$\ln q_e = \ln X_m - K_{DR} \epsilon^2 \quad (4)$$

where  $K_{DR}$  is the Dubinin-Radushkevich isotherm constant ( $\text{mol}^2 (\text{kJ}^2)^{-1}$ ),  $\epsilon$  is the Polanyi constant which is calculated using the following equation:

$$\epsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \quad (5)$$

where  $R$  is the universal gas constant ( $\text{J (mol K)}^{-1}$ ),  $T$  is temperature (K).

The mean free energy of adsorption ( $E_s$ ) can be calculated from  $K_{DR}$  as shown in Eq. (6). This energy can be used to determine the adsorption between Pt(IV) and yeast-functionalised bentonite either as physisorption or chemisorption.

$$E_s = \frac{1}{\sqrt{2K_{DR}}} \quad (6)$$

The mean free energy was found to be 12.35  $\text{kJ mol}^{-1}$ , indicating that the adsorption process between Pt(IV) and yeast-functionalised bentonite was through chemical ion exchange mechanism.

The statistical coefficient ( $R^2$ ) was used to determine the isotherm model that best describes the data and the results as presented in Table 3 showed that the Langmuir isotherm described the data better ( $R^2 = 0.99$ ) and was chosen as the thermodynamic model for the adsorption of Pt(IV) onto yeast-functionalised bentonite. This means that maximum adsorption of Pt(IV) corresponds to saturated surface of yeast-functionalised bentonite by Pt(IV) through monolayer adsorption. Thus, no transmigration of Pt(IV) on the surface occurred and this can be attributed to strong interactions with N of the amino acids. Moreover, the energy of adsorption was constant.

**Table 3**

The Langmuir, Freundlich and Dubinin-Radushkevich isotherm constants for Pt(IV) recovery by yeast-functionalised bentonite.

| Langmuir                |                          |       | Freundlich                                          |     |       | Dubinin-Radushkevich    |                           |       |
|-------------------------|--------------------------|-------|-----------------------------------------------------|-----|-------|-------------------------|---------------------------|-------|
| $q_m(\text{mg g}^{-1})$ | $K_L(\text{L mol}^{-1})$ | $R^2$ | $K_f((\text{mg g}^{-1})/(\text{mol L}^{-1})^{1/n})$ | $n$ | $R^2$ | $X_m(\text{mg g}^{-1})$ | $E_s(\text{kJ mol}^{-1})$ | $R^2$ |
| 0.546                   | $5.9 \times 10^5$        | 0.99  | 256                                                 | 1.9 | 0.84  | 7.45                    | 12.35                     | 0.86  |

### 3.8. Effect of competing ions

The selectivity for Pt(IV) was determined as this can have implications on efficiency. Since, the adsorbent will be used in platinum mining environments, other platinum group metals (PGMs) i.e. Rh(III), Ir(III), Os(III), Ru(III) and Pd(II) were taken into consideration. Metals ions such as Mg(II), Ni(II), and Zn(II) were included as they are always in host ores of minerals and can affect the efficiency and selectivity of adsorbents. The results as presented in Fig. 4a and b indicated that the adsorption of Pt(IV) was not reduced by the presence of competing ions. Moreover, other metal ions (Os(III), Pd(II), Ru(III), Fe(II), Co(II), Ni(II), Zn(II) and Hf(IV)) were also significantly adsorbed ( $p < 0.05$ ) by yeast-functionalised bentonite and this can be attributed to the availability of binding sites as was shown with the effect of concentration that very high concentrations ( $10 \text{ mg L}^{-1}$ ) of Pt(IV) could be adsorbed. The ability of the adsorbent to remove other PGMs means that there were still vacant N binding sites and that other metals could be bound through different active sites. The adsorption of Rh(III) and Ir(III) was low and this could be due to occupation of binding sites by other PGMs and metal ions. Thus, yeast-functionalised bentonite will be highly selective for Pt(IV), Pd(II), Os(III) and Ru(III). The ability of the adsorbent to adsorb other metal ions means that it has dual efficacy which is to remove precious metals and remove other contaminants.

### 3.9. Indicative cost-benefit analysis

In order to determine if the method used for the removal of Pt(IV) from mine leachate will be potentially economically, a cost-benefit analysis was done. All costs that were used for functionalisation of bentonite were taken into consideration and the current prices of bentonite and energy were used. Bentonite is naturally readily available in many parts of the world including South Africa, USA and Canada, and is not commercialised in other countries where it is deemed non-industrially required (WHO, 2005; Tito et al., 2016). The cost-benefit analysis was calculated using Eq. (7). It was determined from the optimised conditions and parameters that 700 g of Pt(IV) can be removed with 1 kg of yeast-functionalised bentonite. The prices used were in USD. The price of 1 g of platinum amounts to USD29.45 (Markets Insider, 2018).

#### 3.9.1. Recovery of Pt only

$$\begin{aligned}
 700 \text{ g Pt} &= 700 \times \text{USD}29.45 = \text{USD}20615 \\
 \text{Net profit} &= \text{USD}20615 - \text{functionalisation costs} \\
 &= \text{USD}20615 - (\text{cost of bentonite} + \text{energy}) \text{ kg}^{-1} \text{ bentonite} \\
 &= \text{USD}20615 - (\text{USD}22.40 + \text{USD}11.86) \\
 &= \text{USD}20580.74
 \end{aligned}
 \tag{7}$$

#### 3.9.2. Combined cost-benefit analysis of Pt, Rh, Pd and Ir

The results of the effect of competing ions were used to determine combined cost-benefit analysis of Pt(IV), Rh(III), Pd(II) and Ir(II) which are some of the most expensive PGMs. The prices of 1 g

Rh, Pd and Ir were found to be USD39.22, USD30.24 and USD35.45, respectively. The amounts of Rh, Pd and Ir were found to be 254.52 g (USD9982), 700.28 g (USD21177) and 173.88 g (USD6164), respectively. The net profit of more than USD57000 can be made with 1 kg yeast-functionalised bentonite when these metals are included.

From this analysis, it can be concluded that the proposed yeast-functionalised bentonite has potential to be used in the natural environment to remove PGMs from discharged solutions of PGM processing. The remaining PGMs (Ir(III) and Rh(III)) in solution due to lower selectivity in the presence of other ions can be further removed by adding more of the adsorbent after the first recovery until significant amounts have been obtained. The adsorbent can be applied on sites where PGMs processing waste solution is discharged. Since the yeast that can be used is waste from the brewing or food industry, no desorption studies were conducted because there is no intention of reusing the adsorbent. Thus, more of this waste can be used to functionalise more adsorbent for significant removal of PGMs. Once platinum has been captured from wastewater, the adsorbent can be added to the process feed points so that it can be processed with the new ore hence, a cheaper process as no extra chemicals will be required for desorption. The desorption can however, be done by exposing the Pt(IV)-adsorbed-yeast-functionalised bentonite to the mixture of EDTA-H<sub>2</sub>SO<sub>4</sub> as indicated by Zhou et al. (2009) or thiourea-HCl as indicated by Fujiwara et al. (2007) and more than 95% recovery was achieved. These authors targeted more than  $100 \text{ mg L}^{-1}$  Pt(IV) or more and used concentrations between 0.5 and 2 M thus, even lower concentrations of these desorbing agents can be used to capture Pt(IV) from yeast-functionalised bentonite as very low concentrations were considered in this study. When using these desorbing agents, the adsorbent can be reused. It should be noted here that the cost-benefit analysis given is only a guideline or rough estimate as other costs such as labour, transportation and so on have not been considered.

## 4. Conclusion

The removal of Pt(IV) from aqueous solutions with yeast-functionalised bentonite was studied. The functionalisation of bentonite with the yeast waste from brewing was successful. The optimum conditions for the adsorption of Pt(IV) with yeast-functionalised bentonite were; 100 mg dosage,  $2 \text{ mg L}^{-1}$  concentration, 180 min and pH 2. The maximum adsorption efficiency of Pt(IV) by the adsorbent at these conditions was found to be 98.5%. The ability of the adsorbent to remove Pt(IV) at highly acidic regions makes it a suitable adsorbing agent as PGMs processing environments are highly acidic. The natural bentonite could not capture Pt(IV) from aqueous solution hence the adsorption was through the spent yeast. The fact that the adsorption of Pt(IV) was not reduced in the presence of competing ions, makes yeast-functionalised bentonite a competitive and a cheap adsorbent for efficient recovery of Pt(IV) including other platinum group metals (PGMs) from wastewater. Some contaminants such as Zn(II) and Ni(II) were efficiently removed from aqueous solutions, thus the yeast-functionalised bentonite acts as a dual efficacy adsorbent. The indicative cost benefit-analysis showed that an estimated

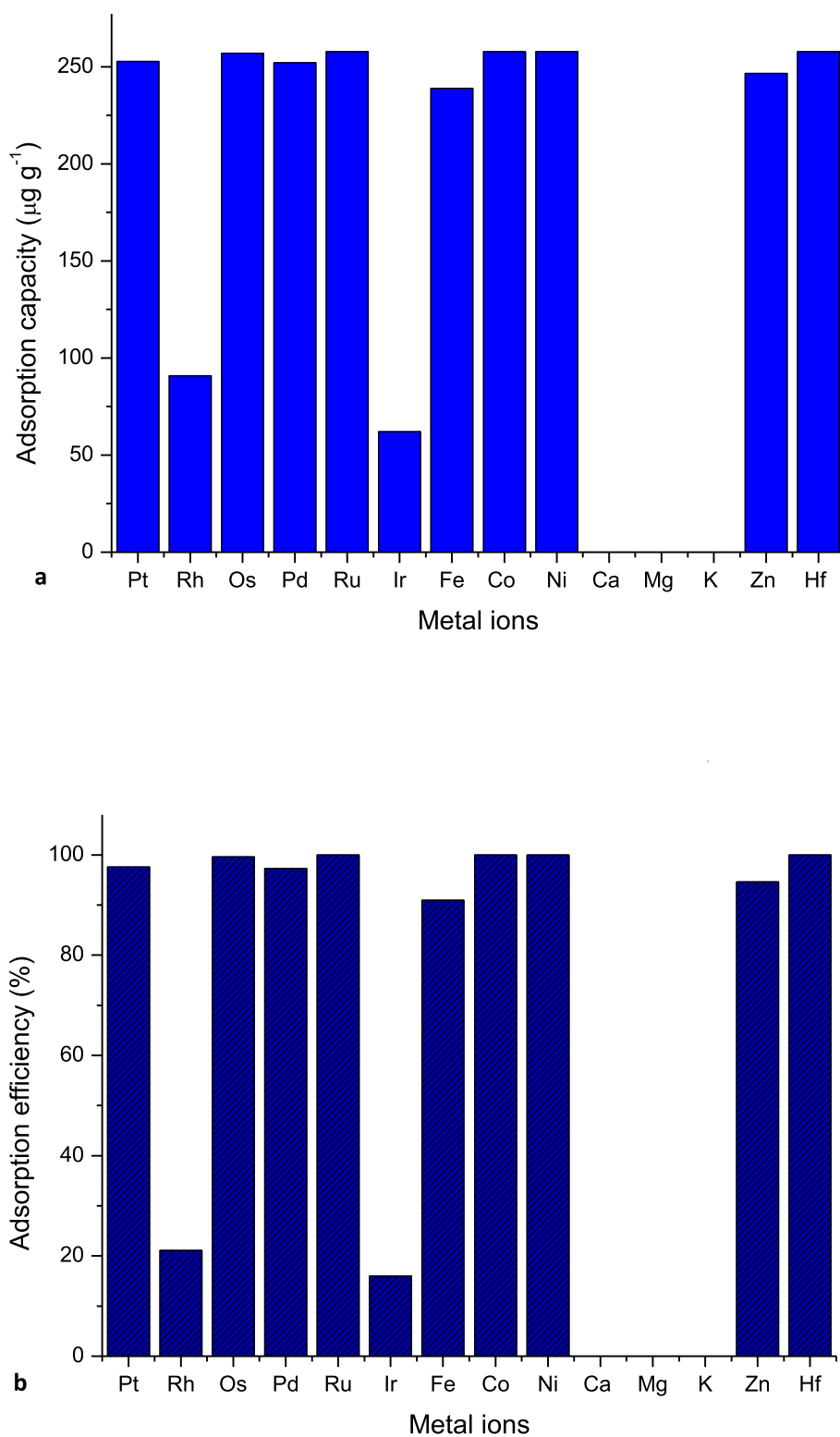


**Fig. 4.** Effect of competing ions on the adsorption of Pt(IV) by yeast-functionalised bentonite indicating adsorption capacity (a) and adsorption efficiency (b) (pH 2, conc = 2 mg L<sup>-1</sup>, time = 180 min, temp = 25 °C, V = 10 mL, n = 3, RSD <10%).

profit of more than USD20000 can be made from the recovery of Pt(IV) alone with 1 kg of the adsorbent, and more than USD57000 when other PGMs are included.

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# PAPER III

**This paper investigated the recovery of Pt(IV) from aqueous solutions by APDEMS-functionalised zeolite.**

**This is a conference paper that I presented at:**

**11th ICARD | IMWA | MWD Conference**

**“Risk to Opportunity”, South Africa.**

**International Mine Water (IMWA). 2018**

**Contribution:** lead author, conducted experimental work and data modelling, conceptualization, methodology, software validation, formal analysis, investigation, writing - original draft and visualization.



# The recovery of Pt(IV) from aqueous solutions by APDEMS-functionalised zeolite ©

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## Abstract

The recovery of Pt(IV) from aqueous solutions by zeolite functionalised with 3-aminopropyl(diethoxy)methylsilane (APDEMS) was studied at various adsorbent dosage, pH, time, concentration and competing ions. The adsorbent was highly efficient at pH 2 and the maximum adsorption was reached at 180 min. The adsorption of Pt(IV) was not affected by the presence of competing ions instead, other precious metals and trace elements were adsorbed. The strong Pt-adsorbent interaction concluded from kinetic and isotherms models makes the adsorbent suitable for the recovery of Pt(IV) and other metals from mining wastewater.

**Keywords:** Pt(IV), recovery, platinum group elements, APDEMS-functionalised zeolite

## Introduction

Large amount of water is used during mineral processing and the resulting wastewater is discharged into the environment (Lottermoser 2003). The discharged water normally contains significant concentrations of metals. Studies have shown that platinum group metals (PGMs) are discharged along with wastewater as by-products of nickel and copper mining (Xiao and Laplante 2004). Moreover, PGMs mining plants lose significant amounts of PGMs during processing (Hunt et al. 2013). Thus, the accumulation of PGMs could be quite significant in the environment and their recovery could add value to the economy of many countries dependant on them. PGMs are widely used in jewellery, catalytic converters, laboratory equipment and medicine (Chassari et al 2005; Xiao and Laplante 2004). The production of PGMs has increased over the years due to their increasing demand and since only a few countries (South Africa, Canada and Russia) have large reserves, there is a danger of the scarcity of their minerals worldwide and thus a need for recovery from wastewater solutions (Alonso et al 2009).

Zeolites are aluminosilicate clay minerals which are among the cheapest naturally available adsorbents. They consist of  $\text{SiO}_4$  and  $\text{AlO}_4$

frameworks which are linked through oxygen atoms in a three-dimensional array. The overall charge of zeolite is negative due to the replacement of  $\text{Si}^{4+}$  with  $\text{Al}^{3+}$  and is balanced by cations such as Ca, Mg, Na and K in the cavities of the zeolite (Malamis and Katsou 2013). Zeolites have been found to be good adsorbents for trace metals due to their high cation exchange capacity and molecular sieve properties (Bakatula et al. 2015). Moreover, studies have shown that the adsorption capacities of zeolites can be improved by modification where the zeolite acts as a support (Ren et al. 2016). Platinum has been found to interact strongly with nitrogen and thus, the aim of the study to use zeolite functionalised with 3-aminopropyl(diethoxy)methylsilane (APDEMS) which has a primary amine group to recover Pt(IV) from aqueous solutions.

## Materials and methods

### Chemicals

The chemicals used in this study were of analytical reagent grade and were obtained from Sigma Aldrich, South Africa. The  $10 \text{ mg L}^{-1}$  platinum stock solution was prepared from Pt(IV) standard and deionised water in 1 L volumetric flask and was stored in the refrigerator ( $4^\circ\text{C}$ ) until required. Working solutions with specific concentrations were pre-



pared daily from the stock solution through serial dilutions. The pH of the solutions was controlled with 0.01 mol L<sup>-1</sup> NaOH and 0.01 mol L<sup>-1</sup> HCl. The stock solution of the mixed metals was prepared in the same way.

### Functionalisation of zeolite and characterisation

The zeolite was purchased from Sigma Aldrich (Steinheim, Germany). The chemical functionalization was achieved by mixing 5g zeolite with 10 mL of 3-aminopropyl(diethoxy)methylsilane (bp: 85 – 88°C) in a glass vial and the contents were interacted at 180°C for 30 min in an automated Microwave-assisted Extraction monowave 450 (Anton Paar, South Africa). The contents were cooled to room temperature and filtered using 0.45µm cellulose natrete filtech filter paper using suction and rinsed with ethanol. The functionalised zeolite was then dried at 100°C for 24 h.

The natural and functionalised zeolite were characterised with fourier transform infrared (FTIR) spectroscopy in the range of 4000 – 400 cm<sup>-1</sup> for the determination of functional groups, the mineralogy was determined with powder X-ray diffraction (PXRD) D2 Phaser (Bruker, Germany), X-ray fluorescence (XRF) (PANalytical, Netherlands) was used to determine the chemical composition, varioELcube V4.0.13 (Elementar, Germany) was used for elemental analysis. Textural properties (surface area, pore size and pore volume) were analysed with Micromeritics Flow Prep 060 instrument (Aachen, Germany). The point of zero charge (PZC) was also determined using KCl for ionic strength, HNO<sup>3</sup> and NaOH to control pH.

### Batch adsorption studies

The study was carried out by placing the adsorbent and 10 mL Pt(IV) solution at various conditions in 50 mL polypropylene containers which were shaken at room temperature with an elliptical benchtop shaker (Labcon, USA) to attain equilibrium and the contents were filtered with 0.45 µm cellulose natrete Filtech filter paper and the filtrate was analysed with inductively coupled plasma optical emission spectroscopy (ICP-OES) (Spectro genesis, Germany).

Effect of adsorbent mass (50 – 500 mg) on the adsorption of Pt(IV) by APDEMS-functionalised zeolite was determined at pH 2 and room temperature (25°C). Effect of pH (2 – 9), concentration of Pt(IV) (0.5 – 5 mg L<sup>-1</sup>) and contact time (0 – 540 min) on the adsorption of Pt(IV) was determined. Competing ions (Rh(III), Pd(II), Ir(III), Ru(III), Os(III), Fe(III), Ca(II), Mg(II), K(I), Co(II), Ni(II), Hf(IV), Zn(II) and Au(I)) were prepared with Pt(IV) and exposed to APDEMS-functionalised zeolite to determine their effect on adsorption or recovery of Pt(IV).

### Data treatment

The adsorption capacity,  $q_e$  (mg g<sup>-1</sup>) and the adsorption efficiency were calculated using equations 1 and 2, respectively.

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (1)$$

$$\text{adsorption efficiency} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

where  $C_0$  and  $C_e$  are initial and equilibrium concentrations of metals (mg L<sup>-1</sup>),  $V$  is the volume of the solution used (L) and  $M$  is the mass of the adsorbent (g).

### Adsorption isotherms

The type of adsorption occurring between Pt(IV) and APDEMS-functionalised zeolite was determined with Langmuir, Freundlich and Dubinin Radushkevich (D-R) adsorption isotherms. The Langmuir isotherm describes the monolayer adsorption between adsorbents and substances (Mushtaq et al. 2016). The Freundlich isotherm describes the non-ideal and reversible adsorption of elements onto the heterogeneous surface (Chen 2015; Mushtaq et al. 2016). The Dubinin-Radushkevich (D-R) isotherm describes the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface (Chen 2015). The Langmuir, Freundlich and Dubinin Radushkevich (D-R) adsorption can be expressed as, respectively:

$$\frac{C_e}{q_e} = \left( \frac{1}{q_m} \right) C_e + \left( \frac{1}{K_L q_m} \right) \quad (3)$$

$$q_e = K_f C_e^{\frac{1}{n}} \quad (4)$$

$$\ln q_e = \ln X_m - K_{ad} \varepsilon^2 \quad (5)$$



where  $q_e$  ( $\text{mg g}^{-1}$ ) is the quantity of the adsorbate adsorbed per gram of adsorbent at equilibrium,  $q_m$  ( $\text{mg g}^{-1}$ ) is the maximum monolayer coverage capacity and  $K_L$  is the Langmuir isotherm constant ( $\text{L mol}^{-1}$ ),  $K_f$  ( $(\text{mg g}^{-1})/(\text{mol L}^{-1})^{1/n}$ ) is the Freundlich isotherm constant and  $n$  is the adsorption intensity,  $K_{ad}$  ( $\text{mol}^2 (\text{kJ}^2)^{-1}$ ) is the Dubinin-Radushkevich isotherm constant,  $X_m$  ( $\text{mg g}^{-1}$ ) is theoretical isotherm saturation capacity and  $\varepsilon$  is the Polanyi constant.

### Kinetic models

The adsorption process controlling mechanism between Pt(IV) and APDEMS-functionalised zeolite was determined with pseudo first- and second order kinetic models represented by equations 6 and 7, respectively (Bakatula et al 2015). The correlation coefficient ( $R^2$ ) and the closeness of the experimental adsorption capacity,  $q_{exp}$  to the calculated,  $q_{cal}$  were used to determine the model that best describes the kinetic data.

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

where  $q_t$  ( $\text{mg g}^{-1}$ ) and  $q_e$  ( $\text{mg g}^{-1}$ ) are the adsorption capacities at time  $t$  and equilibrium, respectively,  $k_1$  ( $\text{min}^{-1}$ ) and  $k_2$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ) are the rate constants.

## Results and discussion

### Characterisation

The results from XRF showed that silica ( $\text{SiO}_2$ ) (68.49%) and alumina ( $\text{Al}_2\text{O}_3$ ) (11.48%) are main components of the zeolite. Other

chemical components are  $\text{K}_2\text{O}$  (3.79%),  $\text{Na}_2\text{O}$  (1.47%),  $\text{CaO}$  (1.22%),  $\text{Fe}_2\text{O}_3$  (1.09%) and loss on ignition of 11.03%. The PXRD results are shown in Fig. 1. The zeolite was mainly composed of clinoptilolite, quartz and sanidine. From these results, it was clear that the natural zeolite can be classified as clinoptilolite. The FTIR spectra of the raw and functionalised zeolite are shown in Fig. 2. The peaks at 695 and 964  $\text{cm}^{-1}$  which are present in both the raw and functionalised zeolite are due to the Si-O and Al-O-Si and Si-OH groups (Guaya et al. 2015). The success of functionalization was confirmed by the peaks at 790 and 765  $\text{cm}^{-1}$  which are due to Si-O-Si bonds of the zeolite and APDEMS. The peak at 1644  $\text{cm}^{-1}$  can be attributed to the deformation vibration of water. The peaks beyond 3300  $\text{cm}^{-1}$  are due to the hydroxyl groups of the zeolite. The  $-\text{CH}_2$  and  $-\text{CH}$  stretching vibrations of APDEMS are represented by the peaks at 2925 and 2872  $\text{cm}^{-1}$ . The peaks at 1182 and 1257  $\text{cm}^{-1}$  on the functionalised zeolite can be attributed to Si- $\text{CH}_2$  and Si- $\text{CH}_3$ , respectively. The presence of the nitrogen groups is represented by the peaks at 1575  $\text{cm}^{-1}$  ( $-\text{NH}$  vibration) and 3366  $\text{cm}^{-1}$  (primary amines). Moreover, the elemental analysis showed that the C and H percentages were high on the functionalised zeolite and that of N was observed on APDEMS-functionalised zeolite which was not present on the raw zeolite. These results show that the functionalization of raw zeolite was successful. The surface area of the raw zeolite decreased from 16.28 to 2.17  $\text{m}^2 \text{g}^{-1}$  due to functionalization with APDEMS and this also confirmed the success of the addition of

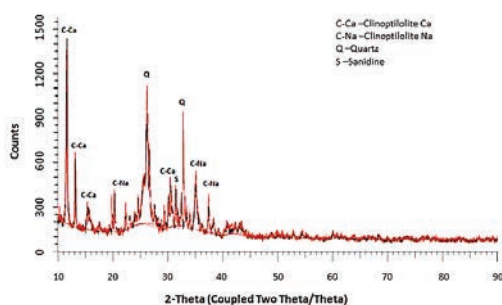


Fig. 1 PXRD pattern of zeolite

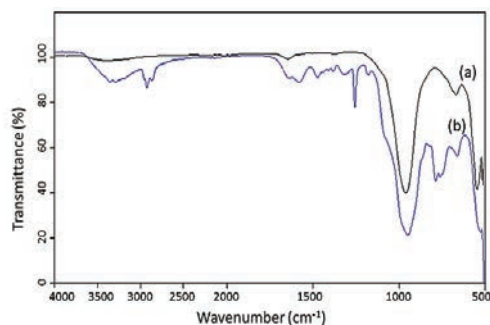


Fig. 2 FTIR spectra of raw zeolite (a) and functionalised zeolite (b)



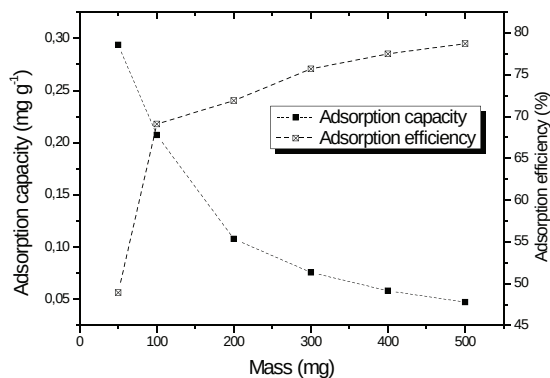


Fig. 3 Effect of mass on the adsorption of Pt(IV) by APDEMS-functionalised zeolite

the ligand on zeolite. This reduction can be attributed to the smothering of the pores by APDEMS as the pore size and pore volume also decreased from 12.97 to 4.50 nm and 0.052 to 0.0045 cm<sup>3</sup>, respectively.

#### Effect of adsorbent mass

The effect of adsorbent mass on the adsorption or recovery of Pt(IV) was studied and the results are shown in Fig. 3. The adsorption efficiency increased with increasing adsorbent mass but the adsorption capacity decreased. For subsequent experiments, 10 g L<sup>-1</sup> adsorbent mass was used as the adsorption capacity and the adsorption efficiency were significant.

#### Effect of pH

Studies have shown that pH can affect the behaviour and hence the adsorption efficiency of adsorbents (Bakatula et al. 2015; Ren et al. 2016). The adsorption capacity decreased with increasing solution pH and this could

be attributed to the speciation of Pt(IV) and the surface charge (Fig. 4). At acidic pH, the surface groups were protonated and thus, –NH<sup>3+</sup> which had high affinity for the anionic Pt(IV) species (PtCl<sub>6</sub><sup>2-</sup>) resulted. The anionic chloride species were more prevalent at acidic pH due to the addition of HCl. During the processing of PGMs, concentrated acids are used for extraction and thus, the discharged water is highly acidic (Nguyen et al. 2016). Thus, the adsorbent will work well and significantly recover Pt(IV) from mining wastewaters which are highly acidic. PZC was found to be 5.3. The adsorption capacity decreased significantly beyond pH 2 and this can be attributed to the low amount of chloride species favourable for adsorption as well as electrostatic repulsion between the Pt species and the surface groups.

#### Effect of concentration

The adsorption of Pt(IV) at pH 2 was observed to increase with increasing Pt(IV)

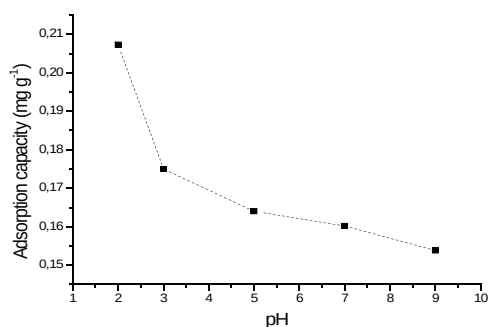


Fig. 4 Effect of pH on Pt(IV) adsorption

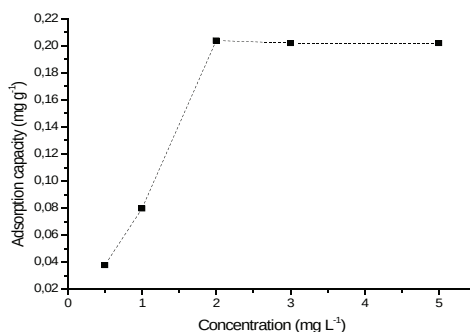


Fig. 5 Effect of concentration on Pt(IV) adsorption



**Table 1** Adsorption isotherm constants

| Langmuir                    |                              |       | Freundlich                                                           |      |       | Dubinin-Radushkevich (D-R)  |                               |       |
|-----------------------------|------------------------------|-------|----------------------------------------------------------------------|------|-------|-----------------------------|-------------------------------|-------|
| $q_m$ (mg g <sup>-1</sup> ) | $K_L$ (L mol <sup>-1</sup> ) | $R^2$ | $K_f$ ((mg g <sup>-1</sup> )/(mol L <sup>-1</sup> ) <sup>1/n</sup> ) | $n$  | $R^2$ | $X_m$ (mg g <sup>-1</sup> ) | $E_s$ (kJ mol <sup>-1</sup> ) | $R^2$ |
| 0.117                       | 3.5x105                      | 0.98  | 32.29                                                                | 1.99 | 0.91  | 1.37                        | 12.42                         | 0.92  |

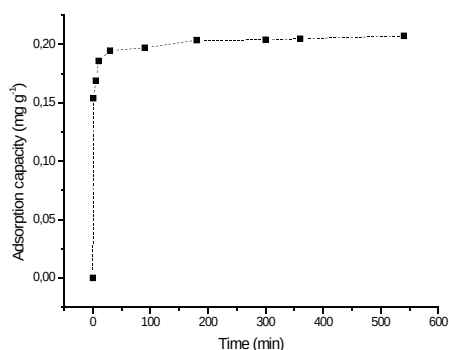
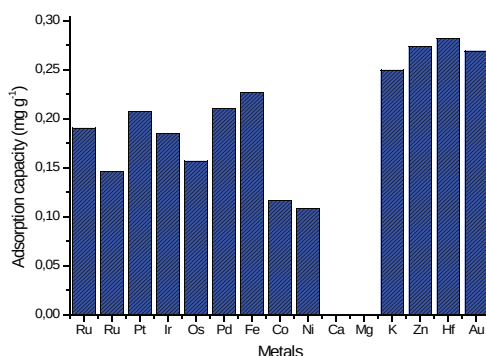
**Table 2** Kinetic parameters for Pt(IV) adsorption by APDEMS-functionalised zeolite

| Pseudo first-order         |                                 |       | Pseudo second-order                           |                                 |       |
|----------------------------|---------------------------------|-------|-----------------------------------------------|---------------------------------|-------|
| $K_1$ (min <sup>-1</sup> ) | $q_{exp}$ (mg g <sup>-1</sup> ) | $R^2$ | $K_2$ (g mg <sup>-1</sup> min <sup>-1</sup> ) | $q_{exp}$ (mg g <sup>-1</sup> ) | $R^2$ |
| 0.0088                     | 0.0061                          | 0.71  | 6.71                                          | 0.103                           | 0.99  |

concentration from 0.5 to 2 mg L<sup>-1</sup> (Fig. 5). The increase in adsorption capacity can be attributed to the availability of binding sites (-NH<sub>3</sub><sup>+</sup>). The adsorption efficiencies were 75.6, 79.7, 78, 3, 57.7 and 40.4% at 0.5, 1, 2, 3 and 5 mg L<sup>-1</sup>, respectively. The ability of the adsorbent to significantly adsorb very low concentrations of Pt(IV) makes it a suitable adsorbent for PGMs wastewater which contains very low concentrations of PGMs (Hunt and Clark 2013, Hunt et al 2015). This also means that there is a strong interaction between Pt(IV) and the adsorbent. Beyond 2 mg L<sup>-1</sup>, no increase in adsorption was observed. The adsorption isotherm results (Table 1) indicated that the interaction of Pt(IV) onto APDEMS-functionalised zeolite is through monolayer adsorption since the experimental data was described better by Langmuir isotherm ( $R^2 > 0.98$ ). The free energy change as determined from D-R isotherm was found to 12.42 kJ mol<sup>-1</sup> indicating that the adsorption process is through ion exchange (Bakatula et al. 2015).

### Effect of contact time

The effect of contact time on the adsorption of Pt(IV) by APDEMS-functionalised zeolite was investigated and the results are shown in Fig. 6. A rapid increase in adsorption was observed between 0 and 30 min after which, a slow uptake was observed until 180 min. Equilibrium was reached at 180 min where the adsorption was controlled by diffusion. Thus, 180 min was chosen as the sufficient time for the recovery of Pt(IV) by the adsorbent. The kinetic data was best described by pseudo second-order indicating that chemisorption was the rate controlling mechanism ( $R^2 > 0.99$ ) (Table 2). This was also supported by the calculated adsorption capacity ( $q_{cal}$ ) (0.102 mg g<sup>-1</sup>) which was very similar to the experimental adsorption capacity (0.103 mg g<sup>-1</sup>). The experimental adsorption capacity determined with pseudo first-order was found to be 0.0061 mg g<sup>-1</sup> which is very different from the calculated capacity, further explaining that there is no good correlation with pseudo first-order.

**Fig. 6** Effect of time on Pt(IV) adsorption**Fig. 7** Effect of competing ions on Pt(IV) adsorption

### Effect of competing ions

A mixture of 2 mg L<sup>-1</sup> Pt(IV) and other ions at pH 2 was exposed to APDEMS-functionalised zeolite to determine the efficiency of the adsorbent on the recovery of Pt(IV) in the presence of other ions. The adsorption capacity of Pt(IV) was not affected by the presence of other ions, some of which are PGMs (Fig. 7). Moreover, these PGMs and other cations except Ca and Mg were adsorbed by the adsorbent making APDEMS-functionalised zeolite a dual efficacy adsorbent. The ability to significantly adsorb Pt(IV) in the presence of other ions makes the APDEMS-functionalised zeolite a suitable adsorbent to be used in mining wastewater.

### Conclusion

In this study, APDEMS-functionalised zeolite was synthesised and used to recover Pt(IV) from aqueous solutions. The characterisation results showed that the functionalization was successful. The experimental studies were carried out under the optimised conditions (100 mg adsorbent, pH 2, 2 mg L<sup>-1</sup> and 180 min) and indicated that 0.207 mg g<sup>-1</sup> of Pt(IV) was removed from aqueous solutions by APDEMS-functionalised zeolite. The adsorbent was significantly adsorbed Pt(IV) at highly acidic pH (pH 2) which makes the adsorbent very suitable for PGM mining wastewater which is highly acidic. The kinetic (pseudo second-order) and isotherm (Langmuir) models as well as the energy from D-R isotherm indicated that there was strong chemisorptive Pt-adsorbent interaction. The presence of competing ions did not affect the adsorption of Pt(IV). The adsorbent can be applied in retaining ponds into which processing solutions are discharged and fed to the processing units together with fresh ore after recovery.

### Acknowledgements

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# PAPER IV

**This paper investigated the recovery of Platinum (IV) from aqueous solutions using APDEMS-functionalised bentonite.**

**The paper is published in the Journal of Dispersion Science and Technology. Impact Factor: 1.701.**

**Contribution:** lead author, conducted experimental work and data modelling, conceptualization, methodology, software validation, formal analysis, investigation, writing - original draft and visualization.



## Recovery of platinum (IV) from aqueous solutions using 3-aminopropyl(diethoxy)methylsilane functionalized bentonite

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# Recovery of platinum (IV) from aqueous solutions using 3-aminopropyl(diethoxy)methylsilane functionalized bentonite

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## ABSTRACT

Platinum, naturally found in a few parts of the world, is one of the most widely used precious elements and its recycling from waste components is very important due to demand. However, not as much attention has been given toward its recovery from aqueous solutions. This present study is aimed at recovering platinum (Pt(IV)) from aqueous solutions such as mining wastewaters using bentonite functionalized with 3-aminopropyl(diethoxy)methylsilane (APDEMS). The study exploited the novelty of using a cost-effective natural mineral, bentonite, as a support base to which amine groups, that have a high affinity for Pt(IV), could be anchored. The approach involved characterizing the natural and functionalized bentonite. Adsorption experiments were conducted in batch mode under varying conditions, namely: adsorbent dosage, pH, initial concentration, and competing ions. The data were fitted using various kinetic and isothermic models to understand the adsorption mechanism. The results showed that >85% of Pt(IV) in solution was recovered at a dosage of  $10 \text{ g L}^{-1}$  of the adsorbent at pH 2, within 90 min of contact. The adsorption of Pt(IV) increased by >5% in the presence of other ions, most likely due to synergistic effects. The adsorption of Pd(II), Ir(III), Rh(III), Os(III), and Ru(III) was also enhanced along with that for Pt(IV). Adsorption was found to proceed *via* the Langmuir isotherm and the pseudo second-order kinetic model, implying monolayer coverage and chemisorption, respectively. The successful synthesis of APDEMS-functionalized bentonite and its efficiency in adsorbing Pt(IV) from aqueous solutions make it a potential adsorbent for application in the mining industry.

## ARTICLE HISTORY

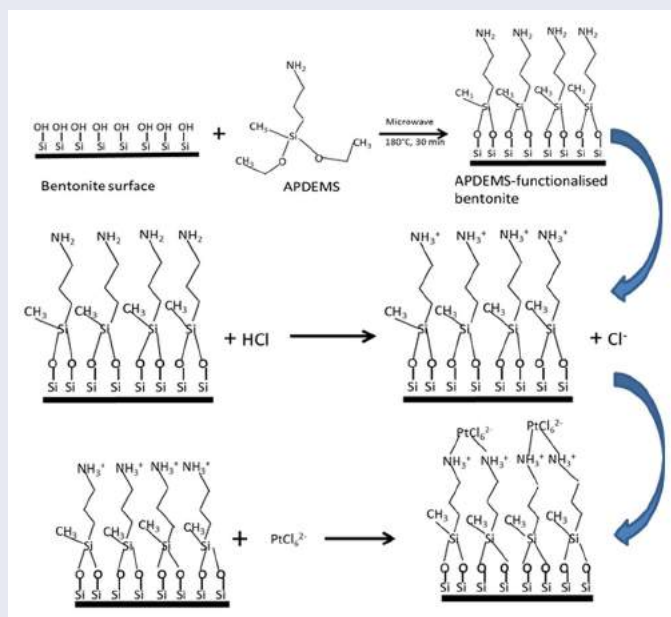
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## KEYWORDS

Adsorption capacity; bentonite clay; isotherm models; kinetic models; platinum group elements

## GRAPHICAL ABSTRACT



## Introduction

Platinum has favorable physical and chemical properties that make it one of the most important precious elements for various applications such as in catalysts (for fuel cells, sensors, petroleum, and automotive industries), medicine, and jewelry.<sup>[1–4]</sup> It occurs in few parts of the world including, notably in: South Africa, Canada, Zimbabwe, Russia, and the United States, with South Africa accounting for >70% of the world's reserves and resources.<sup>[5,6]</sup> Supply of platinum has increased over the years due to high demand, with some studies raising concerns that the current high supply may lead to the scarcity of this element in the future.<sup>[6,7]</sup> Platinum is mined with a host of other platinum group elements (PGEs) *viz* palladium, rhodium, ruthenium, osmium, and iridium. During mineral processing, the PGEs are separated from base elements using many steps including leaching, flotation, and volatilization.<sup>[8,9]</sup> There have been reported losses of PGEs during crushing, grinding, and flotation.<sup>[8,10]</sup> The lost PGEs may accumulate in mining wastewater ponds and the environment over the years, leading to potentially economically recoverable amounts, but also potential toxicity.<sup>[11]</sup> Exposure to high concentrations of platinum can have negative side effects in humans such as problems in the respiratory tract and skin.<sup>[12]</sup> Some cellular functions can be inhibited by the presence of platinum complexes.<sup>[13]</sup> Platinum was also found to cause DNA damage and protein denaturing in rats.<sup>[14]</sup> Thus, the removal of platinum from aqueous solutions will be important both for economic and health reasons. The maximum permissible limit of platinum in water as determined by the United States Environmental Protection Agency (USEPA) is 0.1 mg L<sup>-1</sup>, but mining wastewaters normally contain >2 mg L<sup>-1</sup>.<sup>[15,16]</sup>

One of the most effective methods of removing elements from aqueous solutions is adsorption using nanoparticles and clay-based adsorbents such as zeolite, montmorillonite, and bentonite.<sup>[17–20]</sup> Bentonite is a naturally abundant<sup>[21]</sup> layered clay mineral consisting of Al (Al (O<sub>5</sub>, OH)) and Si (SiO<sub>4</sub>) sheets with an overall negative structural charge, making it react with electron acceptors.<sup>[22,23]</sup> The selectivity of bentonite can be improved by anchoring various functional groups on its surface that have varying affinities for elements of interest in the solution. This study accomplished the effective adsorption of platinum from aqueous solutions simulating PGE mining wastewaters by using bentonite functionalized with 3-aminopropyl(diethoxy)methylsilane (APDEMS) as an adsorbent. APDEMS (CH<sub>3</sub>Si(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub>) contains a carbon chain with nitrogen (amine), for which platinum has an affinity.<sup>[24,25]</sup> The novelty of the work has been in irreversibly anchoring a functional group (that would otherwise be ineffective as a standalone) onto a support structure provided by bentonite (cost-effective mineral), forming a hybrid adsorbent that has potential application in the PGE industry.

## Materials and methods

### Functionalization of bentonite with 3-aminopropyl(diethoxy)methylsilane

Bentonite was chemically functionalized by interacting 10 mL of 3-aminopropyl(diethoxy)methylsilane (MW

191.34 g mol<sup>-1</sup>, bp 85 – 88 °C) with 5 g bentonite in a glass vial using a Monowave 450 instrument (Anton Paar, South Africa). The reactants were reacted at 180 °C with a holding time of 30 min. They were then filtered using suction, rinsed with methanol, and dried at 100 °C for 24 h before usage.

### Characterization

Qualitative and quantitative information of bentonite was determined by powder X-ray diffraction (PXRD) D2 Phaser (Bruker, Germany) at a range of 10 – 90 2 $\theta$ , Chemical composition was done using X-ray fluorescence (XRF) (PAAnalytical, Netherlands) while functional groups were determined using Fourier transform infrared (FTIR) spectroscopy (Tensor 27, Bruker, Germany).<sup>[26]</sup> Elemental analysis was conducted on natural functionalized bentonite using the VarioELcube V4.0.13 (Elementar, Germany). Textural properties were determined using the Micromeritics instrument (Aachen, Germany). The point of zero charges (PZC) was determined using Surpass 3 electrokinetic analyzer (Anton Paar, South Africa).

### Chemicals

The chemicals used were analytically pure and purchased from Sigma Aldrich, South Africa. A stock solution (1 L) of 10 mg L<sup>-1</sup> Pt(IV) was prepared from 1000 mg L<sup>-1</sup> platinum standard in 5% w/w of c(HCl) and kept cool in the refrigerator at 4 °C until required for usage. Serial dilutions were done daily from the stock solution to make working solutions. A stock solution containing a mixture of PGEs was prepared as described above. A stock solution of other elements (Fe, Ca, Mg, K, Co, Ni, and Zn) was prepared from the nitrate salts of the elements to make a stock solution which was mixed with the solution containing Rh, Pd, Ir, Ru, Os, Pt, Hf, and Au to make a final solution of 2 mg L<sup>-1</sup> of all the elements.

### Batch adsorption experiments

Experiments were done in triplicates ( $n = 3$ ) and percentage relative standard deviation (RSD) was used to confirm the reliability of the data. Thus, only those values that agreed up to 5% RSD were considered. The adsorption of Pt(IV) was first done using natural bentonite. However, the adsorbed amount was very low ( $\sim 0.002 \mu\text{g g}^{-1}$ ) and insignificant ( $p > 0.05$ ) at different conditions (adsorbent mass, concentration, and pH). Therefore, those results have not been included in the manuscript.

Optimum conditions of the functionalized adsorbent for significant recovery of Pt(IV) were investigated by studying the effect of adsorbent dosage (50 – 400 mg) while keeping other variables (pH and concentration) constant. The effect of initial concentration (0.5 – 10 mg L<sup>-1</sup>) of Pt(IV) on adsorption was also investigated since other studies have indicated that different concentrations can affect the behavior of adsorbents.<sup>[18,30]</sup> The pH of discharged solutions can change overtime hence, the consequences of different pH

values (2–9) on the removal of Pt(IV) were investigated. The Pt(IV) solutions were added to the adsorbent at the mentioned conditions and the ability of the adsorbent to remove Pt(IV) from the solutions was assessed at  $\pm 25^\circ\text{C}$  using an elliptical bench-top shaker (Labcon, South Africa). The effect of competing ions (Rh(III), Pd(II), Ir(III), Ru(III), Os(III), Fe(III), Ca(II), Mg(II), K(I), Co(II), Ni(II), Hf(IV), Zn(II), and Au(I)) was determined by mixing all the ions with Pt(IV) at pH 2. The equilibration time was determined by shaking Pt(IV) and the adsorbent at different times. The solutions were analyzed with inductively coupled plasma optical emission spectroscopy (ICP-OES) (Spectro Genesis, Germany). An optic flush of  $1.0\text{ L min}^{-1}$ , Hvps current and voltage of 52 mA and 290 V, respectively were used in ICP-OES for the determination of Pt(IV) concentration. The optic temperature used was between 29 and  $31^\circ\text{C}$  with argon and nebulizer pressure between 6–7 bar and 2–4 bar, respectively.

The adsorption capacity ( $q_e$ ) ( $\mu\text{g g}^{-1}$ ) and adsorption percentage were determined using Equations (1) and (2), respectively:<sup>[27]</sup>

$$q_e = \frac{(C_o - C_e)V}{w} \times 1000 \quad (1)$$

$$\text{Adsorption efficiency} = \frac{(C_o - C_e)}{C_e} \times 100 \quad (2)$$

where  $C_o$  ( $\text{mg L}^{-1}$ ) and  $C_e$  ( $\text{mg L}^{-1}$ ) are starting and equilibrium concentrations, respectively,  $V$  (L) is the volume of the solution, and  $w$  (g) is the mass of bentonite.

### Kinetic models

The adsorption process between Pt(IV) and APDEMS-functionalized bentonite was determined using pseudo first- and second-order, Elovich, Weber-Morris intraparticle diffusion, film diffusion, and Vermeulen film diffusion kinetic models. The pseudo first-order which was proposed by Lagergren, describes the physical adsorption or bonding of elements to adsorbents through Van der Waals forces and can be expressed as:<sup>[28]</sup>

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (3)$$

where  $q_e$  is the equilibrium adsorbed amount ( $\text{mg g}^{-1}$ ),  $q_t$  is the experimental adsorbed amount ( $\text{mg g}^{-1}$ ) of elements at time  $t$  and  $k_1$  is the rate constant ( $\text{min}^{-1}$ ).

The pseudo second-order kinetic model which demonstrates the dependence of rate on sorption capacity was also used (Equation (4)).<sup>[29–30]</sup> The experimental data that can be described by this model, normally have strong interactions which involves valency forces through the exchange or sharing of electrons between the elements and adsorbents as covalent forces.<sup>[31]</sup>

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_{et}} \quad (4)$$

where  $k_2$  ( $\text{g mg}^{-1} \text{ min}^{-1}$ ) is rate constant and  $k_2 q_e^2$  is the initial adsorption rate.

Elovich kinetic model was also used. It is based on the assumption that adsorbent surfaces are energetically heterogeneous and that the kinetics of adsorption is not significantly affected by the interaction between the elements adsorbed (Equation (5)).<sup>[32]</sup>

$$\frac{dq_t}{dt} = a \cdot \exp(-b \cdot q_t) \quad (5)$$

where  $a$  is the initial adsorption rate ( $\text{g mg}^{-1} \text{ min}^{-1}$ ) and  $b$  is a constant ( $\text{g mg}^{-1} \text{ min}^{-1}$ ).

The Weber-Morris intraparticle diffusion model was also used to fit the kinetic data. This model will be useful when there is a linear relationship between the adsorbed amount of the analyte and the square root of time. The model can determine if the rate-limiting step is intraparticle diffusion, external mass transfer, or both.<sup>[33]</sup> The Weber-Morris intraparticle diffusion model can be expressed as:

$$q_t = k_{id} t^{1/2} + C \quad (6)$$

where  $C$  ( $\text{mg g}^{-1} \text{ min}^{-1}$ ) is the thickness of a boundary layer and  $k_{id}$  ( $\text{mg g}^{-1} \text{ min}^{1/2}$ ) is a rate constants.

The film diffusion model is often applied when the transport of an analyte from the liquid phase to the solid phase is paramount.<sup>[34]</sup> The film diffusion model can be presented as follows:

$$\ln(1 - F) = -K_F t + I_F \quad (7)$$

where  $F$  is the fractional attainment of equilibrium ( $F = q_t/q_e$ ),  $K_F$  is the adsorption rate constant, and  $I_F$  is the diffusion constant that can tell whether the kinetics of the adsorption process is controlled by diffusion through the liquid film surrounding the solid adsorbent ( $I_F = 0$ ) or not.

The Vermeulen film diffusion model which is good for processes where there is an ion-exchange occurring between the ions of the adsorbent and the analyte was also used. The flux of the ions on the adsorbent to the solution and the flux of the analyte from the solution to the adsorbent depends on the diffusion coefficient and the ion concentration on the adsorbent.<sup>[35]</sup> The model can be described as:

$$\ln(1 - F^2) = -\frac{\pi^2 D t}{r^2} \quad (8)$$

where  $F$  is the fraction of analyte bound at time  $t$ ,  $r$  is the medium radius of the adsorbent, and  $D$  ( $\text{m}^2 \text{ min}^{-1}$ ) is the diffusion coefficient.

### Adsorption isotherms

The sorption relationship of the analyte and APDEMS-functionalized bentonite was determined using two and three-parameter adsorption isotherm models. The two-parameter isotherms (Langmuir, Freundlich, Dubinin-Radushkevich, and Temkin) are known for their simplicity and the ability to be easily linearized. The three-parameter isotherms (Sips, Redlich-Peterson, Toth, and Fitz-Schlunder) are more complicated than the two-parameter models since they have three unknowns that have to be determined.

**Two-parameter isotherm models.** The Langmuir isotherm was used to fit the experimental adsorption data. An assumption used in this isotherm is that the adsorbed element cannot interact with other elements and that the surface has a finite number of identical sites hence, a monolayer adsorption results.<sup>[36]</sup> Thus, Langmuir isotherm describes the distribution of elements onto a homogeneous surface and can be expressed as:

$$\frac{C_e}{q_e} = \left(\frac{1}{q_m}\right)C_e + \left(\frac{1}{K_L q_m}\right) \quad (9)$$

where  $q_m$  ( $\text{mg g}^{-1}$ ) is the maximum amount of adsorption that can be achieved and  $K_L$  is a constant ( $\text{L mol}^{-1}$ ). The slope was used to determine  $q_m$  whilst the intercept was used to determine  $K_L$  from the plot of  $(C_e/q_e)$  and  $C_e$ .

The Freundlich isotherm which describes the adsorption of elements onto a heterogeneous surface was used (Equation (10)). The model assumes that the elements can be adsorbed or captured by different active sites with different adsorption energies.<sup>[37]</sup>

$$q_e = K_f C_e^{1/n} \quad (10)$$

where  $K_f$  ( $(\text{mg g}^{-1})/(\text{mol L}^{-1})^{1/n}$ ) and  $n$  are empirical constants.<sup>[38]</sup> If  $n > 1$  then the adsorption between the elements and adsorbents is favorable.<sup>[39]</sup>

The Dubinin-Radushkevich (D-R) which describes the adsorption between adsorbents and adsorbates with Gaussian energy distribution onto a heterogeneous surface was used.<sup>[40]</sup>

$$\ln q_e = \ln X_m - K_{DR} \varepsilon^2 \quad (11)$$

where  $X_m$  is the theoretical coverage ( $\text{mg g}^{-1}$ ),  $K_{DR}$  ( $\text{mol}^2/\text{kJ}^2$ ), and  $\varepsilon$  are D-R constants and  $\varepsilon$  can be expressed as:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e}\right) \quad (12)$$

where  $R$  is the universal gas constant ( $\text{J (mol K)}^{-1}$ ),  $T$  is the temperature (K).

The  $K_{DR}$  can be used to determine the mean free energy of adsorption ( $E_{DR}$ ) using the equation:

$$E_{DR} = \frac{1}{\sqrt{2K_{DR}}} \quad (13)$$

The experimental data was fitted using the Temkin adsorption isotherm. It has the assumption that the heat of adsorption decreases linearly rather than logarithmically. Moreover, the heat of adsorption decreases in a linear fashion with coverage as a result of adsorbent-analyte interaction.<sup>[41]</sup> The Temkin isotherm can be expressed as:

$$q_e = \frac{RT}{b_T} \ln K_T C_e \quad (14)$$

where  $K_T$  ( $\text{L mol}^{-1}$ ) is the Temkin isotherm constant related to the heat of adsorption,  $R$  ( $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ) is a gas constant and  $T$  (K) is the absolute temperature.

**Three-parameter isotherm models.** The Sips adsorption isotherm is a three-parameter model that fits data where there

is a heterogeneous adsorption surface and localized adsorption with no analyte-analyte interactions.<sup>[42]</sup> The model is a combination of both the Langmuir and Freundlich isotherms but it reduces to the Freundlich at lower equilibrium analyte concentrations and to Langmuir at higher concentrations. The Sips model linear equation can be expressed as:

$$\frac{1}{q_e} = \frac{1}{q_m K_s} \left(\frac{1}{C_e}\right)^{1/n} + \frac{1}{q_m} \quad (15)$$

where  $K_s$  ( $\text{L mg}^{-1}$ ) is the Langmuir isotherm constant,  $n_s$  is the Freundlich heterogeneity factor.

The Redlich-Peterson (R-P) isotherm model is another three-parameter isotherm model that also combines the Langmuir and Freundlich isotherms. It can be used for homogeneous or heterogeneous surface adsorption data. It has parameter  $\beta$  which can be between 0 and 1.<sup>[43]</sup> When it is at 1, the R-P equation reduces to the Langmuir equation. The linear R-P isotherm model can be expressed as:

$$\ln \left( K_{RP} \frac{C_e}{q_e} - 1 \right) = \beta \ln C_e + \ln \alpha \quad (16)$$

Where  $K_{RP}$  ( $\text{mg g}^{-1}$ ) is the R-P adsorption isotherm constant,  $\alpha$  ( $\text{mg L}^{-1}$ ) is the R-P isotherm constant, and  $\beta$  is the R-P isotherm constant which should be between 0 and 1.

The Toth isotherm model can well describe the adsorption data where there is a multilayer and a heterogeneous surface adsorption where both low and high analyte concentrations are considered.<sup>[44]</sup> The linear expression of the Toth model is as follows:

$$\ln \left( \frac{q_e}{q_m - q_e} \right)^{n_T} = n_T \ln K_T + n_T \ln C_e \quad (17)$$

where  $K_T$  is the Toth isotherm constant and  $n_T$  is the Toth isotherm exponent.

The Fritz-Schlunder (F-S) isotherm model also combines the Langmuir and Freundlich isotherms (Equation (18)). When the parameter  $M$  is 1 then the equation reduces to Langmuir model and reduces to Freundlich model at high analyte concentration.<sup>[45]</sup>

$$q_e = \frac{q_{mFS} K_{FS} C_e}{1 + q_{mFS} C_e^M} \quad (18)$$

where  $q_{mFS}$  ( $\text{mg g}^{-1}$ ) is the F-S maximum adsorption capacity,  $K_{FS}$  ( $\text{mg g}^{-1}$ ) is the F-S model equilibrium constant and  $M$  is the F-S model exponent.

## Results and discussion

### Characterization

The chemical composition of bentonite was determined using XRF and the results indicated that silica ( $\text{SiO}_2$ ) (51.49%) and alumina ( $\text{Al}_2\text{O}_3$ ) (16.67%) were the main components of the adsorbent.<sup>[18,46]</sup> Other components of bentonite were;  $\text{Fe}_2\text{O}_3$  (5.03%),  $\text{MgO}$  (3.55%),  $\text{CaO}$  (1.95%),  $\text{K}_2\text{O}$  (1.37%), and  $\text{TiO}_2$  (0.40%) with a loss of ignition of 18.41%. The PXRD results (Figure 1) indicated that the main minerals of bentonite were montmorillonite, kaolite, gibbsite, quartz, and pyrophyllite-

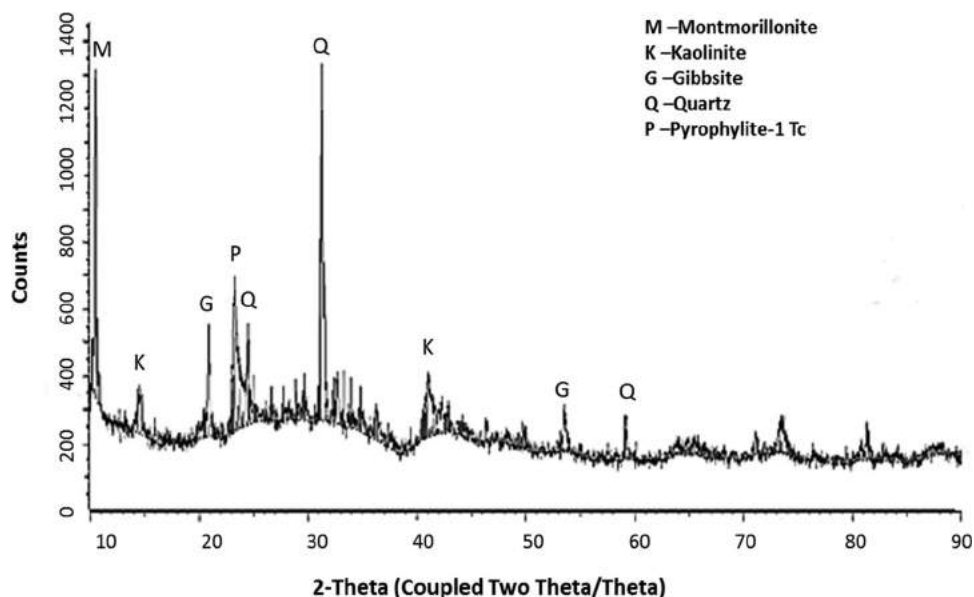


Figure 1. PXRD pattern of bentonite.

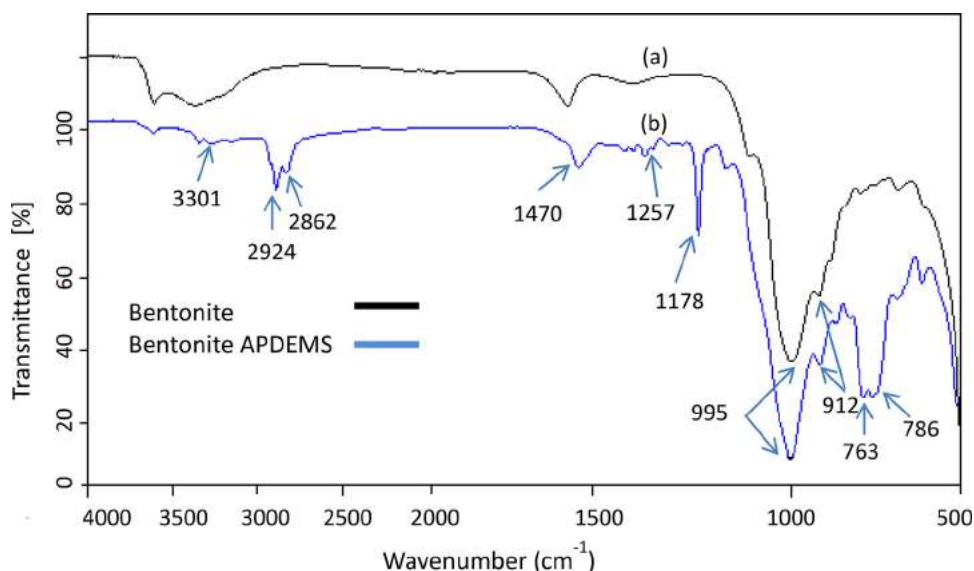


Figure 2. FTIR spectra of (a) natural bentonite and (b) APDEMS-functionalized bentonite.

1 Tc which, have a high content of Al, Si, and O. The silica that was observed in XRF was in the form of quartz. The PXRD analysis was also done on the functionalized bentonite and no change in mineralization was observed thus, the addition of APDEMS on to bentonite did not affect the characteristics of the support.

Functional groups on bentonite and APDEMS-functionalized bentonite were determined using FTIR (Figure 2). The peaks at around 995 and 912  $\text{cm}^{-1}$  on both bentonite and APDEMS-functionalized bentonite were due to Si-O and Al-O stretching vibrations, respectively.<sup>[47,48]</sup> These peaks were as a result of Al-, Si-, and O-rich minerals as indicated by PXRD and XRF results. The Si-O-Si peak resulting from the interaction of Si from APDEMS and Si-O from bentonite overlapped with the peak at  $\sim 995 \text{ cm}^{-1}$ . At 2862 and 2924  $\text{cm}^{-1}$  the -CH and -CH<sub>2</sub> stretching vibrations of the APDEMS long chain were detected, respectively.<sup>[47]</sup> The Si-O-C and Si-CH<sub>3</sub>

bonds of APDEMS were represented by peaks at 1178 and 1257  $\text{cm}^{-1}$ , respectively. The almost overlapping peaks at 763 and 786  $\text{cm}^{-1}$  were due to C-O stretching of APDEMS. The amine groups in APDEMS were represented by peaks at 3301 and 1470  $\text{cm}^{-1}$ . The peaks at 1410 and 1443  $\text{cm}^{-1}$  were indicative of CH<sub>3</sub> asymmetric deformation. CHNS analysis was done to determine the amount of C, H, and N before and after functionalization (Table 1). These results complemented the FTIR results as they showed that functionalized bentonite had nitrogen which was not present on the natural bentonite. Moreover, the percentage of C and H increased due to the presence of APDEMS on the surface of bentonite. These results also give evidence of the success of functionalization of bentonite with APDEMS. The proposed mechanism for the reaction of APDEMS and bentonite is presented (Figure 3).<sup>[47]</sup>

Textural properties of natural bentonite and APDEMS-functionalized bentonite are reported in Table 2. The surface

area of natural bentonite decreased after functionalization with APDEMS due to the smothering of the pores. This also confirms the functionalization of bentonite with APDEMS. SEM images of bentonite before and after functionalization are also presented (Figure 4). The smoothness of bentonite decreases after functionalization and pores which were clearly visible decreased after the addition of APDEMS. Furthermore, bentonite consisted of irregular shaped particles of different sizes. Smaller bentonite particles ranged between 2 and 10  $\mu\text{m}$  whilst bigger particles ranged between 20 and 200  $\mu\text{m}$ .

### Effect of adsorbent mass

The effect of adsorbent mass on the uptake of Pt(IV) was investigated and the results indicated that adsorption

**Table 1.** Elemental analysis data of bentonite and APDEMS-functionalized bentonite (replicates ( $n$ ) = 3, RSD <5%).

| Sample                          | C (%) | H (%) | N (%) | S (%) |
|---------------------------------|-------|-------|-------|-------|
| Bentonite                       | 0.65  | 1.72  | 0.00  | 0.00  |
| APDEMS-functionalized bentonite | 22.09 | 5.31  | 5.84  | 0.00  |

efficiency increased with increasing mass of APDEMS-functionalized bentonite from 50 to 100 mg (Figure 5). However, a reduction in adsorption was observed beyond 100 mg.<sup>[49]</sup> The adsorption capacity of Pt(IV) decreased as adsorbent mass was increased. For subsequent experiments, 10 g L<sup>-1</sup> APDEMS-functionalized bentonite adsorbent dosage was used since it gave the optimal adsorption capacity.

### Effect of pH

The effect of pH on the uptake of Pt(IV) by APDEMS-functionalized bentonite was investigated and adsorption was found to decrease with pH because of the changing surface charge of the adsorbent and the speciation of Pt(IV) (Figure 6). The PZC of APDEMS-functionalized bentonite was found to be 5.3, meaning that experiments conducted below pH 5.3 (i.e., pH 2 – 5), led to the interaction of Pt(IV) with a positively charged surface of the adsorbent.<sup>[50]</sup> At acidic pH, the hydronium ions ( $\text{H}_3\text{O}^+$ ) protonated the amine groups of APDEMS leading to  $\text{CH}_3\text{Si}(\text{OC}_2\text{H}_5)_2(\text{CH}_2)_3\text{NH}_3^+$  as described in Figure 7.<sup>[51]</sup> Since hydrochloric acid (HCl) was used to control the solution pH in the acidic region, a

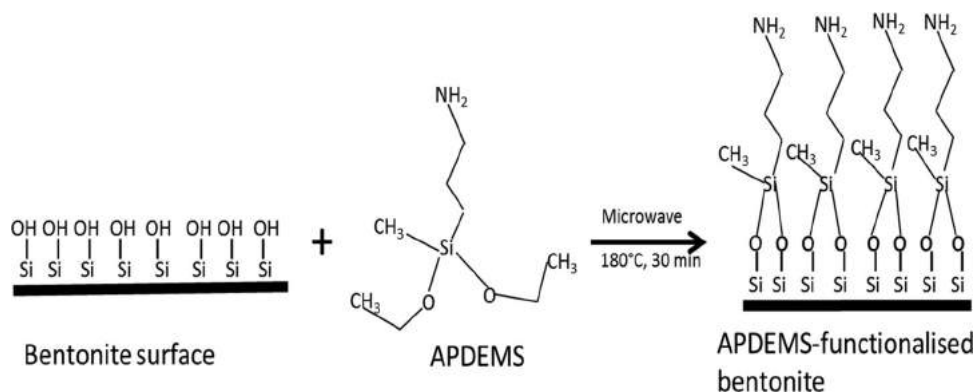


**Figure 3.** Schematic representation of the formation of APDEMS-functionalized bentonite.

**Table 2.** Textural properties of bentonite and APDEMS-functionalized bentonite (replicates ( $n$ ) = 3, RSD <5%).

| Sample                          | Pore size (nm) | Pore volume ( $\text{cm}^3 \text{g}^{-1}$ ) | Surface area ( $\text{m}^2 \text{g}^{-1}$ ) |
|---------------------------------|----------------|---------------------------------------------|---------------------------------------------|
| Bentonite                       | 10.38          | 0.054                                       | 21.29                                       |
| APDEMS-functionalized bentonite | 4.15           | 0.0019                                      | 1.20                                        |

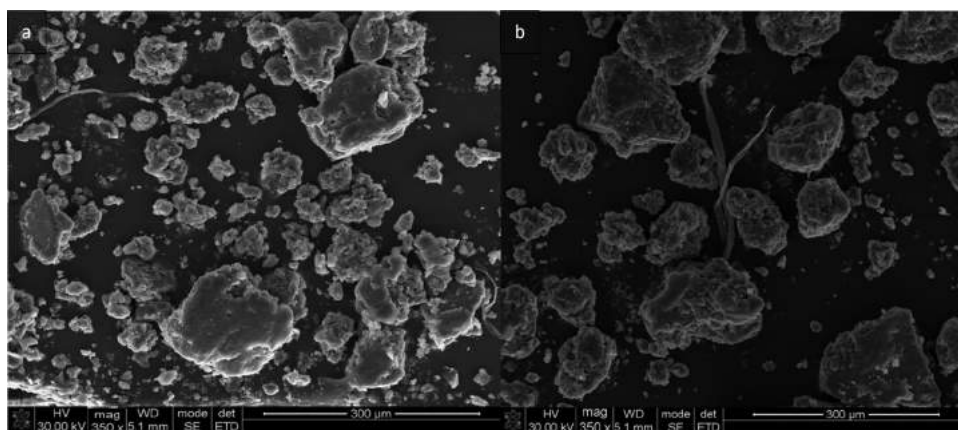
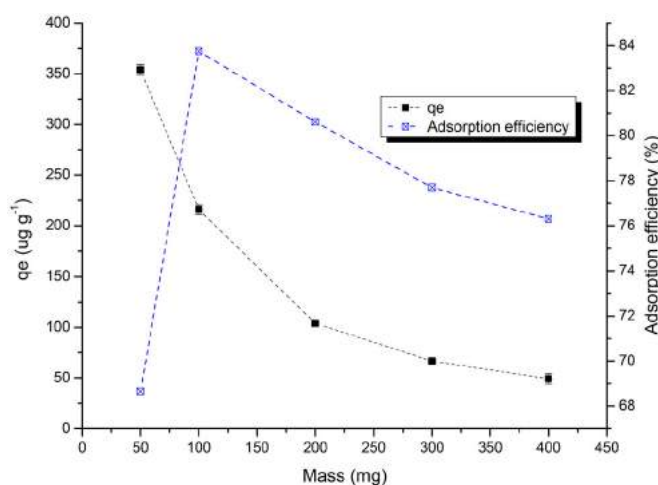


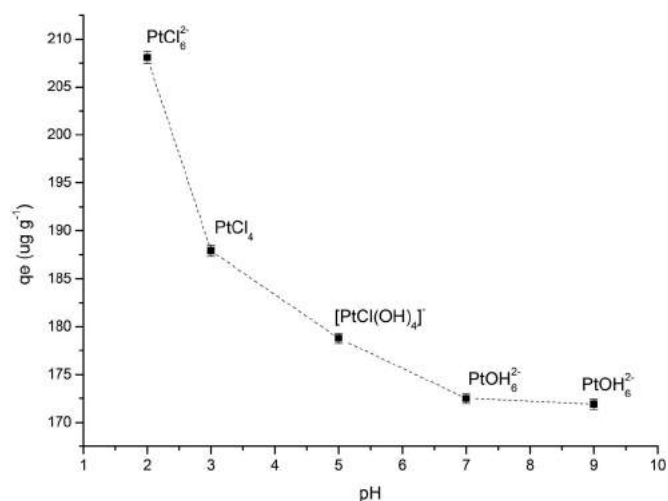
**Figure 4.** Scanning electron microscope images of (a) natural and (b) APDEMS-functionalized bentonite.

**Table 3.** Kinetic parameters of the adsorption of Pt(IV) onto APDEMS-functionalized bentonite (replicates ( $n$ ) = 3, RSD <5%).

| Kinetic model                        | Parameters                                        | Parameter values       |
|--------------------------------------|---------------------------------------------------|------------------------|
| Pseudo first-order                   | $k_1$ ( $\text{min}^{-1}$ )                       | 0.0073                 |
|                                      | $q_e$ ( $\text{mg g}^{-1}$ )                      | 0.028                  |
|                                      | $R^2$                                             | 0.56                   |
|                                      | RMS error                                         | 2.65                   |
| Pseudo second-order                  | $k_2$ ( $\text{g mg}^{-1} \text{min}^{-1}$ )      | 5.72                   |
|                                      | $q_e$ ( $\text{mg g}^{-1}$ )                      | 0.113                  |
|                                      | $R^2$                                             | 0.99                   |
|                                      | RMS error                                         | 0.44                   |
| Elovich                              | $a$ ( $\text{kgmol}^{-1} \text{min}^{-1}$ )       | 0.00010                |
|                                      | $b$ ( $\text{g mg}^{-1} \text{min}^{-1}$ )        | 99.60                  |
|                                      | $R^2$                                             | 0.79                   |
|                                      | RMS error                                         | 0.41                   |
| Weber-Morris intraparticle diffusion | $K_{id}$ ( $\text{mg g}^{-1} \text{min}^{-0.5}$ ) | 0.0024                 |
|                                      | $C$                                               | 0.074                  |
|                                      | $R^2$                                             | 0.47                   |
|                                      | RMS error                                         | 0.81                   |
| Film diffusion                       | $K_F$ ( $\text{min}^{-1}$ )                       | 0.0061                 |
|                                      | $I_F$                                             | -1.75                  |
|                                      | $R^2$                                             | 0.56                   |
|                                      | RMS error                                         | 1.13                   |
| Vermeulen film diffusion             | $D$ ( $\text{m}^2 \text{min}^{-1}$ )              | $9.20 \times 10^{-11}$ |
|                                      | $R^2$                                             | 0.60                   |
|                                      | RMS error                                         | 1.04                   |

**Figure 5.** Effect of mass on the recovery of Pt(IV) by APDEMS-functionalized bentonite (pH 2, concentration =  $2 \text{ mg L}^{-1}$ , temperature =  $25^\circ\text{C}$ , time = 90 min, replicates ( $n$ ) = 3, RSD <5%).

high concentration of  $\text{Cl}^-$  ions resulted, which favored the formation of chloro-complexes ( $\text{PtCl}_6^{2-}$ ) that prefer electrostatic interactions with positively charged groups on the surface of bentonite.<sup>[26,52]</sup> Hence, the highest adsorption capacity was observed when the most acidic pH was reached. This was corroborated by a study by Anbia and Rahimi (2017) that found that the uptake of Pt(IV) ions was high at pH 2.<sup>[11]</sup> Beyond pH 2, the positive character of APDEMS-functionalized bentonite surface decreased due to a low concentration of hydronium ions which then led to the reduction of Pt(IV) capture. There is also a possibility of electrostatic repulsion between the negatively charged Pt(IV) species and negatively charged adsorbent beyond pH 5 due to the high concentration of hydroxide ions.<sup>[11,26]</sup> Thus, the recovery of Pt(IV) by APDEMS-functionalized bentonite will be more effective in highly acidic environments. Other

**Figure 6.** Effect of pH on the recovery of Pt(IV) by APDEMS-functionalized bentonite (concentration =  $2 \text{ mg L}^{-1}$ , mass = 100 mg, temperature =  $25^\circ\text{C}$ , time = 90 min, replicates ( $n$ ) = 3, RSD <5%).

studies have come up with similar results.<sup>[41,52]</sup> The ability of the adsorbent to recover Pt(IV) at very low pH values makes it a suitable adsorbent to use in real wastewaters which are exposed to high concentrations of acids such as HCl and  $\text{HNO}_3$  that are used during the processing of minerals.<sup>[53]</sup>

### Effect of contact time

The relationship between the amount of Pt(IV) adsorbed by APDEMS-functionalized bentonite and contact time is presented in Figure 8. The results indicated that there was fast adsorption of Pt(IV) by the adsorbent between 0 and 30 min which resulted in an exponential growth in adsorption. The increase can be attributed to the availability of active sites ( $-\text{NH}_3^+$  at pH 2) for Pt(IV) as well as high adsorbent-adsorbate affinity.<sup>[54]</sup> An equilibrium phase was observed beyond 90 min and similar results were obtained by Ramesh et al. (2008).<sup>[37]</sup> A contact time of 90 min was chosen as the optimum to attain equilibrium.

### Kinetic models

The coefficient of determination ( $R^2$ ) was used to determine the model that best fits the kinetic experimental data. The pseudo second-order model fitted the data better ( $R^2 > 0.99$ ), meaning that the rate-controlling mechanism for the adsorption of Pt(IV) onto APDEMS-functionalized bentonite was through chemisorption and not mass transfer (Table 3). Thus, the reaction between Pt(IV) and the adsorbent may be due to the exchange of electrons.<sup>[38]</sup> Further validation of the results obtained can be deduced from the experimental and calculated adsorption capacities. The experimentally determined adsorption capacity,  $q_e$  ( $0.113 \text{ mg g}^{-1}$ ) for pseudo second-order was close to the calculated adsorption capacity ( $0.10 \text{ mg g}^{-1}$ ). The experimental adsorption capacity determined from pseudo first-order ( $0.028 \text{ mg g}^{-1}$ ) was significantly different from the calculated value indicating that this model cannot describe the adsorption of Pt(IV) by

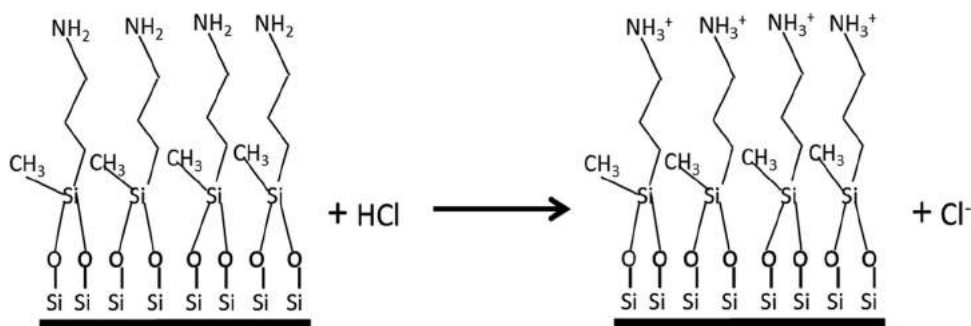


Figure 7. The reaction of APDEMS-functionalized bentonite with HCl.

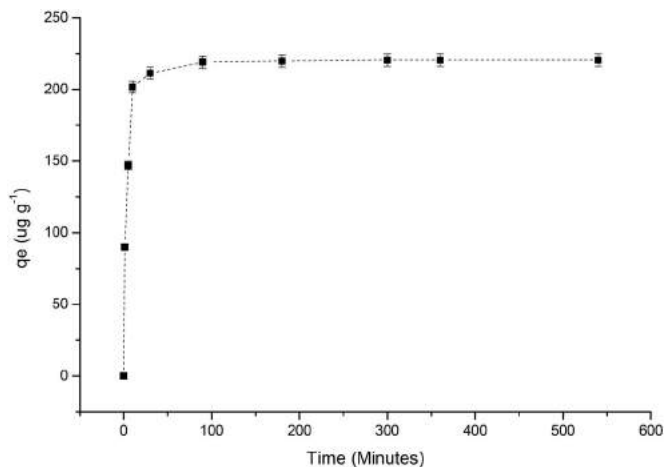


Figure 8. Effect of contact time on the adsorption of Pt(IV) by APDEMS-functionalized bentonite (pH 2, concentration = 2 mg L<sup>-1</sup>, temperature = 25 °C, mass = 100 mg, replicates (n) = 3, RSD < 5%).

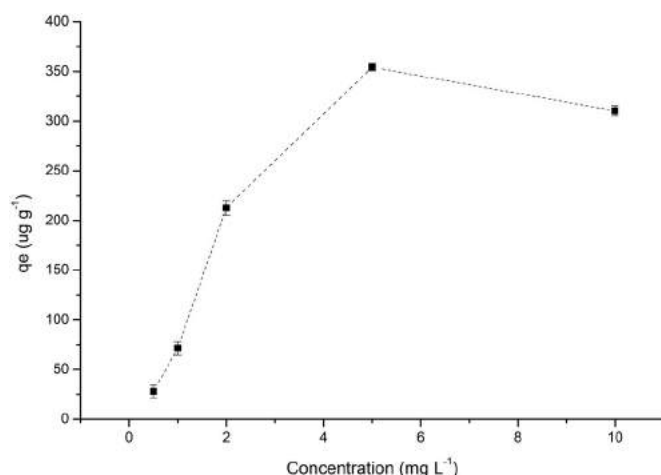


Figure 9. Effect of initial concentration on the adsorption of Pt(IV) by APDEMS-functionalized bentonite (pH 2, temperature = 25 °C, mass = 100 mg, time = 90 min, replicates (n) = 3, RSD < 5%).

APDEMS-functionalized bentonite. The intraparticle, film, and Vermeulen diffusion models poorly described the kinetic data, meaning that diffusion was not the only contributing factor to the adsorption of Pt(IV) onto the adsorbent. The nonlinear relative error (Equation (19)) was also used to evaluate the applicability of the models in predicting the quantitative data.<sup>[54]</sup>

$$\text{RMS error} = \frac{q_{e, \text{cal}} - q_{e, \text{exp}}}{q_{e, \text{exp}}} \quad (19)$$

where  $q_{e, \text{cal}}$  (mg g<sup>-1</sup>) and  $q_{e, \text{exp}}$  (mg g<sup>-1</sup>) are then calculated and experimental adsorption capacities. The RMS error from the pseudo second-order model was very small which further indicated that the model gives an accurate representation of the rate controlling mechanism of Pt(IV) uptake by APDEMS-functionalized bentonite.<sup>[54,55]</sup>

### Effect of concentration

Studies have shown that initial concentration can affect the efficiency of adsorbents hence, the role of concentration on the adsorption of Pt(IV) by APDEMS-functionalized bentonite was studied.<sup>[26,37]</sup> The adsorption capacity of Pt(IV) increased with concentration from 0.5 to 5 mg L<sup>-1</sup> due to the availability of active sites and the concentration gradient driving force (Figure 9).<sup>[18]</sup> The adsorbed amount of Pt(IV) decreased significantly ( $p < 0.05$ ) beyond 5 mg L<sup>-1</sup> and this

can be due to the high concentration of Pt(IV) on a limited number of active sites. The adsorption efficiencies were found to be 55.8, 71.3, 85.1, 64.4, and 29% at 0.5, 1, 2, 5, and 10 mg L<sup>-1</sup>, respectively.

### Adsorption isotherms

The results for the two and three-parameter isotherm models are given in Tables 4 and 5, respectively. Using the coefficient of determination from both types of models, the Langmuir isotherm ( $R^2 > 0.93$ ) was found to fit the experimental data better. This means that Pt(IV) adsorption onto APDEMS-functionalized bentonite was likely to occur through identical adsorption sites in a monolayer fashion since all the multilayer adsorption and heterogeneous surface models poorly described the adsorption data.<sup>[11]</sup> Important features of the Langmuir isotherm were expressed using equilibrium parameter ( $R_L$ ) expressed as:

$$R_L = \frac{1}{1 + C_0 K_L} \quad (20)$$

The adsorption can be deemed unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), irreversible ( $R_L = 0$ ) and favorable ( $0 > R_L > 1$ ).<sup>[56]</sup> The  $R_L$  value between Pt(IV) and the modified bentonite was found to be 0.379, meaning that the adsorption of Pt(IV) by APDEMS-functionalized bentonite was favorable. All three-parameter isotherm models poorly described

**Table 4.** Two-parameter adsorption isotherm models constants for the adsorption of Pt(IV) onto APDEMS-functionalized bentonite (replicates ( $n$ ) = 3, RSD <5%).

| Isotherm model       | Isotherm parameters                                                  | Parameter values   |
|----------------------|----------------------------------------------------------------------|--------------------|
| Langmuir             | $q_m$ (mg g <sup>-1</sup> )                                          | 0.312              |
|                      | $K_L$ (L mol <sup>-1</sup> )                                         | $1.3 \times 10^5$  |
|                      | $R^2$                                                                | 0.93               |
|                      | RMS error                                                            | 0.98               |
| Freundlich           | $n$                                                                  | 1.69               |
|                      | $K_F$ ((mg g <sup>-1</sup> )/(mol L <sup>-1</sup> ) <sup>1/n</sup> ) | 136                |
|                      | $R^2$                                                                | 0.74               |
|                      | RMS error                                                            | 1.21               |
| Dubinin-Radushkevich | $E_s$ (kJ mol <sup>-1</sup> )                                        | 11.05              |
|                      | $X_m$ (mg g <sup>-1</sup> )                                          | 4.53               |
|                      | $R^2$                                                                | 0.77               |
|                      | RMS error                                                            | 1.13               |
| Temkin               | $b_T$ (J mol <sup>-1</sup> )                                         | $7.53 \times 10^6$ |
|                      | $K_T$ (L mol <sup>-1</sup> )                                         | $1.81 \times 10^6$ |
|                      | $R^2$                                                                | 0.91               |
|                      | RMS error                                                            | 1.26               |

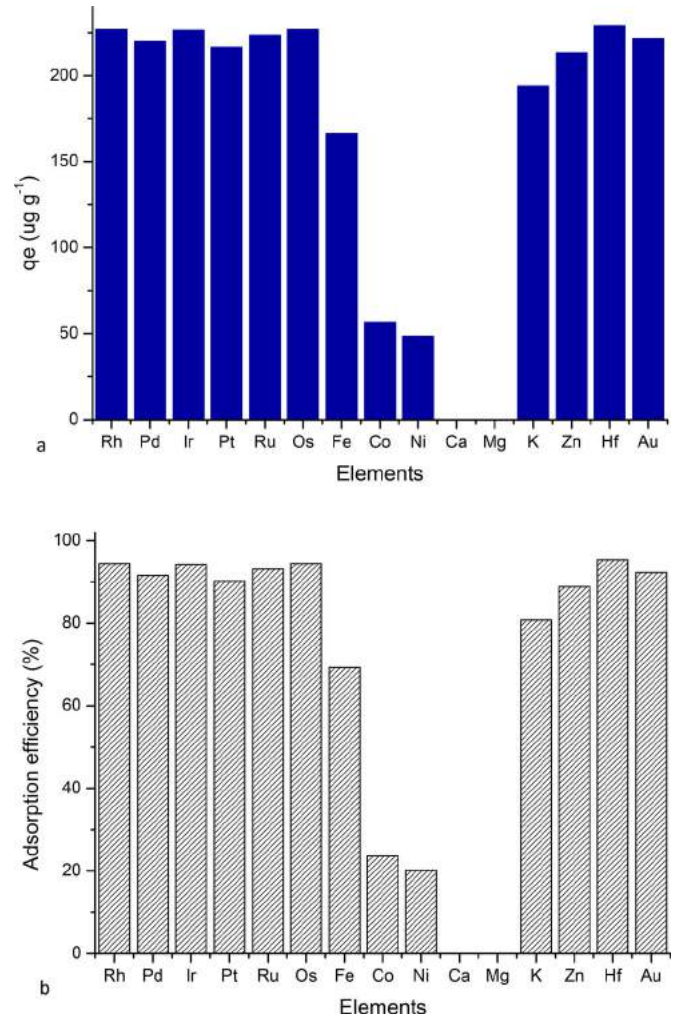
**Table 5.** Three-parameter adsorption isotherm models constants for the adsorption of Pt(IV) onto APDEMS-functionalized bentonite (replicates ( $n$ ) = 3, RSD <5%).

| Isotherm model   | Isotherm parameters             | Parameter values |
|------------------|---------------------------------|------------------|
| Sips             | $q_m$ (mg g <sup>-1</sup> )     | 0.27             |
|                  | $n_s$                           | 0.22             |
|                  | $K_s$ (L mg <sup>-1</sup> )     | 105              |
|                  | $R^2$                           | 0.71             |
| Redlich-Peterson | RMS error                       | 1.59             |
|                  | $\alpha$ (mg L <sup>-1</sup> )  | 0.95             |
|                  | $B$                             | 0.85             |
|                  | $K_{RP}$ (mg g <sup>-1</sup> )  | 0.51             |
| Toth             | $R^2$                           | 0.50             |
|                  | RMS error                       | 1.91             |
|                  | $q_m$ (mg g <sup>-1</sup> )     | 0.29             |
|                  | $K_T$                           | 0.69             |
| Fitz-Schlunder   | $n_T$                           | 1.00             |
|                  | $R^2$                           | 0.86             |
|                  | RMS error                       | 1.23             |
|                  | $q_{mFZ}$ (mg g <sup>-1</sup> ) | 0.72             |
| Fitz-Schlunder   | $M$                             | 1.67             |
|                  | $K_{FS}$ (mg g <sup>-1</sup> )  | 0.49             |
|                  | $R^2$                           | 0.53             |
|                  | RMS error                       | 1.58             |

the adsorption data. The RMS error of the Langmuir isotherm was very small, implying that experimental and calculated adsorption capacities were very close to each other and that the Langmuir isotherm gave an accurate representation for Pt(IV) adsorption onto APDEMS-functionalized bentonite.<sup>[55]</sup>

### Role of competing ions

Wastewater released from mining operations usually contains a number of other elements that constitute the ore body.<sup>[57]</sup> Thus, the role of competing ions was determined and the results are shown in Figure 10a and 10b for adsorption capacity and adsorption efficiency, respectively. The presence of other ions did not decrease the uptake of Pt(IV). Instead, there was an increase of uptake from 85% to 90.2% ( $p > 0.05$ ). Similar results were observed by Mosai et al. (2019).<sup>[26]</sup> The concentrations of elements such as Mg and Ca were more than the initial concentrations used after the equilibration time, meaning that there is a possibility that some of the competing ions were taken up by the

**Figure 10.** Effect of competing ions on adsorption capacity (a) and adsorption efficiency (b) of Pt(IV) by APDEMS-functionalized bentonite (pH 2, concentration = 2 mg L<sup>-1</sup>, temperature = 25 °C, mass = 100 mg, time = 90 min, replicates ( $n$ ) = 3, RSD <5%).

adsorbent as a result of ion exchange. Other precious elements (Rh(III), Pd(II), Ir(III), Ru(III), Os(III), and Au(I)) were notably adsorbed, a phenomenon that would be desirable for the adsorbent as it is an added advantage. The percentage recoveries of these elements including Pt(IV) were >90%. Thus, APDEMS-functionalized bentonite is a promising adsorbent for the recovery of precious elements as well as for the removal of other elements such as K and Ni, making it important in water purification.<sup>[58]</sup>

The selectivity of the adsorbent for Pt(IV) in a mixture with other competing ions was determined using the selectivity coefficient ( $\alpha$ ) (Equation (21)).<sup>[59]</sup>

$$\alpha = \frac{K_{d, \text{Pt(IV)}}}{K_{d, I}} \quad (21)$$

where  $K_{d, \text{Pt(IV)}}$  (L g<sup>-1</sup>) is the distribution coefficient of Pt(IV) and  $K_{d, I}$  (L g<sup>-1</sup>) is the distribution coefficient of the competing ions in the mixture. The distribution coefficient can be described as:<sup>[59]</sup>

$$K_d = \frac{V(C_o - C_e)}{wC_e} \quad (22)$$

The selectivity coefficient indicated that APDEMS-functionalized bentonite preferred Pt(IV) over other elements such as Ni, Co, and Zn which are considered as contaminants in most mining wastewaters. The selectivity coefficients of Pt(IV) over other elements was found to be  $\alpha_{\text{Pt/Fe}} = 4.07$ ,  $\alpha_{\text{Pt/Co}} = 29.7$ ,  $\alpha_{\text{Pt/Ni}} = 36.8$ ,  $\alpha_{\text{Pt/K}} = 2.19$ , and  $\alpha_{\text{Pt/Zn}} = 1.15$ .

### Recommendations

- The adsorbent can be applied for a short period of time in the wastewater since the results indicated that 90 min of contact was enough.
- The amount of Pt(IV) adsorbed increased with starting concentration from 0.5 to 5 mg L<sup>-1</sup> and decreased beyond 5 mg L<sup>-1</sup>. It is therefore recommended that the adsorbent be assessed for wastewaters with low concentrations of Pt(IV) (<5 mg L<sup>-1</sup>).
- An adsorbent dosage of 10 g L<sup>-1</sup> should be considered when applying the adsorbent and the wastewaters should have a pH ≤ 2. Thus, it is best to use the adsorbent before the neutralization of the wastewater.
- After the adsorption process from mining wastewaters, the adsorbent can be collected and transported to the processing feed plants so that it can be processed with the current ore. This means that there is no need for desorption studies as this is a cheaper way of recovering Pt(IV) from the adsorbent.

### Conclusion

The natural and readily available adsorbent, bentonite was successfully functionalized with 3-aminopropyl(diethoxy)methylsilane (APDEMS) and used to recover Pt(IV) from aqueous solutions. The Pt(IV) uptake was due to the electrostatic interactions with amine groups of the APDEMS. The highest adsorption efficiency was achieved at 10 g L<sup>-1</sup> adsorbent dosage at pH 2 and a concentration of 2 mg L<sup>-1</sup>. The uptake of other PGEs was >90% and did not affect that of Pt(IV) as depicted by high selectivity coefficients, making this a potential adsorbent for use in low pH mining wastewaters containing Pt(IV) and a host of PGEs. The key adsorption mechanism was *via* chemisorption, implying strong binding of Pt(IV) to the adsorbent, a property that is important for effective adsorption. Overall, the adsorbent is a promising cost-effective potential alternative to other methods, giving properties such as: applicability, selectivity, robustness, and dual usage.

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**SECTION 4.2:**  
**RECOVERY OF**  
**PALLADIUM,**  
**IRIDIUM AND**  
**RHODIUM USING**  
**ENGINEERED**  
**MATERIALS**

# PAPER I

**This paper investigated the Recovery of Pd (II), Ir (III) and Rh (III) from aqueous solutions with Brewer's Yeast-functionalised bentonite.**

**The paper is published in Minerals Engineering.  
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**Contribution:** lead author, conducted experimental work and data modelling, conceptualization, methodology, software validation, formal analysis, investigation, writing - original draft and visualization.



# Recovery of Pd(II), Ir(III) and Rh(III) from aqueous solutions with Brewer's Yeast-functionalised bentonite

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## ABSTRACT

The scarcity of precious elements such as Pd(II), Ir(III) and Rh(III) has been increasing over the years hence, their recovery from wastewaters using efficient and cheap recovery techniques is becoming more important. In this study, the spent yeast collected after brewing was used to functionalise bentonite clay material to obtain very cheap material for recovery. The functionalised bentonite was characterised using Fourier transform infrared (FTIR) spectroscopy and element analyser. The textural properties of the natural and functionalised bentonite were determined. The effect of adsorbent dosage, pH, concentration, contact time and competing ions on the adsorption of Pd(II), Ir(III) and Rh(III) by yeast-functionalised bentonite was determined. The adsorbent dosage of  $10 \text{ g L}^{-1}$  and 360 min were chosen as optimum for this study. The pH of 2 was used since; it is the typical pH of the processing plant wastewater under investigation. The adsorption of Pd(II) and Ir(III) decreased as the pH increased whilst that of Rh(III) increased with pH. The adsorption of Pd(II) increased with concentration and this was attributed to the ability of Pd(II) to adsorb on different active sites of the adsorbent. This was substantiated by the adsorption isotherm study since, the adsorption of Pd(II) onto the adsorbent was best described by the Freundlich isotherm, meaning that the adsorption occurs on different active sites. Beyond  $2 \text{ mg L}^{-1}$ , the adsorption capacity of Ir(III) and Rh(III) remained the same. In the presence of other ions, Pd(II) adsorption increases due to the synergistic Fe-Pd interaction but, the adsorption of Ir(III) and Rh(III) decreased by 57 and 17%, respectively. Therefore, to significantly recover Ir(III) and Rh(III), the old adsorbent which contains a significant amount of other elements should constantly be replaced by the new one and as other elements decrease, the adsorption of Ir(III) and Rh(III) will increase. The yeast-functionalised bentonite is a potential cheap adsorbent for the adsorption of precious elements.

## 1. Introduction

A number of studies have alluded to the fact that there is high possibility of the future scarcity of precious elements such as platinum group elements (PGEs) (*vis* Pt, Pd, Ru, Ir, Os and Rh), gold (Au) and rare earth elements (Gd, Hf, Eu, etc.) due to limited natural resources and thus, their recovery from aqueous solutions to which they are contained such as industrial wastewater and mining holding ponds is necessary (Fujiwara et al., 2007; Alonso et al., 2009; Nakamura and Sato, 2011). It is for this reason that, cheap and effective methods for the recovery of precious elements from wastewaters should be invented especially in this time of declining commodity prices and weak economic growth of many countries. Current widely used methods for the recovery of PGEs by some large companies in the world such as Umicore, Johnson Matthey and Techemet are hydrometallurgy and pyrometallurgy. Hydrometallurgy uses acids ( $\text{HCl}$ ,  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ ), iodine, bromine and

other chemicals in the presence of oxygen whilst in pyrometallurgy, the PGEs are concentrated and mixed with fluxes, collector (Cu, Fe) and reductant which will then undergo smelting (Dong et al., 2015; Kolliopoulos et al., 2014). The issue with these methods is that they are non-selective, require high energy, high operational costs and are suitable for the primary ore (Chassary et al., 2005). Due to these limitations, such methods are not suitable for the treatment of wastewaters because they do not perform well for low element solutions since, the discharged wastewaters from processing of minerals contain very low concentrations of precious elements thus; a method of recovery at this point is of importance. The current typical treatment of mining wastewater by most mining companies is the adjustment of pH of the water so that the elements can form insoluble precipitates and a coagulant is often used in the mixing tank so that the elements can combine to form a larger particles that can be easily removed from the wastewater. The particles are then bound by a polymer to form even larger substances

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which will then settle in sediments and removed (Barakat, 2011). This treatment combines a host of elements together and some elements still find their way to water bodies since they are not completely removed from the wastewaters. Current successful methods for the recovery of precious elements from wastewaters include bio-metallurgy where microorganisms are used and bioelectrical where microorganisms and solid electron acceptors are used (Zhuang et al., 2015; Nanchaiah et al., 2016).

PGEs have been found to have a strong affinity with nitrogen and thus N-containing ligands can be used to separate PGEs from aqueous solutions (Chassary et al., 2005). In this study, brewer's yeast, *Saccharomyces cerevisiae* (*S. cerevisiae*) used for brewing beer contain a high amount of nitrogen which is required for yeast growth and metabolism (Jiranek et al., 1995; Platikanov et al., 2014). To ensure proper fermentation during brewing, there should be a significant amount of nitrogen content and most of the nitrogen is due to ammonium and amino acids such as glycine, aspartame, tyrosine, alanine, histidine, threonine, etc. (Jiranek et al., 1995). A large amount of used yeast is released as a by-product during the production of beer (Bryant and Cohen, 2015). Large beer manufacturers can produce thousands of litres of yeast by-product per week and since; beer consumption has increased over the years, more by-product has been produced (Ferreira et al., 2010; Amienyo and Azapagic, 2016). The release of yeast into the environment increases environmental pollution due to a high composition of organic matter and thus, ways of utilising the by-product to benefit the economy is of high value (Mathias et al., 2015).

The low-cost natural adsorbents such as bentonite and zeolite have been found to be highly effective on the removal of pollutants from aqueous solutions (Misaelides, 2011; Abollino et al., 2003; Tahervand and Jalali, 2017). Moreover, their effectiveness in removing pollutants as well as selectivity have been improved through modifications with various ligands interacting strongly with pollutants of interest (Bakatula et al., 2015; Camacho et al., 2011; Zhou et al., 2010). In order to add to the current knowledge, the naturally available bentonite was modified with the freely available yeast by-product from brewing and used to adsorb PGEs (Pd, Ir and Rh) from aqueous solutions. In this context, the study seeks to develop very cheap and highly effective adsorbent that can be used in wastewater for the recovery of precious elements that can help improve the economy of many countries dependent on their production. The optimum conditions for the adsorbent were determined to assess the applicability to real solutions.

## 2. Materials and methods

### 2.1. Functionalization

The bentonite used in this study was purchased from Sigma Aldrich, South Africa. The spent yeast waste used was obtained from the Wits Microbrewery, Johannesburg, South Africa. The liquid solution of the yeast waste (pH 5.4) was collected and no treatment or purification was done on it. To obtain the yeast-functionalised bentonite, the waste was mixed with bentonite and shaken for 24 h in an automated elliptical bench top shaker (Labcon, USA) at 25 °C. The contents were filtered using suction and a 0.45 µm filter paper (Advantec®, Japan) was used. The functionalised bentonite was rinsed with deionised water and dried at 100 °C. The obtained yeast-functionalised bentonite was stored until required for usage. The chemical composition and the mineralogy of the bentonite were determined with X-ray fluorescence (XRF) (PANalytical, Netherlands) and powder X-ray diffraction (PXRD) (Bruker D2 Phaser, Germany), respectively. To confirm if the functionalisation was successful, Fourier transform infrared (FTIR) spectroscopy (Tensor 27, Bruker, Germany) was used to determine the functional groups on raw and functionalised bentonite. The amount of nitrogen, carbon and hydrogen before and after functionalisation of bentonite was determined with element analyser; varioELcube V4.0.13 (Elementar, Germany). The point of zero charge (pHpzc) of the raw and functionalised

bentonite was determined using a method described by (Smičiklas and Onjia, 2005). The textural properties (surface area, pore volume and pore size) of the raw and functionalised bentonite were determined with the Micromeritics Flow Prep 060 instrument (Aachen, Germany).

### 2.2. Reagents and standards

All the chemicals used in this study were of analytical reagent grade and were purchased from Sigma Aldrich, South Africa. The 10 mg L<sup>-1</sup> stock solutions of Pd(II), Ir(III) and Rh(III) were prepared from the HCl standards of the respective elements and deionised water prepared from Direct-Q® 3, 5, 8 Laboratory Water Purification Systems (MilliporeSigma, South Africa) in 1 L volumetric flasks. The stock solution containing a mixture of Fe, Co, Ni, Ca, Zn, Mg, Zn and Hf was prepared by dissolving appropriate masses of the elements in deionised and filled to the mark of 1 L volumetric flask to get 1000 mg L<sup>-1</sup>. The solutions were preserved by further adding drops of HCl and were stored in the refrigerator at 4 °C. The working solutions were prepared from the stock solutions on the day of experiments. To get the desired pH of the solutions, 0.01 mol L<sup>-1</sup> NaOH and HCl were used and a pH meter from Mettler Toledo, Switzerland was used. The stock solution of a mixture of PGEs was prepared in the same way as the individual elements.

### 2.3. Adsorption experiments

The effect of the dosage of yeast-functionalised bentonite on the recovery of the elements (Pd, Ir and Rh) was studied to determine the amount of the adsorbent that can be used for a specific volume of wastewater. Different masses (50–300 mg) were used with 10 mL (optimised) of solutions of Pd(II), Ir(III) and Rh(III) at pH 2. This pH was chosen since it is the pH of the platinum group elements (PGEs) processing plant wastewater. The contents were shaken for 6 h (optimised equilibration time) and filtered. The effect of pH (2–9), concentration (0.5–10 mg L<sup>-1</sup>), time (0–360 min) and competing ions (Pt(IV), Ru(III), Os(III), Fe(III), Ca(II), Mg(II), K(I), Co(II), Ni(II), Hf(IV) and Zn(II)) on the recovery of the elements was studied. The raw bentonite was also used to recover Pd(II), Ir(III) and Rh(III) from aqueous solutions and the results were compared to those of the functionalised bentonite under similar conditions. The experiments were done in triplicates (n = 3) and percentage relative standard deviation (%RSD) was used to validate the experimental results. The concentrations of the elements were determined using inductively coupled plasma optical emission spectroscopy (ICP-OES) (Spectro Genesis, Germany). Prior to analysis with ICP-OES, the samples were spiked with Scandium (Sc) so that the solutions have a final concentration of 0.01 mg L<sup>-1</sup> Sc as an internal standard.

The adsorption capacities,  $q_e$  (µg g<sup>-1</sup>) of Pd(II), Ir(III), Rh(III) and other elements were determined using equation (1). The adsorption efficiency (%) was calculated using equation (2).

$$q_e = \frac{(C_0 - C_e)V}{M} \times 1000 \quad (1)$$

$$\% \text{ adsorption} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

where  $C_0$  and  $C_e$  are initial and equilibrium liquid-phase concentrations of the elements, respectively,  $V$  (L) is the volume of the solutions and  $M$  (g) is the mass of the adsorbent used.

## 3. Results and discussion

### 3.1. Characterisation

The raw bentonite was composed of SiO<sub>2</sub> (51.5%) and Al<sub>2</sub>O<sub>3</sub> (16.7%) with a loss of ignition of 18.4%. The Si/Al ratio was found to

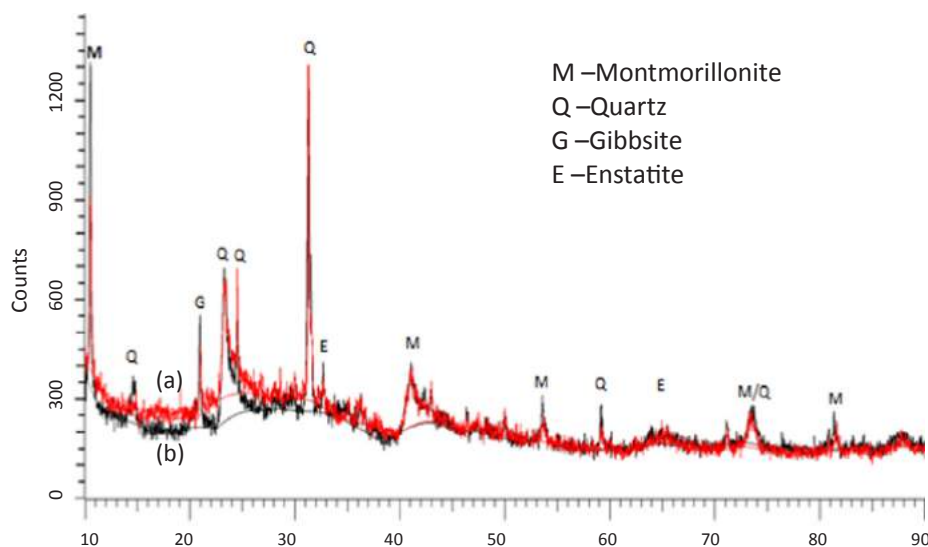


Fig. 1. PXRD pattern of (a) raw and (b) yeast functionalised bentonite.

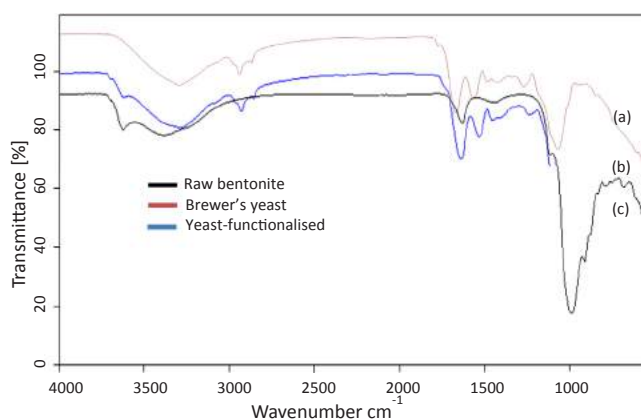


Fig. 2. FTIR spectra of (a) yeast waste, (b) raw bentonite and (c) yeast-functionalised bentonite.

be 3. Other compounds;  $\text{Fe}_2\text{O}_3$  (5.0%),  $\text{MgO}$  (3.6%),  $\text{CaO}$  (2.0%) and  $\text{K}_2\text{O}$  (1.4%) were also in significant amounts. These compounds were involved in the interaction of the yeast waste groups with bentonite. The mineralogy of the raw and functionalised bentonite was determined with PXRD and the results are shown in Fig. 1. The functionalisation did not have a significant effect on the mineralogy of bentonite and thus, the PXRD patterns were similar. The main minerals of bentonite were found to be; montmorillonite ( $\text{Na,Ca}_{0.3}(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n(\text{H}_2\text{O})$ ), quartz ( $\text{SiO}_2$ ), gibbsite ( $\text{Al}(\text{OH})_3$ ) and enstatite ( $\text{MgSiO}_3$ ). To confirm the success of the functionalisation of bentonite, FTIR spectra of the yeast, raw bentonite and Yeast-functionalised bentonite were compared (Fig. 2). The bands at  $\sim 999.6 \text{ cm}^{-1}$  on the raw and functionalised bentonite were due to the overlapping Si-O bending vibrations due to the presence of  $\text{SiO}_2$ . The bands at  $\sim 3283 \text{ cm}^{-1}$  were due to the hydroxyl groups which are bonded through hydrogen bonds (Zhirong et al., 2011). The bands at  $1632 \text{ cm}^{-1}$  were also attributed to the hydroxyl groups frequencies of the water molecule (Alabarse et al., 2011). The brewer's yeast and yeast-functionalised bentonite spectra showed similar bands at 1235, 1537 and  $1637 \text{ cm}^{-1}$  which were due to the sugar region, N-H bend and C-N stretch, respectively. The bands at 1395 and  $2925 \text{ cm}^{-1}$  were due to the asymmetric C-H stretch (Aydin et al., 2011). The presence of these bands can be attributed to the presence of amino acids such as leucine, serine and lysine which have N-H, C-H and C-N bonds (Iraqi et al., 1999). The presence of bands due to N-groups are good for this study since, the recovery of Pd

(II), Ir(III) and Rh(III) is prone to be due to N-PGE interaction (Fujiwara et al., 2007).

The percentage amount of carbon, hydrogen and nitrogen on the raw bentonite as determined from elemental analysis was found to be 0.65, 1.7 and 0%, respectively. After functionalisation, these amounts changed to 18.2, 3.4 and 3.48%, respectively. This further confirms that bentonite was indeed functionalised with the yeast. The textural properties of the raw and functionalised bentonite are shown in Table 1. The pore volume and the surface area reduced drastically after functionalisation whilst the pore size increased, and this can be attributed to the smothering of the bentonite pores by the yeast.

### 3.2. Effect of adsorbent dosage

The effect of adsorbent dosage on the adsorption of Pd(II), Ir(III) and Rh(III) was studied and the results are shown in Fig. 3. The adsorption capacity of Pd(II) with yeast-functionalised bentonite was higher than that of Ir(III) and Rh(III) at all dosages. This can be attributed to the Pd(II) species which are favourable for adsorption on the yeast-functionalised bentonite. At 100 mg, the adsorption efficiency of Pd(II) was found to be  $> 97\%$  compared to 52 and 44% of Ir(III) and Rh(III), respectively. The lower adsorption of Ir(III) and Rh(III) can be attributed to their speciation and the nature of the yeast-functionalised bentonite. Also, the ionic radii of both elements are  $\sim 200 \text{ pm}$  compared to  $165 \text{ pm}$  of Pd(II). Thus, other factors such as the size and oxidation states might have had an impact on the adsorption of these elements. A study by Chantawong (2004) indicated that elements with small ionic radii are more reactive than those with high radii (Chantawong, 2004). The adsorption efficiency of Rh(III) was in the range of 42 to 44.7% at all the adsorbent dosages (50–300 mg). The adsorption efficiency of Ir(III) increased with increasing adsorbent dosage and this can be attributed to the increase of active sites for the element. Based on these results,  $10 \text{ g L}^{-1}$  dosage was chosen for the subsequent experiments. Thus, the recovery of the elements will be in the order: Pd(II)  $>$  Ir(III)  $>$  Rh(III). The raw bentonite was also used

Table 1

Textural properties of the raw and yeast-functionalised bentonite.

| Sample                         | Pore size (nm) | Pore volume ( $\text{cm}^3 \text{ g}^{-1}$ ) | Surface area ( $\text{m}^2 \text{ g}^{-1}$ ) |
|--------------------------------|----------------|----------------------------------------------|----------------------------------------------|
| Raw bentonite                  | 10.38          | 0.054                                        | 21.29                                        |
| Yeast-functionalised bentonite | 57.46          | 0.0050                                       | 0.39                                         |

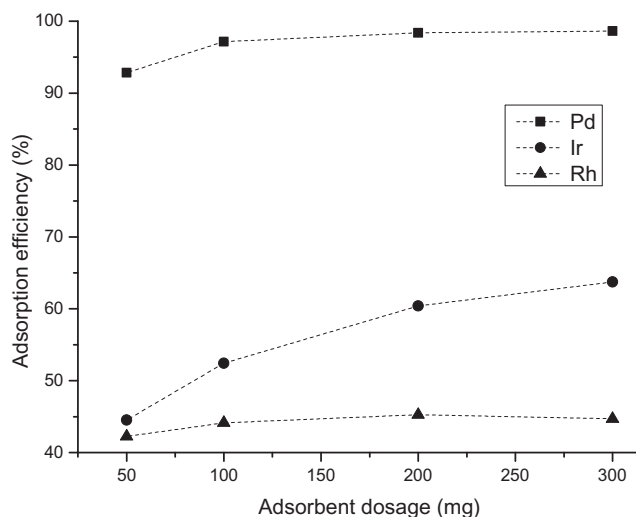


**Fig. 3.** Effect of dosage on the adsorption of Pd(II), Ir(III) and Rh(III) by yeast-functionalised bentonite zeolite (pH = 2, temp = 25 °C, concentration = 2 mg L<sup>-1</sup>, volume = 10 mL, time = 180 min, n = 3 and RSD < 5%).

to adsorb the elements from aqueous solutions using the same range of dosages and conditions. The results (not shown) indicated that the adsorption efficiency of Pd(II) ranged from 1.2 to 9.7%, whilst that of Ir(III) and Rh(III) was less than 0.8 and 0.3%, respectively at all adsorbent dosages. Therefore, the yeast-functionalised bentonite works significantly better ( $p < 0.05$ ) than the raw bentonite.

### 3.3. Effect of pH

The changing pH of the solutions affected the adsorption capacities of the elements (Fig. 4). The adsorption capacity of Pd(II) decreased as pH increased. At highly acidic pH, the Pd(II) species exist mainly as  $\text{PdCl}_6^{4-}$  and are favourable for adsorption onto the positively charged surface functional groups due to the amount of hydronium ions ( $\text{H}_3\text{O}^+$ ). Thus, surface groups such as the amine groups of the yeast probably due to amino acids, were protonated, leading to the formation of  $-\text{NH}_3^+$  groups which form strong electrostatic interactions with the negatively charged Pd(II) species. At pH 5 the adsorption of Pd(II) significantly decreased due to the reduction in chloro complexes and high

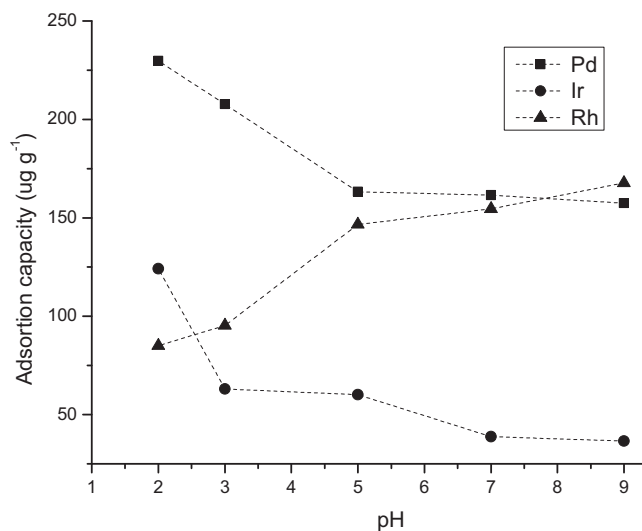


**Fig. 4.** Effect of pH on the adsorption of Pd(II), Ir(III) and Rh(III) by yeast-functionalised bentonite zeolite (mass = 100 mg, temp = 25 °C, concentration = 2 mg L<sup>-1</sup>, volume = 10 mL, time = 180 min, n = 3 and RSD < 5%).

concentration of hydroxide ions which led to the formation of negatively charged adsorbent surface. Thus, the hydroxide species of Pd(II) were not favourable for adsorption by the negatively charged adsorbent. This indicates that the interaction of Pd(II) with the adsorbent was through electrostatic attraction (Chassary et al., 2005). The adsorption capacity of Pd(II) did not change significantly beyond pH 5. The adsorption capacity of Ir(III) also decreased as pH was increased and this can be attributed to the speciation that changes with pH. Contrary to Pd(II) and Ir(III), the adsorption capacity of Rh(III) increased with pH. Since the concentration of chloride ions is high at acidic pH values, there is a possibility of competition with the negatively charged,  $\text{RhCl}_6^{3-}$  species for the adsorbent (Labib et al., 2018). As the amount of chloride ions decrease due to increasing pH, the ability of Rh(III) to attach onto the adsorbent increases. This is also due to the formation of aqua/chloro complexes of Rh(III) such as  $[\text{RhCl}_2(\text{H}_2\text{O})_4]^+$  and  $[\text{RhCl}(\text{H}_2\text{O})_5]^{2+}$  at higher pH values. These complexes are positively charged and are therefore favourable for adsorption onto the non-protonated adsorbent surface (Labib et al., 2018). The pH<sub>pzc</sub> of the adsorbent was found to be 5.3 and thus, the adsorbent was negatively charged beyond pH 5.3 and positively charged below this pH. Since the platinum industrial wastewater is acidic, pH 2 was chosen for subsequent experiments. The pH<sub>pzc</sub> of the raw bentonite was found to be 7.68 and the adsorption capacities of the elements at all pH values were significantly lower ( $p < 0.05$ ) than those of the functionalised bentonite. Thus, even though the raw bentonite was positively charged over a wide range of pH than the functionalised bentonite, because of the lack of functional groups such as amine from the spent yeast, the adsorption was still low. Thus even though the raw bentonite was positively charged over a wide range of pH than the functionalised bentonite, because of the lack of functional groups such as amine from the spent yeast, the adsorption was still low, further confirming the importance of functionalisation.

### 3.4. Effect of concentration

The effect of concentration on the adsorption of Pd(II), Ir(III) and Rh(III) by yeast-functionalised bentonite was studied and the results are reported in Fig. 5. The adsorption capacity of Pd(II) increased with concentration and the adsorption efficiency was > 99% at all concentrations. The high adsorption efficiency can be attributed to the ability of Pd(II) to adsorb on different sites of the yeast-functionalised bentonite and not just on the N-containing groups. The adsorption capacities of Ir(III) and Rh(III) were not significantly ( $p > 0.05$ ) different from each other. The adsorption capacities of these elements increased

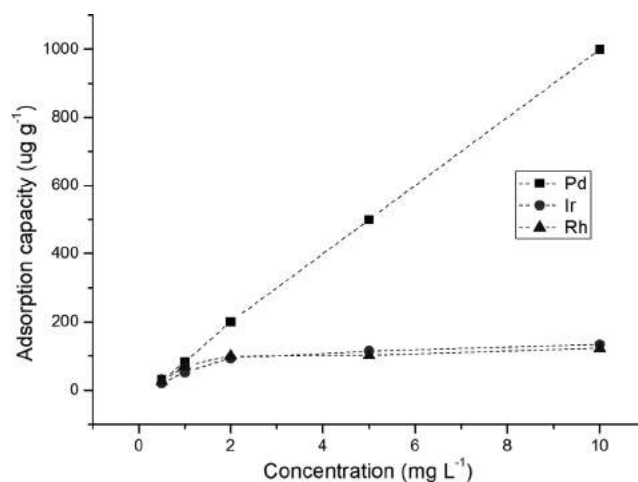


**Fig. 5.** Effect of concentration on the adsorption of Pd(II), Ir(III) and Rh(III) by yeast-functionalised bentonite zeolite (pH = 2, mass = 100 mg, temp = 25 °C, volume = 10 mL, time = 180 min, n = 3 and RSD < 5%).

**Table 2**  
Adsorption isotherm parameters for Pd(II), Ir(III) and Rh(III) adsorption by yeast-functionalised bentonite.

| Metal   | Langmuir                    |                              |       | Freundlich                                                           |      |       | Dubinin-Radushkevich        |                               |       |
|---------|-----------------------------|------------------------------|-------|----------------------------------------------------------------------|------|-------|-----------------------------|-------------------------------|-------|
|         | $q_m$ (mg g <sup>-1</sup> ) | $K_L$ (L mol <sup>-1</sup> ) | $R^2$ | $K_F$ ((mg g <sup>-1</sup> )/(mol L <sup>-1</sup> ) <sup>1/n</sup> ) | $n$  | $R^2$ | $X_m$ (mg g <sup>-1</sup> ) | $E_s$ (kJ mol <sup>-1</sup> ) | $R^2$ |
| Pd(II)  | 1.51                        | 77,706                       | 0.87  | 4509                                                                 | 1.35 | 0.98  | 25.80                       | 10.40                         | 0.97  |
| Ir(III) | 0.15                        | 1.75x10 <sup>5</sup>         | 0.99  | 1.65                                                                 | 2.15 | 0.57  | 0.40                        | 12.37                         | 0.82  |
| Rh(III) | 0.13                        | 1.06x10 <sup>5</sup>         | 0.98  | 1.91                                                                 | 3.37 | 0.69  | 0.37                        | 15.25                         | 0.69  |

from 0.5 mg L<sup>-1</sup> to 2 mg L<sup>-1</sup> after which no significant increase was observed. The almost constant adsorption at concentrations > 2 mg L<sup>-1</sup> can be attributed to the exhaustion of active sites by these elements and thus, no further adsorption could occur. In other words, there are limited active sites on the yeast-functionalised bentonite for the adsorption of Ir(III) and Rh(III) and they are highly likely to be amine groups (Labib et al., 2018; Nikoloski et al., 2015). Therefore, the yeast-functionalised bentonite favours the adsorption of high concentrations of Pd(II) whilst the adsorption of Ir(III) and Rh(III) remains significant only at low concentrations. A study by Lusk et al. (2018) indicated that the concentration of PGEs in mining wastewaters range from 5 to 10 mg L<sup>-1</sup> and thus, to significantly recover Ir(III) and Rh(III), high amounts of the adsorbent will have to be used (Lusk et al., 2018).

### 3.5. Adsorption isotherms

The type of interaction between the elements and the yeast-functionalised bentonite was assessed with Langmuir, Freundlich and Dubinin-Radushkevich (D-R) adsorption isotherms. The Langmuir isotherm describes the monolayer adsorption of elements onto the surface of the adsorbent. The assumptions made using this model is that there are identical sites to which the elements adsorb and the energies of adsorption are the same. Also, it is assumed that no further adsorption takes place once the active site has been occupied (Dada et al., 2012). The Langmuir isotherm can be described as:

$$\frac{C_e}{q_e} = \left(\frac{1}{q_m}\right)C_e + \left(\frac{1}{K_L q_m}\right) \quad (3)$$

where  $C_e$  (mg L<sup>-1</sup>) is the equilibrium concentration of the elements,  $q_e$  (mg g<sup>-1</sup>) is the equilibrium adsorption capacity,  $q_m$  (mg g<sup>-1</sup>) is the maximum monolayer adsorption coverage and  $K_L$  (L mol<sup>-1</sup>) is the Langmuir isotherm constant.

The separation factor,  $R_L$ , described in Eq. (4) was used to determine the affinity of the elements for the adsorbent.

$$R_L = \frac{1}{1 + C_o K_L} \quad (4)$$

where  $C_o$  (mg L<sup>-1</sup>) is the initial concentration of the elements. The following limits were used to determine if the adsorption of Pd(II), Ir(III) and Rh(III) onto the yeast-functionalised bentonite was unfavourable ( $R_L > 1$ ), linear ( $R_L = 1$ ), irreversible ( $R_L = 0$ ) or favourable ( $0 < R_L < 1$ ).

The Freundlich adsorption isotherm is used to describe the adsorption of elements onto a heterogeneous surface and thus, different adsorption energies will result (Freundlich, 1907; Song et al., 2017). The expression of the Freundlich isotherm is shown below:

$$q_e = K_F C_e^{\frac{1}{n}} \quad (5)$$

where  $K_F$  ((mg g<sup>-1</sup>)/(mol L<sup>-1</sup>)<sup>1/n</sup>) is the Freundlich isotherm constant and  $n$  is the adsorption intensity.

The D-R adsorption isotherm which describes the adsorption mechanism between the elements and adsorbent with Gaussian energy distribution onto a heterogeneous surface was also used and the linear expression is represented by Eq. (6) (Tran et al., 2017).

$$\ln q_e = \ln X_m - K_{ad} \varepsilon^2 \quad (6)$$

where  $K_{ad}$  (mol<sup>2</sup> (kJ<sup>2</sup>)<sup>-1</sup>) is the Dubinin-Radushkevich (D-R) isotherm constant,  $X_m$  (mg g<sup>-1</sup>) is the theoretical isotherm saturation capacity and  $\varepsilon$  is the Polanyi constant which can be expressed as:

$$\varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \quad (7)$$

where  $R$  is the universal gas constant (J (mol\*K)<sup>-1</sup>) and  $T$  is temperature (K).

The D-R isotherm has a parameter known as the mean free energy ( $E$ ) which can be used along with other tests to determine whether the adsorption of the elements is physisorption or chemical adsorption. The mean free energy change,  $E_s$  (kJ mol<sup>-1</sup>) can be calculated using Eq. (8).

$$E_s = \frac{1}{\sqrt{2K_{ad}}} \quad (8)$$

The correlation coefficient ( $R^2$ ) was used to select the isotherm that best fit the experimental data of the elements. The adsorption of Pd(II) onto the adsorbent was best described by the Freundlich and the D-R isotherm models since their  $R^2$  values were 0.98 and 0.97, respectively (Table 2). This means that Pd(II) possibly adsorbed onto different adsorption sites of the adsorbent and not only through Pd(II)-N interaction. Since, Freundlich isotherm described the experimental data for Pd(II), it is possible that there was multilayer adsorption of Pd elements and also, the possibility of adsorbent-metal-Pd(II) interaction. Hence, the adsorption capacity increased with increasing concentration. The adsorption of Ir(III) and Rh(III) was better described by the Langmuir isotherm meaning that their interaction with the adsorbent was through monolayer adsorption and on one type of active site. Thus, their interaction was through (Ir or Rh)-N-adsorbent reaction. Moreover, the Langmuir isotherm constants for these elements were higher than that of Pd(II). The separation factor for all the elements was between 0 and 1 (Table 3) at all concentrations and thus, the adsorption of the elements by yeast-functionalised bentonite was favourable. The  $E_s$  values for all the elements were between 8 and 16 kJ mol<sup>-1</sup> and thus, a possibility of chemical ion exchange reaction between the elements and the adsorbent.

### 3.6. Effect of contact time

The time it takes for the maximum recovery of the elements was studied and the results are reported in Fig. 6. There was fast adsorption of the elements within the first 10 min of contact after which, a slow increase was observed. For Pd(II), the adsorption increased for up to

**Table 3**  
Separation factors of Pd(II), Ir(III) and Rh(III) adsorption by yeast-functionalised bentonite at different concentrations.

| Concentration (mg L <sup>-1</sup> ) | Pd(II)   | Ir(III)  | Rh(III)  |
|-------------------------------------|----------|----------|----------|
| 0.5                                 | 0,732514 | 0,156321 | 0,659547 |
| 1.0                                 | 0,577927 | 0,084788 | 0,492033 |
| 2.0                                 | 0,406397 | 0,044271 | 0,326289 |
| 5.0                                 | 0,214979 | 0,018191 | 0,162287 |
| 10.0                                | 0,110698 | 0,009179 | 0,077686 |

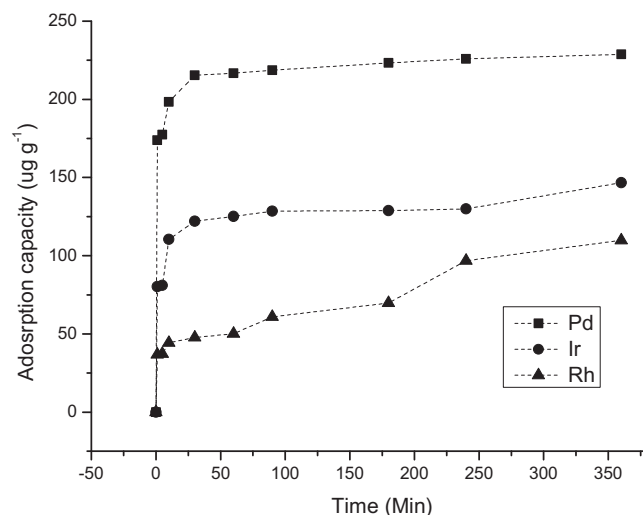


Fig. 6. Effect of contact time on the adsorption of Pd(II), Ir(III) and Rh(III) by yeast-functionalised bentonite zeolite (pH = 2, temp = 25 °C, mass = 100 mg, concentration = 2 mg L<sup>-1</sup>, volume = 10 mL, n = 3 and RSD < 5%).

30 min and a very slow insignificant increase was observed. The adsorption capacity of Pd(II) was higher than that of Ir(III) and Rh(III). The adsorption capacity of Ir(III) also increased for about 30 min and then a slight increase was observed which took place until 360 min. There was fast adsorption within 1 min with Rh(III) and a slight increase was observed until 180 min. Beyond 180 min, the adsorption capacity significantly increased until 240 min after which a slight increase was observed. Based on this study, 360 min was chosen as the optimum time. Since, the adsorption of the elements is significant within the first 30 min of contact with the solutions, the brewer's yeast-functionalised bentonite can be employed for this time and the recovery of the elements will be desirable.

### 3.7. Adsorption kinetics

The kinetic data obtained from the effect of contact time study was used to fit the pseudo first- and second-order and Elovich kinetic models. These kinetic models can assist with identifying the adsorption controlling mechanism between the elements and the yeast-functionalised bentonite (Tran et al., 2017). The model that best fits the kinetic was determined from the correlation coefficient ( $R^2$ ) and how close the experimental adsorption capacity,  $q_{e(\text{exp})}$ , is to the calculated adsorption capacity,  $q_{e(\text{cal})}$ . Eqs. (9), (10) and (11) represent the linear expressions of the pseudo first-, second-order and Elovich kinetic models, respectively.

$$\log(q_e - q_t) = -\frac{k_1 t}{2.303} + \log q_e \quad (9)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (10)$$

$$\frac{dq_t}{dt} = a \cdot \exp(-b \cdot q_t) \quad (11)$$

The kinetic data was better represented by pseudo second-order for all the elements since the correlation coefficient was high ( $> 0.99$ ) and the  $q_{e(\text{exp})}$  is similar to the  $q_{e(\text{cal})}$  from pseudo-second order and thus, further confirming the conformity of the adsorbent-adsorbate interaction with the model (Table 4). These results together with the isotherm model (D-R mean free energy change) allude there is strong chemical interaction between the elements and the yeast-functionalised bentonite.

### 3.8. Effect of competing ions

Since, during the processing of PGEs large amount of wastewater is released which contain different kinds of elements, the effect of competing ions (Pt, Ru, Os, Au, Hf, Co, Ni, Ca, Mg, Fe, K and Zn) on the adsorption of Pd(II), Ir(III) and Rh(III) was studied and the results are shown in Fig. 7. The adsorption capacity of Pd(II) increased by 8.4% in the presence of other ions and this can be attributed to the adsorbent-Fe-Pd synergistic effect. A study by Zhang et al. (2018) found that Pt(II) can bind to Fe which is strongly attached to the MgO surface (Zhang et al., 2018). Moreover a study by Babu et al. (2009) also indicated that there is a strong interaction between Pd and Fe attached on alumina (Al<sub>2</sub>O<sub>3</sub>) (Babu et al., 2009). Thus, iron (Fe<sup>2+</sup>) can bind to the oxides of the adsorbent which are not involved in functionalisation and a multilayer adsorption is possible where Pd(II) bind to Fe, forming the synergistic interaction hence, an increase in adsorption was observed. Therefore, in the presence of other ions, the adsorbent will still be selective for Pd(II). However, the adsorption capacities of Ir(III) and Rh(III) decreased by 57 and 17%, respectively in the presence of other ions and this can be attributed to the competition for active sites with other elements. Thus, to significantly remove Ir(III) and Rh(III) from industrial wastewaters, the amount of the adsorbent will have to be increased and the concentrations of these elements in wastewaters can be measured first so that the amount of the adsorbent to be added is well estimated. Thus, in the presence of other elements, Pd(II) will be removed first followed by Rh(III) and Ir(III). Other elements (Pt, Os, Ru, Fe, Co, Ni, Zn and Hf) were significantly adsorbed but Ca, Mg and K were not adsorbed and their concentrations were higher than the initial concentrations used and this could be due to the detachment of these elements from the adsorbent and thus, a cation exchange reaction with elements such Ni and Co.

### 3.9. Proposed application of the adsorbent

The wastewater from PGEs processing plants is transported to water retaining ponds and has a pH of 2. The yeast-functionalised bentonite can be packed in columns into which the wastewater can be passed through. The appropriate columns could be situated between the pipes transporting wastewater and the retaining ponds. The setup of an ion exchange column will make it possible to establish parameters that will determine when the adsorbent has been saturated and make it possible to optimise the recovery process. Based on the established parameters e.g. column length, flow through speeds and breakthrough points, it will be possible to determine the time at which the adsorbent has to be replaced. The adsorbent can be removed from the column after saturation and the collected adsorbent can be mixed with fresh ore for processing. Thus, desorption studies were not conducted in this study as the suggested recovery method may be an ideal way of retrieving the precious elements from the adsorbent. Further, the indicative value recovered and the cost-effective nature of the adsorbent suggests that its reuse would not be necessary. The functionalisation of bentonite as described in the study should be a cheaper process as it only involves contact of the bentonite with the yeast solution under ambient conditions without any special conditions or treatment e.g. heating, etc. The amount of adsorbent used will depend on the breakthrough quantities established and the column length used.

## 4. Conclusion

The recovery of Pd(II), Ir(III) and Rh(III) from aqueous solutions is important given the high possibility of their loss in industrial wastewaters. The readily available and cheap bentonite clay was functionalised with spent yeast waste from brewing and used as an adsorbent for the recovery of these elements. The functionalised bentonite worked significantly better ( $p < 0.05$ ) than the raw bentonite, indicating that the yeast functional groups attached on bentonite surface have high

**Table 4**  
Kinetic parameters for Pd(II), Ir(III) and Rh(III) adsorption by yeast-functionalised bentonite.

| Metal   | $q_e$ (exp)<br>$\text{mg g}^{-1}$ | Pseudo first-order                      |                             |       | Pseudo-second order                         |                             |       | Elovich                                 |                                         |       |
|---------|-----------------------------------|-----------------------------------------|-----------------------------|-------|---------------------------------------------|-----------------------------|-------|-----------------------------------------|-----------------------------------------|-------|
|         |                                   | $k_1$<br>$\text{min}^{-1}$<br>$10^{-3}$ | $q_e$<br>$\text{mg g}^{-1}$ | $R^2$ | $k_2$<br>$\text{g mg}^{-1} \text{min}^{-1}$ | $q_e$<br>$\text{mg g}^{-1}$ | $R^2$ | A<br>$\text{g mg}^{-1} \text{min}^{-1}$ | b<br>$\text{g mg}^{-1} \text{min}^{-1}$ | $R^2$ |
| Pd(II)  | 0.10                              | 8.80                                    | 0.03                        | 0.56  | 5.51                                        | 0.11                        | 0.99  | 3.58                                    | 106.21                                  | 0.93  |
| Ir(III) | 0.12                              | 1.68                                    | 0.15                        | 0.38  | 3.76                                        | 0.13                        | 0.99  | $5.57 \times 10^{-4}$                   | 192.36                                  | 0.87  |
| Rh(III) | 0.07                              | 1.33                                    | 0.23                        | 0.81  | 0.51                                        | 0.09                        | 0.93  | $1.61 \times 10^{-5}$                   | 113.33                                  | 0.69  |

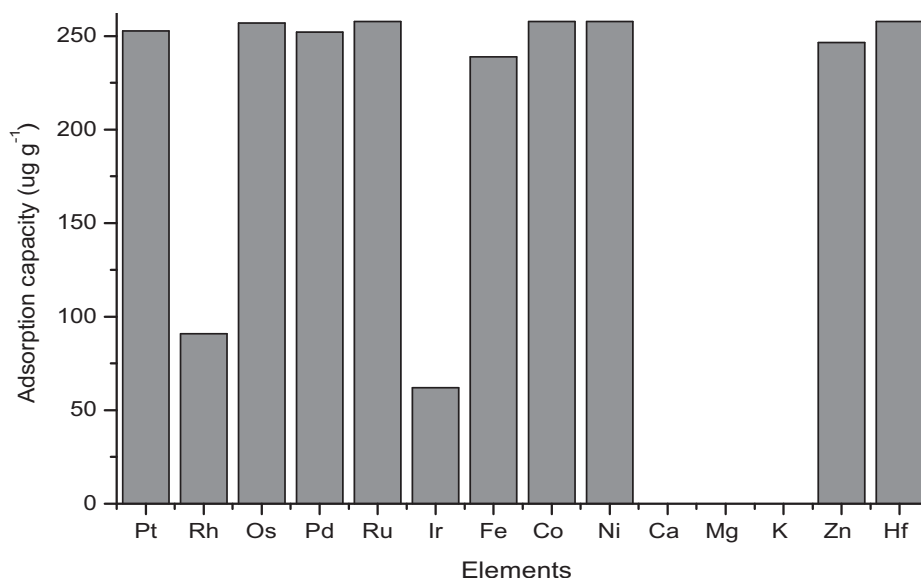


**Fig. 7.** Effect of competing ions on the adsorption of Pd(II), Ir(III) and Rh(III) by yeast-functionalised bentonite zeolite (pH = 2, mass = 100 mg, temp = 25 °C, concentration = 2 mg L<sup>-1</sup>, volume = 10 mL, time = 180 min, n = 3 and RSD < 5%).

affinity for Pd(II), Ir(III) and Rh(III). The optimum conditions for the maximum recovery of all the elements with yeast-functionalised bentonite were found to be at 10 g L<sup>-1</sup> dosage, 2 mg L<sup>-1</sup>, 360 min at 25 °C and pH 2. The fact that the maximum adsorption of Pd(II) and Ir(III) by the adsorbent occurred at pH 2 makes it a suitable adsorbent for the recovery of precious elements since the discharged wastewater from the processing plants is usually at this pH. The ability of the yeast-functionalised bentonite to significantly recover Pd(II), makes the adsorbent potentially suitable for Pd(II) adsorption in real wastewater where a suite of ions can be present alongside Pd(II). The drawback of the adsorbent is that the adsorption of Ir(III) and Rh(III) decreases in the presence of other ions, implying that large amounts of the adsorbent have to be applied. The yeast-functionalised bentonite is a potential cost effective adsorbent for the recovery of PGEs in mine waste streams.

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## Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.mineng.2019.106101>.

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# PAPER II

**This paper investigated the recovery of Pd(II), Ir(III) and Rh(III) from aqueous solutions with yeast-functionalised zeolite.**

**This is a conference paper that I presented at:**

**IMWA 2019 Conference, Mine water:  
Technological and Ecological Challenges.  
International Mine Water (IMWA).**

**Contribution:** lead author, conducted experimental work and data modelling, conceptualization, methodology, software validation, formal analysis, investigation, writing - original draft and visualization.

# The Recovery Of Pd(II), Ir(III) And Rh(III) From Aqueous Solutions With Yeast-functionalised Zeolite ©

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## Abstract

Wastewaters from platinum group metals (PGMs) processing plants can contain substantial amounts of metals including the very PGMs. The recovery of such metals from wastewaters can be of great value especially due to recent declines in commodity prices. The recovery of Pd(II), Ir(III) and Rh(III) by zeolite functionalised with spent yeast waste was studied and the effect of adsorbent dosage, pH, initial concentration, contact time and competing ions was determined. The significant recovery of Pd(II) and Ir(III) was achieved at pH 2, 2 mg L<sup>-1</sup> and 10 g L<sup>-1</sup> adsorbent dosage. The adsorption capacity of Rh(III) increased with pH whilst that of Pd(II) and Ir(III) decreased. The presence of competing ions led to an increase in adsorption capacity due to an adsorbent-Fe-analyte synergistic effect. The adsorbent is suitable for significant recovery of Pd(II), Ir(III) and Rh(III) from PGMs wastewater.

**Keywords:** adsorption capacity, platinum group metals, spent yeast, wastewater

## Introduction

The readily increasing costs of platinum group metals (PGMs) and declining ore grades have been eroding the economic viability of PGMs mines around the world. As a result, some mining plants have closed whilst others are still facing closure. During the processing of minerals, large amount of wastewater is released into the environment and some studies have reported that it may contain traces of valuable minerals such as PGMs (Mosai et al., 2019). Since these metals are in very low concentrations, the current methods used for mining cannot be used to recover the lost minerals hence, a need for cheaper and more efficient methods for recovery. Zeolites are negatively charged aluminium-silicate clay minerals which have micro and mesopores located by water molecules and cations such as Ca<sup>2+</sup> and Mg<sup>2+</sup> (Guaya et al., 2015). Zeolites are readily available in different parts of the world and have been used as natural adsorbents for the removal of metals from wastewaters (Yuna, 2016). Other studies have indicated the efficiency of zeolite can be improved through functionalisation with ligands that have high affinity for target metals (Simsek et al., 2013; Bakatula et al., 2015).

In this study, the zeolite clay mineral was functionalised with spent brewer's yeast waste and used to recover Pd(II), Ir(III) and Rh(III) from aqueous solutions. Thus, this study seeks to come up with a very attractive and cheap material for the recovery of precious metals.

## Materials and methods

### Chemicals

The chemicals used were of analytical reagent grade and were purchased from Sigma Aldrich, South Africa. The 10 mg L<sup>-1</sup> stock solution containing Pd(II), Ir(III) and Rh(III) was prepared and preserved with concentrated nitric acid. Working solutions were prepared daily from the stock solution which was stored in the refrigerator at 4°C when not used. The 0.01 mol L<sup>-1</sup> HCl and NaOH were used to adjust the pH of the working solutions. The spent yeast waste was collected from the Wits Microbrewery, Johannesburg, South Africa using polypropylene plastic containers.

### Functionalisation of zeolite with yeast

The collected yeast waste (40 mL) was added to 2 g zeolite in a 100 mL polypropylene bottle and mixed for 24 h using an elliptical

bench-top shaker at 25°C. The contents were filtered using suction and the unbound yeast was removed by shaking the functionalised zeolite for 5 min with deionised water. The contents were filtered again and the zeolite was dried at 25°C for 24 h.

### Characterisation

The natural zeolite used was characterised with powder X-ray diffraction (PXRD) D2 Phaser (Bruker, Germany) to determine the mineralogy of the adsorbent and X-ray fluorescence (XRF) (PANalytical, Netherlands) for chemical composition. The functional groups of the natural and functionalised zeolite were determined using Fourier transform infrared (FTIR) spectroscopy (Tensor 27, Bruker, Germany). The amount of C, H and N on the natural and functionalised zeolite was determined using varioELcube V4.0.13 (Elementar, Germany). The surface area, pore size and pore volume were determined using TriStar 3000 V6.05 A (Micrometrics, USA).

### Batch adsorption studies

Batch studies were conducted to determine the effect of pH (2-9), initial concentration (0.5-10 mg L<sup>-1</sup>), adsorbent dosage (5-50 g L<sup>-1</sup>), contact time (0-540 min) and competing ions (Pt, Ru, Os, Hf, Au, Fe, Co, Ni, Ca, Mg, K and Zn) on the adsorption of Pd(II), Ir(III) and Rh(III) by yeast-functionalised zeolite. The raw zeolite was also used at the same conditions and the adsorption was not significant ( $p > 0.05$ ). The metals in the above conditions were shaken with the adsorbent to attain equilibrium and filtered. Inductively coupled plasma optical emission spectroscopy (ICP-OES) (Spectro Genesis, Germany) was used to determine the concentration of metals. The equilibrium adsorption capacity ( $q_e$  (μg g<sup>-1</sup>)) and adsorption efficiency of the metals recovered by yeast-functionalised zeolite were determined using Eq. 1 and 2, respectively.

$$q_e = \frac{(C_0 - C_e)V}{M} \times 1000 \quad (1)$$

$$\% \text{ adsorption} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

where  $C_0$  and  $C_e$  (mg L<sup>-1</sup>) are the initial and equilibrium concentrations of the metals, respectively,  $V$  (L) is the volume of the

solution and  $M$  (g) is the mass of the yeast-functionalised zeolite.

## Data treatment

### Adsorption isotherms

The type of adsorption between the metals and yeast-functionalised zeolite was determined using the Langmuir, Freundlich and Dubinin-Radushkevich (D-R) adsorption isotherms. The Langmuir isotherm describes the monolayer adsorption of metals onto a homogeneous surface with a fixed number of active sites. The assumption for this isotherm is that the active sites have equal adsorption energies (Latour, 2015). The Langmuir isotherm can be expressed as:

$$\frac{C_e}{q_e} = \left( \frac{1}{q_m} \right) C_e + \left( \frac{1}{K_L q_m} \right) \quad (3)$$

where  $q_m$  (mg g<sup>-1</sup>) is the maximum monolayer coverage and  $K_L$  (L mol<sup>-1</sup>) is the Langmuir isotherm constant. The affinity of the metals for the adsorbent was determined using the separation factor ( $R_L$ ) which can be determined from the Langmuir constant ( $K_L$ ). The affinity can be expressed as favourable ( $0 < R_L < 1$ ), unfavourable ( $R_L > 1$ ), linear adsorption ( $R_L = 1$ ) and irreversible adsorption ( $R_L = 0$ ). The  $R_L$  is expressed as:

$$R_L = \frac{1}{1 + C_0 K_L} \quad (4)$$

The Freundlich isotherm model describes the adsorption of metals onto a heterogeneous surface where the active sites are assumed to have different energies (Bakatula et al., 2015). The Freundlich isotherm can be expressed as:

$$q_e = K_f C_e^{\frac{1}{n}} \quad (5)$$

where  $K_f$  ((mg g<sup>-1</sup>)/(mol L<sup>-1</sup>)<sup>1/n</sup>) is Freundlich isotherm constant and  $n$  is adsorption intensity.

The Dubinin-Radushkevich (D-R) model is used to describe the adsorption between metals and adsorbents onto a heterogeneous surface with Gaussian energy distribution (Chen, 2015). The D-R model equation is as follows:

$$\ln q_e = \ln X_m - K_{DR} \varepsilon^2 \quad (6)$$

where  $X_m$  is theoretical isotherm saturation capacity ( $\text{mg g}^{-1}$ ),  $K_{DR}$  is the Dubinin-Radushkevich isotherm constant ( $\text{mol}^2 (\text{kJ}^2)^{-1}$ ),  $\epsilon$  is the Polanyi constant which can be expressed as:

$$\epsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \quad (7)$$

where  $R$  is the universal gas constant ( $\text{J (mol K)}^{-1}$ ) and  $T$  is temperature (K). The mean free energy of adsorption ( $E_s$ ) can be calculated from  $K_{DR}$  as shown in Eq. 8.

$$E_s = \frac{1}{\sqrt{2K_{DR}}} \quad (8)$$

### Kinetics study

The adsorption controlling mechanism between the metals and the adsorbent was determined using pseudo first- and second-order kinetic models. The pseudo first-order model has used to describe the rate of adsorption that is controlled by the rate of surface reaction in which case, the transition of metals from free to adsorbed state is considered (Rudzinski and Plazinski 2007). The pseudo second-order model is used to describe a reaction where the adsorption reaction on the surface of adsorbent is the rate-controlling step (Liu, 2008). The pseudo first and second-order kinetic models can be expressed by Eq. 9 and 10, respectively:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (9)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (10)$$

where  $q_t$  is the adsorbed amount ( $\text{mg g}^{-1}$ ) at time  $t$ ,  $q_e$  is the adsorbed amounts ( $\text{mg g}^{-1}$ ) at equilibrium and  $k_1$  is the pseudo first-order rate constant ( $\text{min}^{-1}$ ),  $k_2$  is the pseudo second-order rate constant ( $\text{g mg}^{-1} \text{min}^{-1}$ ) and  $k_2 q_e^2$  is the initial adsorption rate.

## Results and discussion

### Characterisation

The PXRD results showed that the dominant minerals of the zeolite were clinoptilolite ( $(\text{Na,K,Ca})_{2-3}\text{Al}_3(\text{Al,Si})_2\text{Si}_{13}\text{O}_{36} \cdot 12\text{H}_2\text{O}$ ), quartz ( $\text{SiO}_2$ ) and sanidine ( $\text{K(AlSi}_3\text{O}_8)$ ). The results from XRF indicated that the zeolite was mostly composed of silica ( $\text{SiO}_2$ ) (68.5%)

and alumina ( $\text{Al}_2\text{O}_3$ ) (11.6%). Since the yeast waste contains high amounts of amino acids, the possible interaction was through the oxides of the zeolite and these amino acids. The FTIR spectra of the natural and functional zeolite indicated that the functionalisation was successful since, there were N-H and C-N bands at  $1535$  and  $1637 \text{ cm}^{-1}$ , respectively on the functionalised adsorbent, indicative of the amino acid groups in the yeast. Due to the smothering of the zeolite pores by the spent yeast, the surface area and pore volume of the adsorbent decreased whilst the pore size increased. The amount of C, H and N increased after functionalisation due to high amount of amino acids.

### Effect of adsorbent dosage

The effect of adsorbent dosage on the adsorption of Pd(II), Ir(III) and Rh(III) at pH 2 by yeast-functionalised zeolite was studied and the results are presented in Fig. 1. The adsorption capacity of the metals decreased as the dosage increased but, the adsorption efficiency increased with dosage due to increased amount of binding sites. The Pd(II) adsorption capacity was higher than that of Ir(III) and Rh(III) thus, the yeast functional groups on zeolite had high affinity for Pd(II) at pH 2. The adsorption efficiencies of Pd(II) were in the range of 69-91% as the dosage increased from 50 to 500 mg. The adsorption efficiencies of Ir(III) were found to be 33, 54, 59, 62 and 61% at 50, 100, 200, 300 and 500 mg of yeast-functionalised zeolite, respectively and those of Rh were found to be 17, 25, 35, 39 and 61%, respectively. The lower adsorption efficiencies of Ir(III) and Rh(III) can be attributed to high oxidation states and high atomic and ionic radii of the metals thus, only a few could be taken up by the active sites. The recovery of the metals with yeast-functionalised zeolite was in the order: Pd(II) > Ir(III) > Rh(III).

### Effect of pH

The effect of pH on the adsorption of Pd(II), Ir(III) and Rh(III) by yeast-functionalised zeolite was studied and the results (Fig. 2) indicated that the adsorption capacity of Pd(II) and Ir(III) decreased as pH was increased due to the change of species and adsorbent surface. At lower pH, the metals

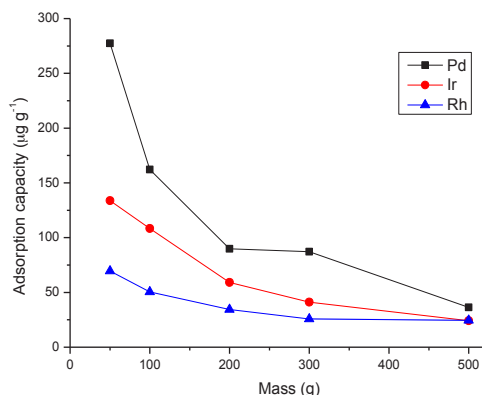


Figure 1 Effect of mass on adsorption of metals

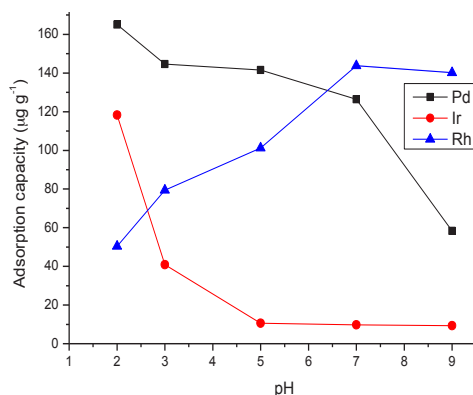


Fig. 2 Effect of mass on adsorption of metals

exist as  $\text{PdCl}_6^{4-}$  and  $\text{IrCl}_6^{3-}$  due to high HCl concentration which was used to adjust the pH. The platinum mining wastewater has high concentration of HCl which is used during processing and thus, the metals exist in their chloride species (Mosai et al., 2019). Since these species are negatively charged, they will interact electrostatically with the positively charged surface which is due to high concentration of hydronium ions ( $\text{H}_3\text{O}^+$ ). Thus at highly acidic regions, the amino acids will be positively charged and interact strongly with negatively charged species. The adsorption capacity of Pd(II) and Ir(III) decreased as pH was increased due to repulsions of the negatively charged hydroxide species and the negatively charged surface. However, the adsorption of Rh(III) increased with pH. A study by Labib et al. (2018) indicated that at higher pH, Rh(III) forms aqua/chloro complexes ( $[\text{RhCl}_2(\text{H}_2\text{O})_4]^+$  and  $[\text{RhCl}(\text{H}_2\text{O})_5]^{2+}$ ) which are positively charged and would electrostatically interact with the negatively charged surface. Thus, to substantially recover Rh(III) from wastewater, pH should be adjusted.

### Effect of initial concentration

The effect of initial concentration on the adsorption of Pd(II), Ir(III) and Rh(III) by the adsorbent at pH 2 was studied and the results are shown in Fig. 3. The adsorption capacity of Pd(II) increased with concentration from 0.5 to 10 mg L<sup>-1</sup> due to favourable adsorption. The adsorption capacity of Ir(III) and Rh(III) however, increased up to 2 mg L<sup>-1</sup> and remained fairly the same beyond this. This can be attributed to the limited binding sites

for these metals which are swiftly occupied hence, no further increase in adsorption was observed. The adsorption efficiencies of Pd(II) were found to be 83, 83, 81, 74 and 64% at 0.5, 1, 2, 5 and 10 mg L<sup>-1</sup>, respectively. The adsorption efficiencies for Ir(III) and Rh(III) were less than 25% beyond 2 mg L<sup>-1</sup>.

The type of adsorption occurring between the metals and yeast-functionalised zeolite was determined using adsorption isotherms and the data is presented in Table 1. The correlation coefficients ( $R^2$ ) were high for Langmuir isotherm, indicating that the adsorption of the metals to the adsorbent was through monolayer adsorption. The metals were removed from aqueous solutions through the metal-N interaction since, studies have indicated that PGEs have strong interactions with nitrogen (Mosai et al., 2019). The maximum adsorption coverage ( $q_m$ ) of Pd(II) onto the adsorbent was higher than for Ir(III) and Rh(III) which can be attributed to high affinity of the active sites for Pd(II) hence, the adsorption capacity has been higher than that of the other metals. The correlation coefficients for Pd(II) were >0.99 for all isotherms, meaning that there is also a possibility of adsorption on different adsorption sites or different adsorption mechanisms leading to a heterogeneous adsorption. The mean adsorption energy ( $E_s$ ) of Pd(II) determined from D-R isotherm was 10.12 kJ mol<sup>-1</sup> meaning that the interaction with the adsorbent was through chemical ion exchange. The energies of Ir(III) and Rh(III) were greater than 16 kJ mol<sup>-1</sup> indicating that their interaction was possibly chemisorptive in nature (Youssef et al., 2008).

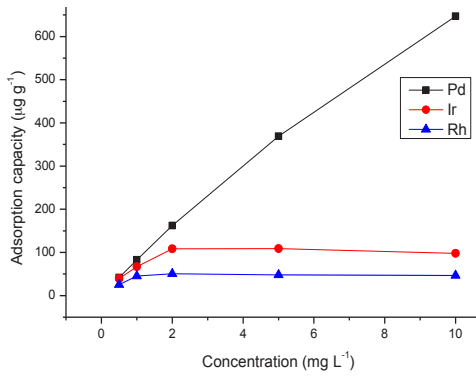


Fig. 3 Effect of concentration on adsorption of metals

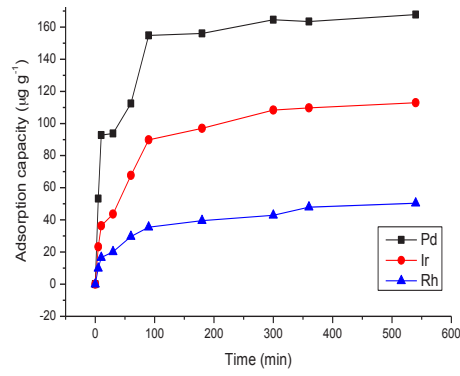


Fig. 4 Effect of time on adsorption of metals

### Effect of contact time

The effect of contact time indicated that there is at first a fast rate of adsorption of the metals which was observed within 10 min (Fig. 4). Beyond 90 min, the increase in adsorption of the metals was insignificant. Even though the adsorption of the metals was substantial within 90 min, a contact time of 6 h was selected for this study to obtain the maximum adsorption. The contact time data was used to fit in the kinetic models and determine the adsorption controlling mechanism. The results in Table 2 showed that pseudo second-order described the data better since the correlation coefficient ( $R^2$ ) was  $> 0.99$  for all the metals, indicating that the interaction of the metals with the adsorbent is strong (Mosai et al., 2019). To further confirm that the data was better described by pseudo second-order, the experimental adsorption capacity ( $q_{e, \text{exp}}$ ) was close to the pseudo second-order calculated adsorption capacity ( $q_e$ ) of the metals. When the adsorption is described by pseudo second-order, the interaction between the metals and the adsorbent is so strong that the detachment of the metals is unlikely to happen, which is a good attribute of the adsorbent especially when it is handled from mining or waste sites.

### Competing ions

The effect of competing ions on the adsorption of Pd(II), Ir(III) and Rh(III) by yeast-functionalised zeolite was studied since, mining wastewaters contain substantial amounts of other metals. The results from this study give an indication of how the adsorbent will behave in real wastewater. The results (Fig. 5) showed that the adsorption capacity of the analytes increased in the presence of other ions and this can be attributed to the possible synergistic interaction of the analytes with other metals such as iron thus, leading to adsorbent-Fe-analyte interaction (Mosai et al., 2019). The percentage increments in adsorption were found to be 14, 27, 58% for Pd(II), Ir(III) and Rh(III), respectively. Other PGEs (Pt, Ru and Os) were substantially removed from the aqueous solutions which is a good attribute of the adsorbent. Thus, in the presence of metals such as Fe, there is a possibility of multilayer adsorption where the Fe is directly connected to the adsorbent and form bonds with the analytes. The ability of the adsorbent to remove metals such as (K, Ni, Co and Zn) means that the yeast-functionalised zeolite has dual efficacy and that is recovering precious metals whilst removing contaminants from wastewaters.

Table 1 Adsorption isotherm parameters for the adsorption of metals by yeast-functionalised zeolite

| Metal   | Langmuir                        |                                  |       | Freundlich                                                  |      | Dubinin-Radushkevich |                                 |                                   |       |
|---------|---------------------------------|----------------------------------|-------|-------------------------------------------------------------|------|----------------------|---------------------------------|-----------------------------------|-------|
|         | $q^m$<br>( $\text{mg g}^{-1}$ ) | $K_L$<br>( $\text{L mol}^{-1}$ ) | $R^2$ | $K_F$<br>( $(\text{mg g}^{-1})/(\text{mol L}^{-1})^{1/n}$ ) | $n$  | $R^2$                | $X_m$<br>( $\text{mg g}^{-1}$ ) | $E_s$<br>( $\text{kJ mol}^{-1}$ ) | $R^2$ |
| Pd(II)  | 0.99                            | 53960                            | 0.99  | 1308                                                        | 1.37 | 0.99                 | 16.7                            | 10.12                             | 0.99  |
| Ir(III) | 0.15                            | $1.10 \times 10^7$               | 0.99  | 0.90                                                        | 4.97 | 0.91                 | 0.29                            | 19.0                              | 0.93  |
| Rh(III) | 0.052                           | $2.75 \times 10^6$               | 0.99  | 0.19                                                        | 7.61 | 0.83                 | 0.09                            | 22.3                              | 0.85  |

**Table 2** kinetic models parameters for the adsorption of Pd(II), Ir(III) and Rh(III) by yeast-functionalised zeolite

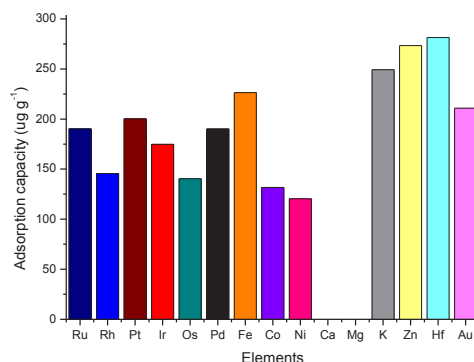
| Metal   | Pseudo first-order                  |                                             |                          |      | Pseudo-second order                        |                          |      |
|---------|-------------------------------------|---------------------------------------------|--------------------------|------|--------------------------------------------|--------------------------|------|
|         | $q_e^{(exp)}$<br>mg g <sup>-1</sup> | k1<br>min <sup>-1</sup><br>10 <sup>-3</sup> | qe<br>mg g <sup>-1</sup> | R2   | k2<br>g mg <sup>-1</sup> min <sup>-1</sup> | qe<br>mg g <sup>-1</sup> | R2   |
| Pd(II)  | 0.20                                | 4.10                                        | 0.12                     | 0.75 | 2.93                                       | 0.17                     | 0.99 |
| Ir(III) | 0.080                               | 1.98                                        | 0.17                     | 0.81 | 4.13                                       | 0.12                     | 0.99 |
| Rh(III) | 0.051                               | 0.61                                        | 0.18                     | 0.78 | 1.65                                       | 0.050                    | 0.99 |

## Conclusion

The ability of zeolite functionalised with yeast waste to recover Pd(II), Ir(III) and Rh(III) from aqueous solutions was studied. The results obtained were compared to those of the raw zeolite and the results were significantly different. The raw zeolite poorly adsorbed the metals but, there was a substantial change when the functionalised zeolite was used. The adsorbent was highly efficient at 2 mg L<sup>-1</sup> and a dosage of 10 g L<sup>-1</sup>. The adsorbent will substantially recover Pd(II) and Ir(III) at highly acidic pH regions but the adsorption of Rh(III) will be more efficient at less acidic pH regions due to the formation of aqua/chloro complexes which are positively charged. The adsorption capacity of Pd(II) was highly preferred more than other metals due to the ability to adsorb onto different active sites of the adsorbent since, both Langmuir and Freundlich described the adsorption data well. The adsorption mechanism of all the analytes was best described by pseudo second-order kinetic model meaning that the interaction of the metals was strong due to chemical adsorption. The adsorption capacities of the analytes increased in the presence of other ions due to adsorbent-Fe-metal synergistic interaction. Desorption studies were not conducted since, the used adsorbent can be processed along with the new ore and thus, no extra chemicals required for recovery. Hence, this will be a very cheap process.

## Acknowledgements

The authors would like to thank the National Research Foundation (NRF) (Grant no: 108556), the University of the Witwatersrand (Enabling grant) and the Water Research Commission (WRC project no. K5/2589) for financial support.

**Fig. 5** Effect of competing ions on adsorption of metals

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# PAPER III

**This paper investigated the recovery of Pd(II), Ir(III) and Rh(III) from aqueous solutions using bentonite functionalised with APDEMS.**

**This paper is submitted to be considered for the C Ellen Gronter Environmental Chemistry Competition.**

**Contribution:** lead author, conducted experimental work and data modelling, conceptualization, methodology, software validation, formal analysis, investigation, writing - original draft and visualization.

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This serves to inform that Alseno did the submitted work with minimal supervision. He conducted the experimental work and compiled the manuscript. You can direct any queries to me directly using my Email.

Regards,  
Hlanganani

# **Recovery of Pd(II), Ir(III) and Rh(III) from aqueous solutions using bentonite functionalised with 3-aminopropyl(diethoxy)methylsilane (APDEMS)**

Alseno K. Mosai and Hlanganani Tutu

## **Abstract**

The recovery of platinum group elements (PGEs) from waste is of high importance due to losses incurred during their processing, high input costs and diminishing primary resources. The recovery of Pd(II), Ir(III) and Rh(III) by bentonite functionalised with 3-aminopropyl(diethoxy)methylsilane (APDEMS) was investigated. Optimum conditions (adsorbent dosage, pH, concentration and competing ions) for the maximum uptake of PGEs by APDEMS-functionalised bentonite were determined. The maximum recovery of Ir(III) and Rh(III) was attained at pH 2, 10 g L<sup>-1</sup> adsorbent dosage and 2 mg L<sup>-1</sup> initial concentration. However, lower adsorbent dosage (5 g L<sup>-1</sup>) was required for maximum adsorption of Pd(II) at all concentrations. The adsorption efficiency of Ir(III) decreased significantly ( $p < 0.05$ ) as pH increased, but was fairly constant for Pd(II) and Rh(III). The adsorption capacity of Ir(III) and Rh(III) increased when competing ions were incorporated. APDEMS-functionalised bentonite proved to be a potential adsorbent for effective recovery of Pd(II), Ir(III) and Rh(III) from mining and industrial wastewaters in order to curb the losses incurred.

**Keywords:** Adsorption capacity; amino acids; cost-benefit analysis; platinum group elements; wastewater

## **Introduction**

The consumption of platinum group elements (PGEs) and the rare earth elements (REEs) has increased due to their unique properties. As a result, losses of these elements from processing plants have also been increasing.<sup>1-3</sup> The high demand of PGEs is mainly due to increasing population and improving technologies, leading to high production. PGEs are widely used in space materials, jewellery, medicine and catalysts.<sup>4,5</sup> The high demand for PGEs has led to high purchase costs from mining industries.<sup>6</sup>

Industrial wastewaters resulting from the processing of PGEs is released into the environment.<sup>6</sup> Other elements such as Mg, Ca, Cu, Ni, Mn and Fe are always in high concentrations in these waters along with lost precious elements.<sup>7</sup> These elements pose serious environmental challenges that can negatively affect living organisms including human beings. There is therefore a need for cheap and easy dual-efficacy methods that can physically remove precious elements and other pollutants from industrial wastewater that would otherwise persist in the environment.

Different methods such as hydrometallurgy and pyro-metallurgy have been used to recover PGEs from aqueous solutions but, they use a lot of energy and the operational costs are high.<sup>8</sup> On the contrary, readily available and relatively cheap materials such as zeolite and bentonite have been used to remove elements from aqueous solutions.<sup>9</sup> Other materials such as composite materials, biosorbents and nanomaterials have also been explored with notable success.<sup>10-13</sup> Studies have shown that the selectivity of bentonite can be improved by modification with ligands that have particular functional groups to target specific analytes and, since PGEs have a strong affinity for nitrogen, bentonite can be functionalised with nitrogen containing ligands to target these elements.<sup>9</sup>

In this study, the recovery of Pd(II), Ir(III) and Rh(III) from aqueous solutions using bentonite functionalised with the nitrogen containing 3-aminopropyl(diethoxy)methylsilane (APDEMS) was investigated at different solution conditions. The ability of the adsorbent to act as both the recovery and cleaning agent for industrial wastewaters was assessed.

## **Materials and methods**

### ***Reagents***

Bentonite and 3-aminopropyl(diethoxy)methylsilane ( $C_8H_{21}NO_2Si$ ) (mp: 85 - 88°C, MW: 191.34 g mol<sup>-1</sup>) were purchased from Sigma Aldrich, South Africa. The Rh, Ir and Pd standards were also purchased from Sigma Aldrich and were of analytical reagent grade. The 10 mg L<sup>-1</sup> stock solutions of the elements were prepared in 1000 mL volumetric flasks and stored in the refrigerator (4°C) until

required for usage. Working solutions were prepared daily from the stock solutions. A standard with a mixture of Pt, Rh, Ir, Pd, Os, Ru, Au and Hf was purchased from De Bruyn, Ultraspec, South Africa.

### ***Analytical techniques***

The deionised water used was prepared using Direct Q® 3 Millipore. The pH was measured using a pH meter (Mettler Toledo, Switzerland). The chemical composition of bentonite was determined with X-ray fluorescence (XRF) (PANalytical, Netherlands), mineral composition was analysed with powder X-ray diffraction (PXRD) D2 Phaser (Bruker, Germany), the functional groups on raw and functionalised bentonite were determined with Fourier transform infrared (FTIR) spectroscopy (Bruker, Germany) at a range of 4000 to 500 cm<sup>-1</sup> and the percentage composition of C, H, N and S were analysed with varioELcube V4.0.13 (Elementar, Germany). The point of zero charge (PZC) was determined using KCl as an electrolyte and NaOH and HNO<sub>3</sub> were used to adjust the pH.<sup>14</sup> The surface area, pore size and pore volume were determined using Micromeritics Flow Prep 060 instrument (Aachen, Germany). The concentration of elements was determined using inductively coupled plasma optical emission spectroscopy (ICP-OES) (Spectro Genesis, Germany).

### ***Functionalisation of bentonite with APDEMS***

The chemical functionalisation of bentonite was achieved by reacting 5.0 g bentonite with 10 mL of 3-aminopropyl(diethoxy)methylsilane in an automated microwave-assisted extraction monowave 450 (Anton Paar, South Africa) for 30 min at 180°C. The contents were cooled to room temperature and the functionalised bentonite was separated using suction filtration. The functionalised bentonite was then dried at 60°C for 24 h.

### ***Batch adsorption studies***

Adsorption experiments were conducted to determine the effect of mass (50 – 500 mg), concentration (0.5 – 10 mg L<sup>-1</sup>), pH (2 – 9), time (0 – 360 min) and competing ions (Pt, Ru, Os, Au, Hf, Co, Ni, Ca, Mg, Fe, K and Zn) on the recovery of Pd(II), Rh(III) and Ir(III) from aqueous solutions by

APDEMS-functionalised bentonite. To perform these experiments, 10 mL of solutions containing the analytes were added to APDEMS-functionalised bentonite and were shaken at room temperature until equilibrium was reached. The samples were filtered using 0.45 µm Whatman™ (Buckinghamshire, UK) cellulose filter paper after equilibrium and the filtrate was analysed with ICP-OES. The raw bentonite was used for the recovery of Pd(II), Ir(III) and Rh(III) but, the recovery efficiency was less than 10% and therefore considered non-economical hence, the APDEMS-functionalised bentonite was used. The amount of analytes adsorbed at equilibrium and the adsorption efficiency were determined using the following equations, respectively:

$$q_e = \frac{(C_i - C_e)V}{m} \quad (1)$$

$$\text{adsorption efficiency} = \frac{C_i - C_e}{C_i} \times 100\% \quad (2)$$

where  $q_e$  (µg g<sup>-1</sup>) is adsorption capacity,  $C_i$  and  $C_e$  (mg L<sup>-1</sup>) are initial and equilibrium concentrations, respectively,  $V$  (L) is the volume of solution used and  $m$  is the mass of APDEMS-functionalised bentonite.

## Data treatment

### Kinetic models

The adsorption controlling mechanism between the analytes and the adsorbent was investigated with pseudo first-order, pseudo second-order and Elovich kinetic models.<sup>1,15</sup> The correlation coefficient ( $R^2$ ) was used to determine the model that best fits the kinetic data. In addition, the closeness of the experimental adsorption capacity ( $q_m$ ) to the calculated adsorption capacity ( $q_{cal}$ ) were also used to determine the best fitting model. The equations of the pseudo first-order, pseudo second-order, Elovich and intra-particle diffusion kinetic models are shown below, respectively.

$$\log(q_e - q_t) = -\frac{k_1 t}{2.303} + \log q_e \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

$$\frac{dq_t}{dt} = a \cdot \exp(-b \cdot q_t) \quad (5)$$

where  $q_t$  and  $q_e$  are the adsorption capacities ( $\text{mg g}^{-1}$ ) at time  $t$  (experimentally obtained) and at equilibrium,  $k_1$  ( $\text{min}^{-1}$ ) and  $k_2$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ) are rate constants of pseudo first-order and pseudo second-order models,  $a$  is the initial adsorption rate ( $\text{mg g}^{-1} \text{min}^{-1}$ ) and  $b$  is a constant ( $\text{mg g}^{-1} \text{min}^{-1}$ ).

### **Adsorption isotherms**

The type of adsorption between Pd(II), Rh(III) and Ir(III) was determined using Langmuir, Freundlich and Dubinin-Radushkevich (D-R), Sips and Redlich-Peterson isotherm models. The experimental concentration data of the analytes was used to fit the isotherm models. The Langmuir isotherm assumes that there is one adsorption site for the analytes and thus leading to monolayer adsorption between analytes and the adsorbent.<sup>16</sup> The Langmuir equation can be expressed as:

$$\frac{C_e}{q_e} = \left(\frac{1}{q_m}\right) C_e + \left(\frac{1}{K_L q_m}\right) \quad (6)$$

where  $q_e$  ( $\text{mg g}^{-1}$ ) is the amount of the analyte adsorbed at equilibrium,  $C_e$  is analyte concentration,  $q_m$  ( $\text{mg g}^{-1}$ ) is the maximum mass of the analyte adsorbed at saturation conditions per unit mass of adsorbent and  $K_L$  is the Langmuir isotherm constant ( $\text{L mol}^{-1}$ ).

Freundlich isotherm assumes that the adsorption of analytes occurs through different adsorption sites with different energies. Hence it describes adsorption on a heterogeneous surface and can also be applied to multilayer adsorption.<sup>17</sup> The Freundlich isotherm equation can be described as:

$$q_e = K_f C_e^{\frac{1}{n}} \quad (7)$$

where  $K_f$  ( $(\text{mg g}^{-1})/(\text{mol L}^{-1})^{1/n}$ ) is the Freundlich isotherm constant and  $n$  is the adsorption intensity.

The D-R isotherm describes the adsorption mechanism between analytes and adsorbents with Gaussian energy distribution onto a heterogeneous surface. The isotherm has a parameter known as the mean free energy (E) which can be used to determine whether the adsorption of analytes is physical or chemical.<sup>15</sup>

$$\ln q_e = \ln X_m - K_{ad} \epsilon^2 \quad (8)$$

where  $K_{ad}$  ( $\text{mol}^2 (\text{kJ}^2)^{-1}$ ) is the Dubinin-Radushkevich (D-R) isotherm constant,  $X_m$  ( $\text{mg g}^{-1}$ ) is the theoretical isotherm saturation capacity and  $\epsilon$  is the Polanyi constant.

The three parameter isotherm empirical models were also used and the unknowns were determined using solver. Sips isotherm model (expressed in Eq. 9) is a combination of the Langmuir and Freundlich isotherms and due to the heterogeneity of the surface, the Sips isotherm reduces to Freundlich isotherm at lower concentrations of elements but, predicts Langmuir relationship at higher concentrations. The dimensionless heterogeneity factor ( $n_s$ ) of the Sips model can be used to determine the heterogeneity of systems.<sup>18</sup>

$$q_e = \frac{q_m (K_s C_e)^{n_s}}{1 + (K_s C_e)^{n_s}} \quad (9)$$

where  $K_s$  ( $\text{L mg}^{-1}$ ) is the Langmuir isotherm constant and  $n_s$  is the Freundlich heterogeneity factor. The Redlich-Peterson (R-P) isotherm model (Eq. 10) was also used to fit the adsorption data. It contains elements from the Langmuir and the Freundlich isotherm models.<sup>18</sup>

$$q_e = \frac{k_R C_e}{1 + a_R C_e^\beta} \quad (10)$$

where  $K_R$  ( $\text{mg g}^{-1}$ ) is the R-P adsorption isotherm constant,  $\alpha_R$  ( $\text{mg L}^{-1}$ ) is the R-P isotherm constant and  $\beta$  is the R-P isotherm constant which should be between 0 and 1. The R-P equation can adopt the Langmuir isotherm equation when  $\beta = 1$  and can get adopt the Freundlich isotherm equation when  $\beta = 0$ .

## Results and Discussion

### Characterisation

The chemical composition of bentonite was determined with XRF and the results indicated that the raw bentonite was mostly composed of silica ( $\text{SiO}_2$ ) (68.49%), alumina ( $\text{Al}_2\text{O}_3$ ) (11.58%) and potassium oxide ( $\text{K}_2\text{O}$ ) (3.79%). The results from PXRD indicated that montmorillonite, kaolinite, gibbsite, quartz and pyrophyllite-1 Tc were the main minerals of bentonite. The functional groups of the raw and functionalised bentonite were analysed with FTIR (Figure 1). The Si-O ( $995\text{ cm}^{-1}$ ) and Al-O ( $912\text{ cm}^{-1}$ ) peaks were observed on both materials and this further confirms the results obtained from XRF and PXRD. Absorbance peaks at approximately  $1643\text{ cm}^{-1}$  on both materials are due to the OH stretch of the water molecules on bentonite.<sup>19</sup>

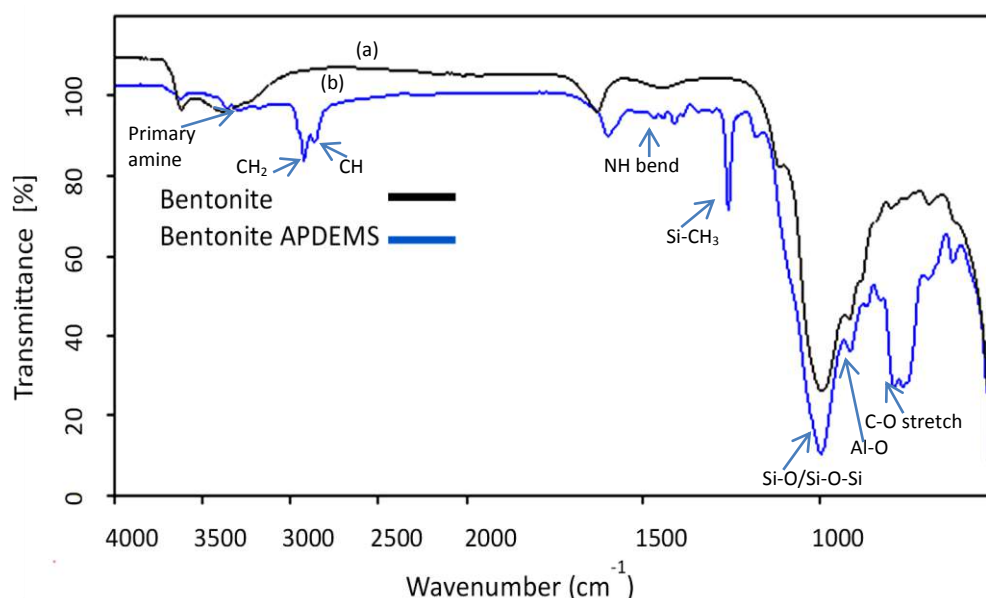


**Figure 1.** FTIR spectra of (a) raw bentonite and (b) APDEMS-functionalised bentonite.

The success of the addition of APDEMS on bentonite was confirmed by new peaks which were observed on the functionalised bentonite. The peak at  $3301\text{ cm}^{-1}$  was as a result of the primary amine of APDEMS. Moreover, the peak at  $1470\text{ cm}^{-1}$  was due to the N-H bend, further indicating the presence of amine groups which have high affinity for PGEs.<sup>20</sup> The carbon chain containing C-H

bonds was represented by the peaks at 2862 and 2924  $\text{cm}^{-1}$  which were due to CH and  $\text{CH}_2$  stretching vibrations of APDEMS, respectively. The proposed mechanism for the interaction of APDEMS on bentonite based on characterisation is shown in Figure 2. The percentages of C and H on the raw bentonite increased from 0.65% and 1.72% to 22.09% and 5.31%, respectively after the addition of APDEMS. The percentage amount of N which was not detected in the raw bentonite was found to be 5.84% on APDEMS-functionalised bentonite, further indicating successful functionalisation. The surface area of bentonite decreased from 21.29 to 1.20  $\text{m}^2 \text{mg}^{-1}$  due to the smothering of the pores upon functionalisation. The pore size decreased from 10.38 to 4.15 nm after the introduction of APDEMS. Moreover, the pore volume decreased to 0.0019 from 0.054  $\text{cm}^3 \text{g}^{-1}$ .

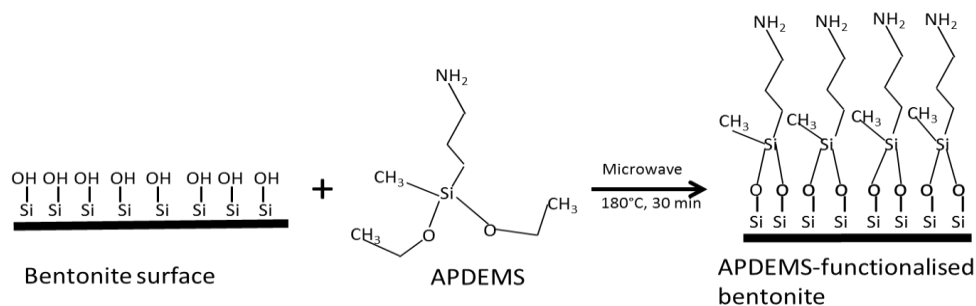


**Figure 2.** Proposed mechanism for the interaction of APDEMS with bentonite.

## Adsorption studies

### Effect of adsorbent mass

The effect of mass (50 – 500 mg) on the adsorption of Pd(II), Ir(III) and Rh(III) by APDEMS-functionalised bentonite was studied (Figure 3). The adsorption capacity decreased with increasing adsorbent mass.

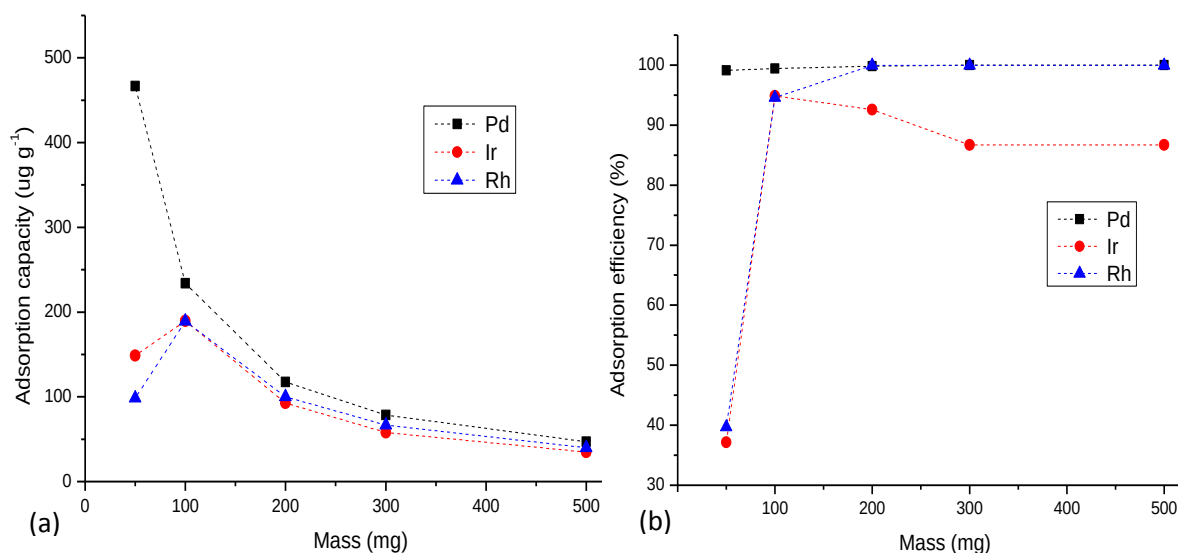


**Figure 3.** The (a) adsorption capacity and (b) adsorption efficiency of Pd(II), Ir(III) and Rh(III) with changing mass (pH 2, concentration = 2 mg L<sup>-1</sup>, temp = 25°C, volume = 10 mL, time = 240 min, n = 3, RSD <5%).

The adsorption efficiency of Pd(II) were not significantly ( $p > 0.05$ ) affected by changing mass. This can be attributed to the high affinity of the adsorbent for Pd(II).<sup>20</sup> The adsorption efficiency of Ir(III) increased with mass up to 100 mg but, decreased beyond this mass. The adsorption efficiency of Rh(III) increased until 200 mg after which no change was observed. 100 mg of APDEMS-functionalised bentonite was chosen as the optimum mass for subsequent experiments (i.e. adsorbent dosage of 10 g L<sup>-1</sup>).

### Effect of pH

The effect of pH on the adsorption of Pd(II), Ir(III) and Rh(III) by APDEMS-functionalised bentonite was investigated (Figure 4). The results indicated that the uptake of Pd(II) was not dependent on pH hence, favourable adsorption was observed across the pH range. The speciation of Pd(II) at different pH values was determined using PHREEQC geochemical modelling.<sup>20</sup> At highly acidic pH regions (pH  $\leq 3$ ), the negatively charged Pd(II)-chloride species ( $\text{PdCl}_4^{2-}$  and  $\text{PdCl}_3^-$ ) were dominant and favourable for adsorption onto the positively charged adsorbent resulting from the protonation of amine

groups. The PZC of the functionalised adsorbent was found to be 5.3, further indicating that the surface of the adsorbent was positively charged at pH values below 5.3. Beyond pH 5, the Pd species precipitated thus, there was little adsorption occurring.

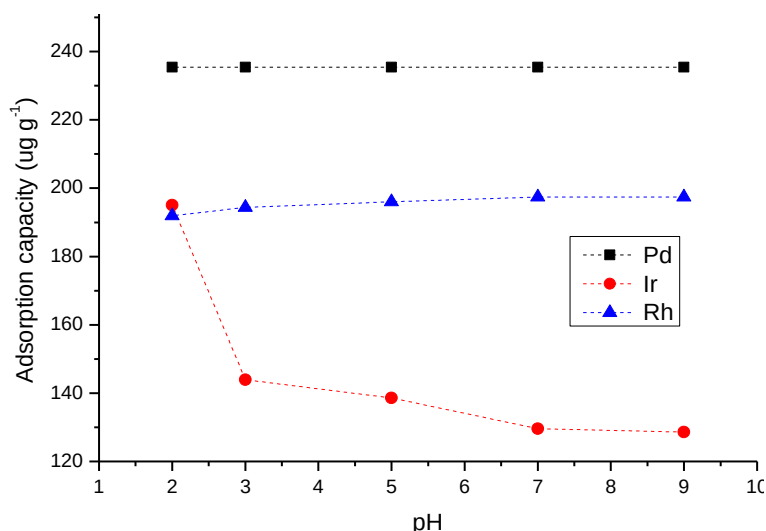


**Figure 4.** Effect of pH on the adsorption of Pd(II), Ir(III) and Rh(III) by APDEMS-functionalised bentonite (mass = 100 mg, concentration = 2 mg L<sup>-1</sup>, temp = 25°C, volume = 10 mL, time = 240 min, n = 3, RSD <5%).

The adsorption of Ir(III) was observed to decrease with increasing pH and the maximum adsorption was obtained at pH 2. At this pH, the Ir(III) species existed mainly as the negatively charged chloride species, IrCl<sub>6</sub><sup>3-</sup> due to the high concentration of chloride ions and thus the adsorption was highly favourable on the positively charged adsorbent. The adsorption of Rh(III) was not significantly affected by changing pH ( $p > 0.05$ ) but, the adsorption capacity was lower than that of Pd(II). This could have been caused by the high oxidation state of Rh(III), which meant that high amounts of amine groups were required. Highly acidic pH will be ideal to administer APDEMS-functionalised bentonite for simultaneous recovery of PGEs from industrial wastewaters.<sup>20</sup>

### Effect of contact time

The effect of contact time on the uptake of Pd(II), Ir(III) and Rh(III) by APDEMS-functionalised bentonite was investigated at pH 2 and the results are shown in Figure 5. There was fast adsorption of the elements within the first 10 min of contact with the adsorbent and, a slow increase in adsorption was observed until equilibrium was reached. The fast adsorption was due to the readily available active sites. Equilibrium was reached after 60 min of contact for Pd(II), 180 min for Ir(III) and 240 min for Rh(III). The slow increase observed on the adsorption capacity of Ir(III) and Rh(III) after the fast adsorption can be attributed to reduced availability of active sites. The adsorbent can be applied for a short period of time (max. 6 h).

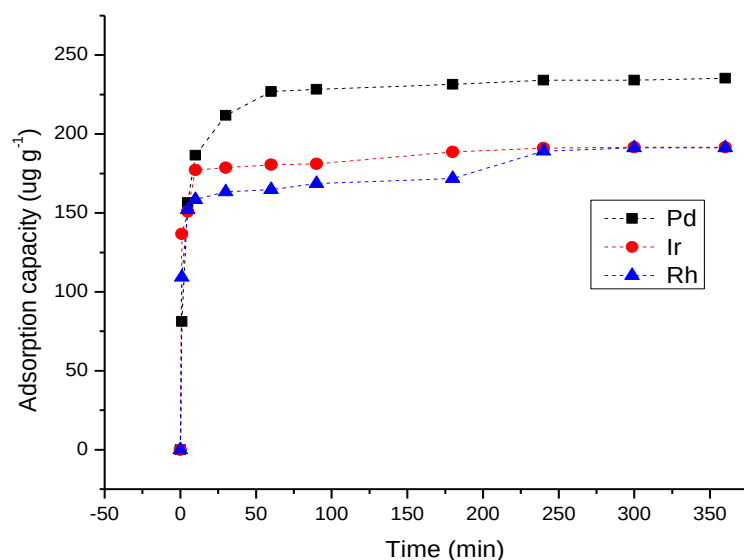


**Figure 5.** Effect of contact time on the adsorption of Pd(II), Ir(III) and Rh(III) by APDEMS-functionalised bentonite (pH = 2, concentration = 2 mg L<sup>-1</sup>, temp = 25°C, volume = 10 mL, mass = 100 mg, n = 3, RSD <5%).

### Adsorption kinetics

The pseudo first-order, pseudo second-order and Elovich kinetic models were used to fit the kinetic data and the results are shown in Table 1. The data was best described by the pseudo second-order model for all elements. The correlation coefficient ( $R^2$ ) was >0.99, indicating strong chemical

interactions between the elements and APDEMS-functionalised bentonite. These results together with the PZC obtained indicated when the optimum pH (pH 2) is used; the reaction of the elements with the adsorbent is highly likely to be due to the sharing of electrons between the negatively charged species and positively charged surface.<sup>21</sup> Moreover, the experimental ( $q_{\text{exp}}$ ) and the pseudo second-order calculated ( $q_{\text{cal}}$ ) adsorption capacities were similar but significantly different with those of pseudo first-order.

**Table 1** Kinetic models parameters

| Metal          | Pseudo first-order                        |                                         |                             |       | Pseudosecond-order                          |                             |       | Elovich                                   |                                           |       |
|----------------|-------------------------------------------|-----------------------------------------|-----------------------------|-------|---------------------------------------------|-----------------------------|-------|-------------------------------------------|-------------------------------------------|-------|
|                | $q_e \text{ (exp)}$<br>$\text{mg g}^{-1}$ | $k_1$<br>$\text{min}^{-1}$<br>$10^{-3}$ | $q_e$<br>$\text{mg g}^{-1}$ | $R^2$ | $k_2$<br>$\text{g mg}^{-1} \text{min}^{-1}$ | $q_e$<br>$\text{mg g}^{-1}$ | $R^2$ | $a$<br>$\text{g mg}^{-1} \text{min}^{-1}$ | $B$<br>$\text{g mg}^{-1} \text{min}^{-1}$ | $R^2$ |
| <b>Pd(II)</b>  | 0.10                                      | 18.20                                   | 0.038                       | 0.83  | 3.18                                        | 0.12                        | 0.99  | $6.30 \times 10^{-6}$                     | 75.05                                     | 0.90  |
| <b>Ir(III)</b> | 0.24                                      | 8.50                                    | 0.052                       | 0.55  | 2.70                                        | 0.23                        | 0.99  | 52.51                                     | 105.39                                    | 0.88  |
| <b>Rh(III)</b> | 0.26                                      | 7.60                                    | 0.073                       | 0.58  | 1.46                                        | 0.24                        | 0.99  | 9.91                                      | 85.07                                     | 0.85  |

### Effect of initial concentration

The initial concentrations ( $0.5 - 10 \text{ mg L}^{-1}$ ) of the analytes were at pH 2 and its effect was assessed. The adsorption capacity of Pd(II) increased with increasing concentration from  $0.5$  to  $10 \text{ mg L}^{-1}$  (Figure 6).

The ability of the adsorbent to significantly recover different concentrations of Pd(II) makes it a suitable adsorbent for industrial wastewaters which may contain varying concentrations of PGEs.<sup>20</sup> The adsorption capacities of Ir(III) and Rh(III) increased only up to  $2 \text{ mg L}^{-1}$  and a decrease in the uptake was observed beyond this. The increase in concentration from  $0.5$  to  $2 \text{ mg L}^{-1}$  can be attributed the availability of binding sites. Higher concentrations of Ir(III) and Rh(III) led to quick exhaustion of limited binding sites hence, no increase in adsorption was observed. Thus,

wastewaters containing high concentrations of Ir(III) and Rh(III) will require high amounts of the adsorbent.

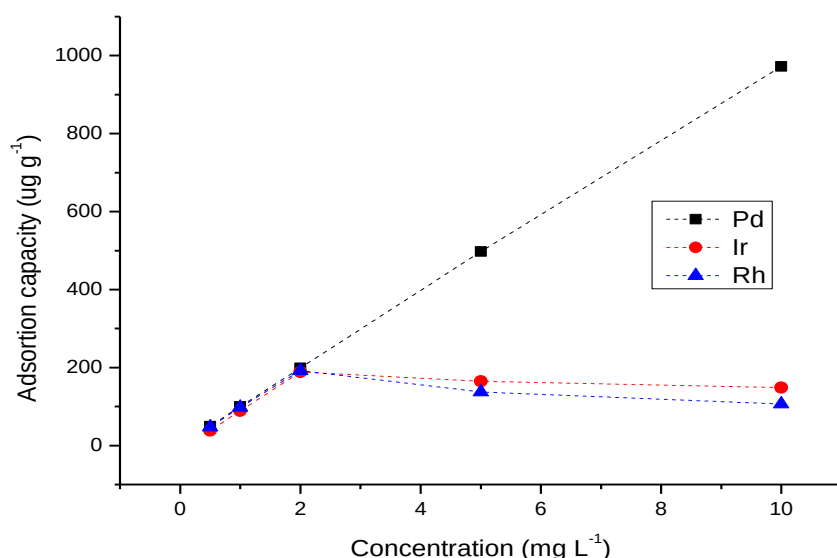


**Figure 6.** Effect of concentration on the adsorption of Pd(II), Ir(III) and Rh(III) by APDEMS-functionalised bentonite (pH = 2, mass = 100 mg, temp = 25°C, volume = 10 mL, time = 240 min, n = 3, RSD <5%).

### Adsorption isotherms

The concentration experimental data was used to fit in the Langmuir, Freundlich and the Dubinin-Radushkevich (D-R) isotherm models and the results are presented in Table 2. The results indicated that Langmuir fitted the experimental data better for all the analytes since the correlation coefficient was >0.99. This means that the interaction of Pd(II), Ir(III) and Rh(III) with APDEMS-functionalised bentonite was mainly through monolayer adsorption onto active sites with similar energies. Thus, adsorption was through the interaction of the analytes with the amine group of ADPDEMS. However, the Freundlich and D-R correlation coefficients for Pd(II) were also high (> 0.93) and this could be due to multisite Langmuir isotherm.<sup>22</sup> This phenomenon can also be supported by the increasing adsorption capacity Pd(II) with concentration. The maximum adsorption capacity,  $q_m$  of Pd(II) as predicted by the Langmuir isotherm was higher than that of other elements hence

increasing uptake was observed with increasing initial concentration (Figure 6). The D-R adsorption isotherm was used to determine the mean free energy of adsorption. The energies of Pd(II), Ir(III) and Rh(III) were found to be 14.13, 22.69 and 21.28 kJ mol<sup>-1</sup>. Thus, the adsorption process between Pd(II) and the adsorbent occurs through chemical ion exchange and that of Ir(III) and Rh(III) through chemisorption.<sup>23</sup> The three parameter isotherm models were also used and the results are shown in Table 3. The Sips model poorly described that experimental data whilst the Redlich-Peterson (R-P) isotherm described the data better, however, the correlation coefficients of Ir(III) and Rh(III) were still lower than those of the Langmuir isotherm. The exponent ( $\beta$ ) was closer to 1 for Ir(III) and Rh(III) further indicating that these elements were bound onto a homogeneous surface.<sup>24</sup> The correlation coefficient of Pd(II) (>0.99) determined from the R-P isotherm as well as the  $\beta$  value (0.64), indicated that there is a possibility of adsorption onto a heterogeneous surface hence, the Freundlich and D-R isotherms showed higher correlation of the data.

**Table 2** The isotherm parameters of Pd(II), Ir(III) and Rh(III)

| Metal          | Langmuir                    |                              |       | Freundlich                                                               |      |       | Dubinin-Radushkevich        |                               |       |
|----------------|-----------------------------|------------------------------|-------|--------------------------------------------------------------------------|------|-------|-----------------------------|-------------------------------|-------|
|                | $q_m$ (mg g <sup>-1</sup> ) | $K_L$ (L mol <sup>-1</sup> ) | $R^2$ | $K_f$ ((mg g <sup>-1</sup> )/<br>(mol L <sup>-1</sup> ) <sup>1/n</sup> ) | N    | $R^2$ | $X_m$ (mg g <sup>-1</sup> ) | $E_s$ (kJ mol <sup>-1</sup> ) | $R^2$ |
| <b>Pd(II)</b>  | 1.04                        | 5.12x10 <sup>6</sup>         | 0.99  | 589.57                                                                   | 2.07 | 0.93  | 14.19                       | 14.13                         | 0.95  |
| <b>Ir(III)</b> | 0.15                        | 2.81x10 <sup>6</sup>         | 0.99  | 0.71                                                                     | 6.81 | 0.23  | 0.29                        | 22.69                         | 0.23  |
| <b>Rh(III)</b> | 0.21                        | 8.84x10 <sup>5</sup>         | 0.99  | 0.97                                                                     | 6.23 | 0.52  | 3.91                        | 21.28                         | 0.55  |

**Table 3** The three parameter isotherm models parameters for Pd(II), Ir(III) and Rh(III)

| Metal          | Sips  |                             |                             |       | Redlich-Peterson                                     |         |                             |       |
|----------------|-------|-----------------------------|-----------------------------|-------|------------------------------------------------------|---------|-----------------------------|-------|
|                | $n_s$ | $K_s$ (L mg <sup>-1</sup> ) | $q_m$ (mg g <sup>-1</sup> ) | $R^2$ | $\alpha_R$ (x10 <sup>3</sup> ) (mg L <sup>-1</sup> ) | $\beta$ | $k_R$ (mg g <sup>-1</sup> ) | $R^2$ |
| <b>Pd(II)</b>  | 0.58  | 1.01x10 <sup>7</sup>        | 0.09                        | 0.86  | 56.9                                                 | 0.61    | 95096                       | 0.99  |
| <b>Ir(III)</b> | 0.67  | 9.8                         | 0.152                       | 0.21  | 8.86                                                 | 0.85    | 1063                        | 0.91  |
| <b>Rh(III)</b> | 0.65  | 381                         | 0.127                       | 0.27  | 5.85                                                 | 0.94    | 663                         | 0.97  |

### Effect of competing ions

The effect of competing ions on the adsorption of Pd(II), Ir(III) and Rh(III) was studied at 25°C by mixing the analytes with other PGEs (Pt, Ru and Os), Hf, Au and contaminants (Fe, Co, Ni, Ca, Mg, K and Zn). The study indicated that APDEMS-functionalised bentonite had high affinity for the analytes even in the presence of other elements (Figure 7). Other precious elements were simultaneously adsorbed onto the adsorbent. The adsorption capacities for Ir(III) and Rh(III) increased by 15.4 and 17.8%, respectively in the presence of other ions. The increase in adsorption capacity can be attributed to their interaction with Fe-O and thus forming Si-O-Fe-O-X(III) ( where X is Ir or Rh).<sup>25</sup> The adsorption of Pd(II) however, decreased by 6.4%. Other elements which are considered contaminants such as Fe, Co, Zn etc. were also removed from aqueous solutions by the adsorbent and thus the adsorbent will act as a recovery agent for precious elements and as a wastewater remediation technique. The ability of APDEMS-functionalised bentonite to significantly recover the analytes of interest in the presence of other elements makes it a good adsorbent for industrial wastewaters which contain significant amounts of different contaminants. Thus, the application of the adsorbent in industrial wastewaters can potentially help mining and other industries gain profit from the waste produced during the processing of PGEs or their use in different fields such as jewellery and automotive. Moreover, the ability to also adsorb contaminants such as Fe, Co and Ni means that the adsorbent can be used to clean industrial wastewaters. The adsorbent can then be

used as a filter in industrial water retaining ponds, where the water from the processing plants will have first contact with the adsorbent before entering the retaining ponds.

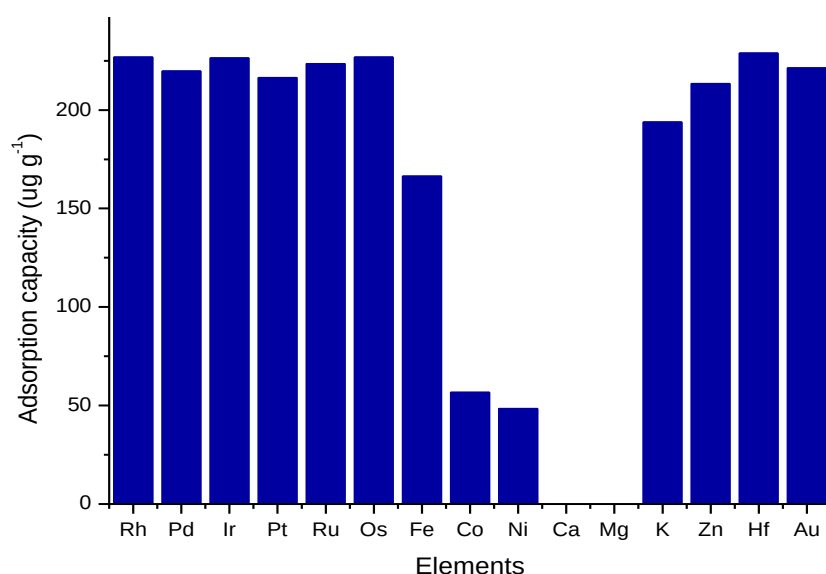


**Figure 7.** Effect of competing ions on the adsorption of Pd(II), Ir(III) and Rh(III) by APDEMS-functionalised bentonite (mass = 100 mg, pH 2, concentration = 2 mg L<sup>-1</sup>, volume = 10 mL, time = 240 min, n = 3, RSD <5%).

## Conclusion

The recovery of Pd(II), Ir(III) and Rh(III) from aqueous solutions using bentonite functionalised with 3-aminopropyl(diethoxy)methylsilane (APDEMS) was studied. Optimum conditions for the maximum uptake of the elements were found to be pH 2 and 10 g L<sup>-1</sup> adsorbent dosage. The discharged wastewater from PGEs processing plants is around pH 2, as a result of high concentrations of acids used. Hence, the adsorbent is suitable for use in industrial wastewaters. The uptake of Pd(II) was higher than that of other elements due to the ability to adsorb on different active sites of the adsorbent. The adsorbent will work best when the concentration of the analytes is low (i.e. 2 mg L<sup>-1</sup>). The selectivity of the elements by the adsorbent increased in the presence of other ions, due to synergistic effects. The cost-benefit analysis for the recovery of Pd(II), Ir(III) and Rh(III) indicated that more than 44 000 USD profit can be gained with 1 kg of APDEMS-functionalised bentonite. Thus,

APDEMS-functionalised bentonite can be used as the potential adsorbent for the recovery of Pd(II), Ir(III) and Rh(III) from wastewater.

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### Conflicts of interest/Competing interests

The authors state that they have no conflict of interest associated with this work.

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**SECTION 4.3:**  
**RECOVERY OF**  
**RARE EARTH**  
**ELEMENTS USING**  
**ZEOLITE AND**  
**BENTONITE**

# PAPER I

**This paper investigated the recovery of rare earth elements (REEs) from aqueous solutions using natural zeolite and Bentonite.**

**The paper is published in Water Air and Soil Pollution.**

**Impact Factor: 1.769.**

**Contribution:** lead author, conducted experimental work and data modelling, conceptualization, methodology, software validation, formal analysis, investigation, writing - original draft and visualization.



# The Recovery of Rare Earth Elements (REEs) from Aqueous Solutions Using Natural Zeolite and Bentonite

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**Abstract** Increasing applications of rare earth elements (REEs) and improving technologies have led to increased demand. Because of their limited availability and depletion of most resources, the recovery of these elements from waste has become important. The use of cost-effective materials for this purpose and the high value that can potentially be recovered would be beneficial and attractive to many industries using REEs. In this study, natural zeolite and bentonite were used in batch studies to recover REEs (La, Y, Lu, Sm, Pr, Tm, Ce, Nd, Yb, Gd, Eu, Er, Ho, Dy, and Sc) from aqueous solutions. The effect of adsorbent dosage, pH, concentration, contact time, and competing ions on recovery was investigated. Desorption studies were conducted using ammonium sulphate. Adsorption onto zeolite was found to increase with pH, whereas uniform adsorption was observed for bentonite, except at pH 2 (16% less efficiency). The pH values of 6.2 and 3.2 were selected as the optimum for zeolite and bentonite, respectively. For zeolite, the average adsorption efficiencies for REEs at 0.5, 1.0, 2.0, 5.0, and 10 mg L<sup>-1</sup> were found to be 91, 96, 89, 40, and 20% respectively but, > 98% adsorption efficiencies were achieved with bentonite at all concentrations. The zeolite and bentonite adsorption data were better described by Langmuir though, for bentonite, the coefficients of determination ( $R^2$  values) for the

Freundlich and Dubinin-Radushkevich isotherm models were also significant. There was no significant difference ( $p > 0.05$ ) on the adsorption of the elements in the presence of competing ions. Bentonite proved to perform better, most likely as a result of its higher surface area. Generally, the good adsorption performance of both adsorbents in their natural forms makes them an attractive and potential cheap option for the recovery of REEs from wastewaters.

**Keywords** Adsorption capacity · Zeolite · Ammonium sulphate · Bentonite

## 1 Introduction

The demand for rare earth elements (REEs) which include europium, yttrium, and lanthanides has been increasing over the years due to improving technologies in cars, smart phones, and catalytic converters (Ogata et al. 2015). This has escalated the exploitation of REEs resources (Shan et al. 2002). The highest REEs reserves are found in China, Brazil, and Russia. Other countries have small concentrations of REEs which have to be handled with caution due to the possibility of scarcity and as a form of resource management. Recently, the trade war between the USA and China has seen a rise in the prices of REEs as China threatened to cut supply. Such factors make the recovery of REEs from wastewaters and mine leachates important as a way of securing alternative sources (Shan et al. 2002). Since, REEs

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exist with a host of elements, cheap and selective techniques are required for their recovery from wastewaters of different industries.

Studies of the recovery or remediation of elements have been conducted using different techniques such as reverse osmosis, ultrafiltration, chemical precipitation, electro-dialysis, and adsorption (Wu et al. 2015). Adsorption has been adopted by a number of researchers due to its low cost, simplicity of operation, and high efficiency (Roosen et al. 2014; Smith et al. 2016; Yanfei et al. 2016). Natural adsorbents such as zeolite, bentonite, kaolin, chitosan, and shells have been used for the adsorption of elements such as Cu, Cd, Cr, and Mg, offering cheaper alternatives as these adsorbents are readily available (Bakatula et al. 2015; Sun et al. 2016; Khan et al. 2018). Zeolite is a crystalline microporous aluminosilicate made up of  $\text{SiO}_4^-$  and  $\text{AlO}_4^-$  tetrahedra which make the surface of the zeolite negative (Weckhuysen and Yu 2015). Zeolite can also be used as an ion exchanger for elements such as Mg, Ca, K, and Na. On the other hand, bentonite contains an octahedral aluminium sheet and two silica tetrahedral sheets and has a structural negative charge due to the substitution of  $\text{Si}^{4+}$  by  $\text{Al}^{3+}$  or  $\text{Al}^{3+}$  by  $\text{Mg}^{2+}$  in the tetrahedral and octahedral layer, respectively (Anirudhan and Ramachandran 2015). Many studies have reported on the use of these adsorbents in their modified form to increase their selectivity for specific elements (Bakatula et al. 2015; Mosai et al. 2018). Thus, they act as supporting materials for ligands and the modification costs will apply which add more expenses on the adsorption of elements. However, these adsorbents have been used in their natural form and have been found to adsorb different elements effectively.

In this study, natural zeolite and bentonite were used to recover REEs from aqueous solutions. The adsorption capacities of these adsorbents were compared to determine the best natural adsorbent. The choice of these adsorbents was based on their availability and cost-effectiveness. Some studies that used these two adsorbents were by Chegrouche et al. (1997) and Jiang et al. (2016) who investigated the recovery of lanthanum from aqueous solutions. Another study by Wu et al. (2012) focused on the adsorption of REEs using synthetic bentonite whilst this study deals with natural zeolite and bentonite, making them cheaper alternatives. In our study, adsorption of a mixture of REEs onto natural zeolite and bentonite was assessed. It further explored the effect of other factors such as initial

concentration and pH which may influence the adsorption capacity of the elements.

## 2 Materials and Method

### 2.1 Reagents and Standards

The standards used were of analytical reagent grade and needed no further purification. The REEs standard solution in concentrated  $\text{HNO}_3$  was obtained from Sigma Aldrich, South Africa. The stock solution of REEs was prepared using the standard solution and was stored in the refrigerator at 4 °C prior to use. The working solutions were prepared daily from the stock solution and the pH of the solutions was adjusted using 0.01 mol L<sup>-1</sup> of  $\text{HNO}_3$  and NaOH. A pH meter (Mettler Toledo, Switzerland) was used to measure the pH. Another stock solution containing platinum group elements (PGEs) was prepared by diluting the standard containing all PGEs with deionised water. The stock solution of other elements (Fe, Co, Ni, Ca, Mg, K, and Zn) was prepared by dissolving nitrate salts of these elements in a volumetric flask using deionised water and concentrated  $\text{HNO}_3$  was added to preserve the solution. Natural zeolite and bentonite used were obtained from Sigma Aldrich, South Africa.

### 2.2 Characterisation

In order to determine the possible reaction between the adsorbent and the elements, the composition of the adsorbents was determined. X-ray fluorescence (XRF) (PANalytical, Netherlands) was used to determine the chemical composition; powder X-ray diffraction (PXRD) D2 Phaser (Bruker, Germany) using Ni-filtered Cu K $\alpha$  radiation for determination of the mineral composition at 10–90 2 $\theta$  range; and Fourier-transform infrared (FTIR) spectroscopy with mid-IR source (4000–400 cm<sup>-1</sup>) and KBr beam splitter for determination of functional groups. The textural properties (surface area, pore size, and pore volume) were determined using TriStar 3000 V6.05 A (Micrometrics, USA). The particle sizes of both adsorbents were determined before and after adsorption using scanning electron microscopy (SEM). The thermal stability (thermogravimetric analysis (TGA) and differential temperature analysis (DTA)) of zeolite and bentonite was determined using the Perkin Elmer Pyris 1 TGA (Massachusetts,

USA). A method by Fiol and Villaescusa (2009) was used to determine the point of zero charge (pHpzc) for both adsorbents.

### 2.3 Adsorption Studies

Batch adsorption experiments were conducted in triplicate to determine the effect of adsorbent dosage on the adsorption of REEs. To validate the results obtained, the relative standard deviation (RSD) was used. For this study, different masses (50–500 mg) of zeolite and bentonite were exposed to 10 mL of 2 mg L<sup>-1</sup> REE solution at pH 6.2 and 3.2 for zeolite and bentonite, respectively in 50-mL centrifuge tubes. The tubes were shaken using an elliptical bench-top shaker (Labcon, South Africa) at 150 rpm. The contents were filtered using a 0.45-μm Whatman filter paper (Whatman™, UK) and the equilibrium concentrations of the REEs were analysed using inductively coupled plasma optical emission spectroscopy (ICP-OES) (Spectro Genesis, Germany). The effect of pH (in the range 2–9) on the adsorption of REEs by both adsorbents was determined by keeping all the other variables constant except the pH. The pHpzc was included to understand the changes in surface charge at different pH values. Since, the industrial wastewaters may contain different concentrations of REEs, the effect of initial concentration (0.5–10 mg L<sup>-1</sup>) on the adsorption of REEs was investigated. The time it takes for the adsorption of REEs to reach equilibrium was determined and a period of 0 to 540 min was selected for this study. To perform this study, the REE solutions were in contact with the zeolite and bentonite at different times and the contents were immediately filtered after a specific time of contact. Since other elements can be present alongside the REEs in wastewaters, the effect of such elements (e.g. Fe, Co, Ni, Ca, Mg, K, and Zn) on the adsorption of REEs was studied. The PGEs (Pt, Pd, Rh, Os, Ir, and Ru) were used since, some industries such as electric automobiles, biomedical equipment and automotive catalytic converters use both REEs and PGEs and thus, the wastewaters may contain their combination (Izatt et al. 2016). Moreover, some mineral ores contain both PGEs and REEs (Xiong et al. 2017), suggesting that mine leachates from these ores would likely contain both suites of elements. The adsorbed REEs were desorbed from the zeolite and bentonite with 0.25, 0.5, and 1 M ammonium sulphate. The choice of ammonium sulphate is based on other studies (Moldoveanu and Papangelakis 2013)

that have indicated that it is effective in removing REEs from clays through ion exchange (NH<sub>4</sub><sup>+</sup> replacing the REEs on the surface).

The adsorption capacities,  $q_e$  (mg g<sup>-1</sup>) and the adsorption efficiency (%) were calculated using Eq. 1 and 2, respectively.

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (1)$$

$$\% \text{adsorption} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

where  $C_0$  and  $C_e$  are initial and equilibrium liquid-phase concentrations of the elements, respectively,  $V$  (L) is the volume of the solutions and  $M$  (g) is the mass of the adsorbent used.

### 2.4 Adsorption Isotherms

The Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) adsorption isotherms were used to determine the adsorption process (typically, the arrangement of ions on the adsorbent surface). The Langmuir isotherm model describes the adsorption of elements onto a homogeneous surface resulting in similar adsorption energies. It also corresponds to monolayer coverage of the adsorbent and can be expressed as (Langmuir 1918; Gerard et al. 2016):

$$\frac{C_e}{q_e} = \left( \frac{1}{q_m} \right) C_e + \left( \frac{1}{K_L q_m} \right) \quad (3)$$

where  $q_{\max}$  (mg g<sup>-1</sup>) is the maximum monolayer adsorption coverage and is obtained from the slope of the plot of  $C_e/q_e$  against  $C_e$ ; and  $K_L$  (L mol<sup>-1</sup>) is the Langmuir isotherm constant which can be obtained from the intercept of the plot. The Langmuir isotherm model has a dimensionless parameter known as the separation factor ( $R_L$ ) which is used to determine if the adsorption is favourable ( $R_L < 1$ ), linear or unchanged ( $R_L = 1$ ), unfavourable ( $R_L > 1$ ) or irreversible ( $R_L = 0$ ). The  $R_L$  can be expressed as:

$$R_L = \frac{1}{1 + C_0 K_L} \quad (4)$$

The Freundlich adsorption isotherm has been widely used for the adsorption of substances onto a heterogeneous surface with the possibility of multilayer

adsorption. Thus, the adsorption energies are expected to be different due to different active sites (Chen 2015).

$$q_e = K_f C_e^{\frac{1}{n}} \quad (5)$$

where  $K_f$  ((mg g<sup>-1</sup>)/(mol L<sup>-1</sup>)<sup>1/n</sup>) and  $n$  are the Freundlich isotherm constant and the adsorption intensity, respectively. The  $K_f$  can be obtained from the slope of the plot of  $\ln q_e$  against  $\ln C_e$  whilst  $n$  can be obtained from the intercept of the plot.

The D-R adsorption isotherm is used to describe the adsorption mechanism between the elements and adsorbents with Gaussian energy distribution onto a heterogeneous surface. The D-R isotherm model equation can be expressed as (Chen and Yang 1994; Mosai et al. 2017):

$$\ln q_e = \ln X_m - K_{ad} \varepsilon^2 \quad (6)$$

where  $K_{ad}$  (mol<sup>2</sup> (kJ<sup>2</sup>)<sup>-1</sup>) is the Dubinin-Radushkevich (D-R) isotherm constant which is determined from the plot of  $\ln q_e$  against  $\varepsilon^2$ ;  $X_m$  (mg g<sup>-1</sup>) is the D-R adsorption capacity which can be determined from the intercept of the plot; and  $\varepsilon$  is the Polanyi constant which can be expressed as:

$$\varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \quad (7)$$

where  $R$  is the universal gas constant (J (mol\*K)<sup>-1</sup>) and  $T$  is temperature (K).

The mean free energy ( $E$ ) of adsorption of REEs onto zeolite or bentonite can be determined using data from the D-R isotherm. The value of the energy can help determine the type of adsorption occurring between the elements and the adsorbents (e.g. physical adsorption or chemical adsorption). The mean free energy change,  $E_s$  (kJ mol<sup>-1</sup>) can be calculated using the following equation:

$$E_s = \frac{1}{\sqrt{2K_{ad}}} \quad (8)$$

## 2.5 Adsorption Kinetics

The controlling mechanism of the adsorption process was analysed using adsorption kinetic models which were deduced from the contact time data of the elements. The pseudo first- and second-order kinetic models were used to help identify the controlling mechanisms affecting the adsorption of REEs onto zeolite or

bentonite. The coefficient of determination ( $R^2$  value) was used to identify the model that best fitted the kinetic data. Moreover, the closeness of the experimental adsorption capacity,  $q_{e(\text{exp})}$ , to the calculated adsorption capacity,  $q_e$  was used together with  $R^2$  to conclude on the models. The pseudo first-order model, also known as the Lagergren pseudo first-order model, assumes that the rate of adsorption of elements onto the active sites is directly proportional to the availability of active sites of the adsorbents and can be expressed as (Babarinde and Onyiaocha 2016):

$$\log(q_e - q_t) = -\frac{k_1 t}{2.303} + \log q_e \quad (9)$$

where  $q_t$  (mg g<sup>-1</sup>) is the amount of elements adsorbed per unit mass of adsorbent at time  $t$ ,  $t$  (min) is time and  $k_1$  (min<sup>-1</sup>) is the Lagergren rate constant. The pseudo second-order kinetic model which describes strong interactions between the elements and the adsorbents was also used and can be expressed as (Ho and McKay 1999; Wu et al. 2009):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \quad (10)$$

where  $k_2$  is the pseudo second-order rate constant.

## 3 Results

### 3.1 Characterisation

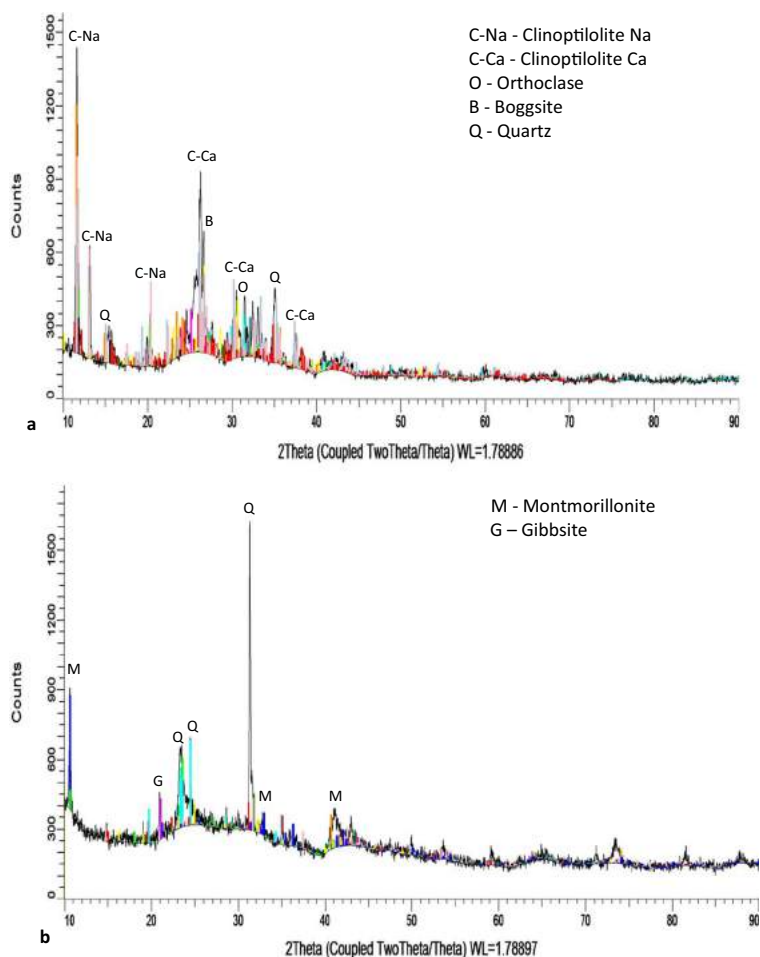
The XRF results indicated that both zeolite and bentonite were dominated by SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> but, in different amounts (Table 1). Zeolite had a higher composition of SiO<sub>2</sub> than bentonite but, the Al<sub>2</sub>O<sub>3</sub> content was higher in bentonite. Sedghi et al. (2014) studied the effect of alumina content in ceramic insulators and found that high alumina content increases the mechanical strength of the insulators. Thus, Al-rich minerals are more stable and can handle surface reactions better. The quartz phase plane intensities reduced as the alumina content was increased. The mineral composition of zeolite and bentonite was determined with PXRD (Fig. 1). Results indicated that zeolite was dominated by clinoptilolite and quartz (Fig. 1a). Orthoclase and boggsite minerals containing Si, Al, and O were also dominant. Bentonite was dominated by montmorillonite, gibbsite, and quartz (Fig. 1b). The FTIR spectra of zeolite and bentonite are

**Table 1** The chemical composition of zeolite and bentonite

| Compound                       | Percentage composition (wt.%) |           |
|--------------------------------|-------------------------------|-----------|
|                                | Zeolite                       | Bentonite |
| SiO <sub>2</sub>               | 68.49                         | 51.48     |
| Al <sub>2</sub> O <sub>3</sub> | 11.58                         | 16.67     |
| Fe <sub>2</sub> O <sub>3</sub> | 1.09                          | 5.03      |
| MnO                            | 0.02                          | 0.06      |
| MgO                            | 0.77                          | 3.55      |
| CaO                            | 1.22                          | 1.95      |
| Na <sub>2</sub> O              | 1.47                          | 0.19      |
| K <sub>2</sub> O               | 3.79                          | 1.37      |
| TiO <sub>2</sub>               | 0.12                          | 0.40      |
| P <sub>2</sub> O <sub>5</sub>  | 0.03                          | 0.09      |
| Cr <sub>2</sub> O <sub>3</sub> | 0.01                          | 0.02      |
| Loss of ignition (LOI)         | 11.3                          | 18.41     |

presented in Fig. 2. The group of peaks between 3450 and 3640 cm<sup>-1</sup> was due to the stretching vibrations of OH groups. The peaks at 1644 and 1632 cm<sup>-1</sup> for zeolite and bentonite, respectively, were due to the OH groups of the water molecules (Özcan and Özcan 2004). The XRF and PXRD results were confirmed by the FTIR results which indicated the presence of strong peaks at ~ 980 cm<sup>-1</sup> which were due to the overlapping peaks of Si-O and Al-O on both adsorbents.

The textural properties of the zeolite and bentonite are presented in Table 2. The surface area of bentonite was higher than that of zeolite and thus, the pore volume of the zeolite was smaller than that of bentonite. A study by Jiang et al. (2011) indicated that the performance of the adsorbents can be improved by increasing their surface areas. They alluded that the uptake of adsorbates such as hydrogen increases with high surface area (Jiang et al. 2011). The TGA and differential temperature

**Fig. 1** PXRD patterns of **a** zeolite and **b** bentonite

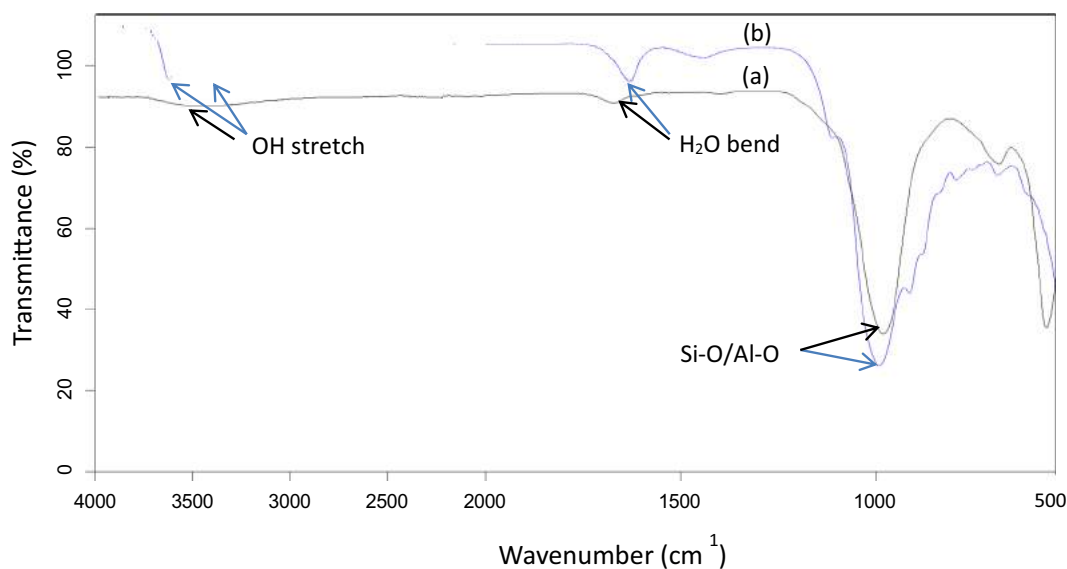


**Fig. 2** FTIR spectra of **a** zeolite and **b** bentonite

analysis (DTA) of the zeolite and bentonite were investigated to determine the thermal stability of the adsorbents. Results (Fig. 3) indicated that moisture loss started at  $\sim 40$  °C and continued until 294 °C and 150 °C for zeolite and bentonite, respectively. Beyond these temperatures, the weight can be attributed to the loss of water from hydration complexes (e.g.,  $\text{Ca}(\text{OH})_2^{2+}$ ). The % weight loss beyond 300 °C for both adsorbents can be attributed to dehydroxylation. The structural collapse of both adsorbents was observed beyond 870 °C indicating a change in the molecular framework. Thus, the adsorbents will be stable up to 870 °C and can be used in high temperature processes. The pH<sub>Hzc</sub> of zeolite and bentonite were found to be 6.47 and 7.68, respectively. The particle sizes of the zeolite and bentonite were found to be in the ranges 108–285  $\mu\text{m}$  and 54–210  $\mu\text{m}$  before adsorption, respectively; and 120–315  $\mu\text{m}$  and 85–281  $\mu\text{m}$  after adsorption, respectively. The increase in particle size after adsorption can be attributed to the occupation of binding sites by the REEs as well as swelling of the particles after hydration (Wang et al. 2012).

**Table 2** Textural properties of zeolite and bentonite

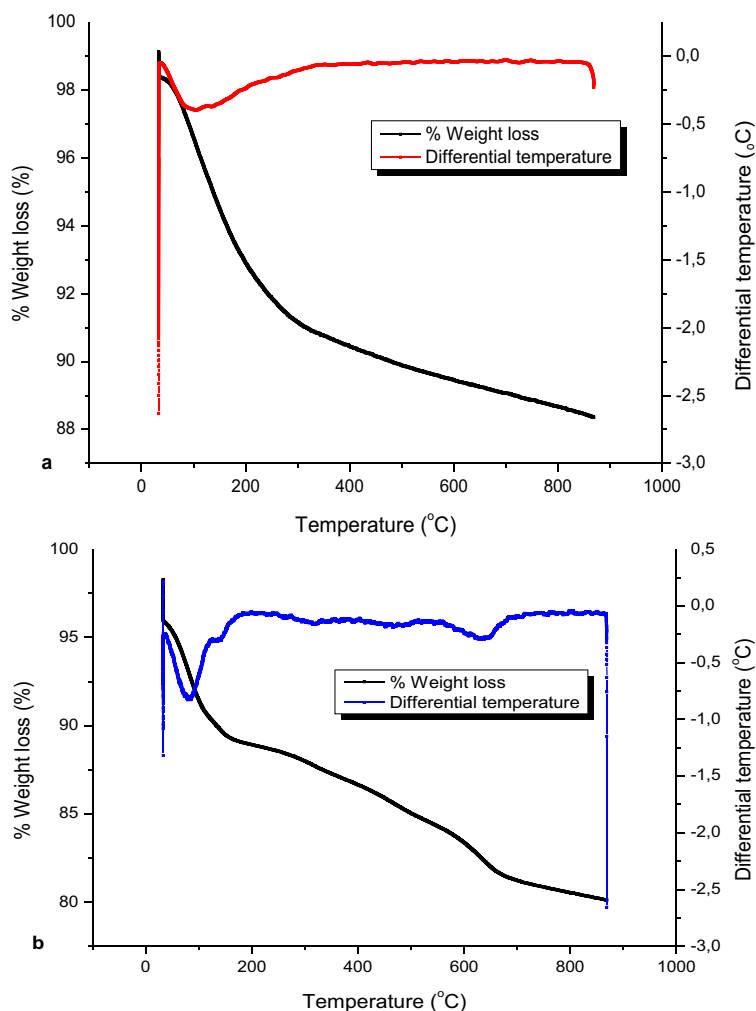
| Sample    | Pore size (nm) | Pore volume ( $\text{cm}^3 \text{g}^{-1}$ ) | Surface area ( $\text{m}^2 \text{g}^{-1}$ ) |
|-----------|----------------|---------------------------------------------|---------------------------------------------|
| Zeolite   | 12.97          | 0.052                                       | 16.28                                       |
| Bentonite | 10.38          | 0.054                                       | 21.29                                       |

## 3.2 Batch Adsorption Studies

### 3.2.1 Effect of Mass

The effect of mass on the adsorption of REEs at pH 3.2 and 6.2 for zeolite and bentonite, respectively, was investigated and the results are presented in Fig. 4 a and b. The adsorption capacities of all the elements were found to decrease with adsorbent dosage when either the zeolite or bentonite was used. However, the zeolite percentage efficiencies were significantly ( $p < 0.05$ ) different from those of bentonite. The adsorption efficiencies for 50 mg zeolite were between 45 and 61%. This increased to 88–93% when 100 mg dosage was used due to the higher amount of adsorption or active sites available. In contrast, the adsorption efficiencies for bentonite were  $> 98\%$  at all dosages. The highest adsorption capacity achieved with bentonite than with zeolite at all dosages can be attributed to the high surface area of bentonite and thus, high amount of active sites for adsorption (Jiang et al. 2011). The capability of bentonite to significantly adsorb elements with the lowest adsorbent mass can also be attributed to different active sites that have affinity for the elements. Thus, for maximum recovery of REEs in industrial wastewaters, 5 and 10  $\text{g L}^{-1}$  should be considered when using bentonite and zeolite, respectively. Thus, for subsequent experiments, 100 mg zeolite was used due to significant adsorption capacity and percentage efficiency, and 50 mg for bentonite. The ability of natural adsorbents to

**Fig. 3** TGA and DTA graphs of **a** zeolite and **b** bentonite



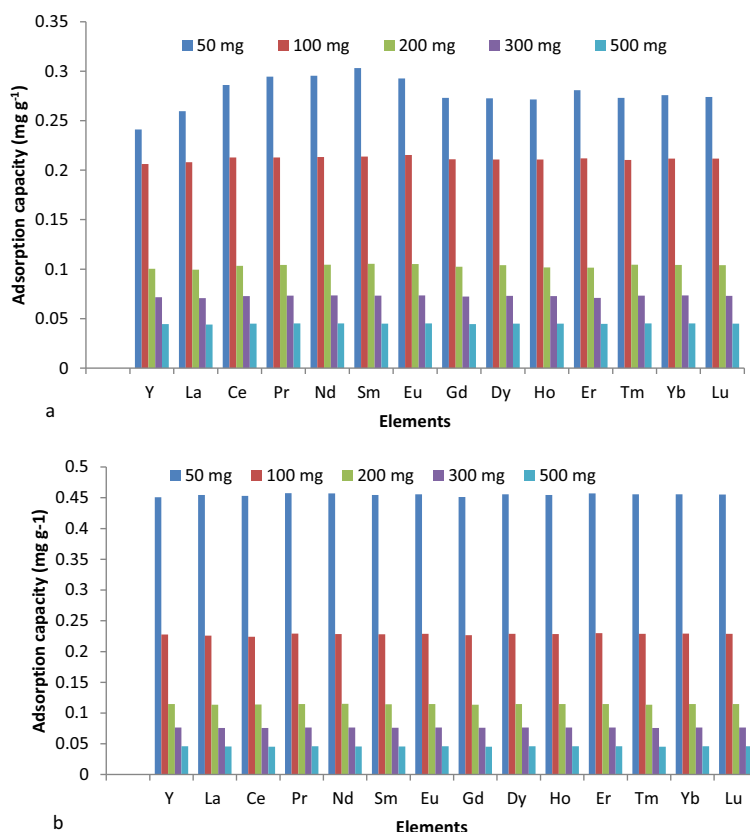
significantly remove REEs from aqueous solutions without any surface modification makes them highly suitable for REEs removal from wastewaters and very attractive due to a cheap process.

### 3.2.2 Effect of pH

The effect of pH on the adsorption REEs by zeolite and bentonite was studied and the results are shown in Fig. 5 a and b. The state of zeolite at highly acidic regions (pH 2–3) was not highly favourable for the adsorption of REEs since the adsorption capacity was low and the adsorption efficiency was 30% lower (Fig. 5a). Thus, the adsorption of the elements by zeolite was controlled by electrostatic interactions (Bakatula et al. 2015). In such highly acidic conditions, the active sites are protonated due to a high amount of hydronium ions ( $\text{H}_3\text{O}^+$ )

leading to a highly positive surface of the zeolite. The positive character of the zeolite decreased with increasing pH (Mosai et al. 2019). The adsorption capacity was observed to increase with pH but was not significantly changed beyond pH 6.2, and this can be attributed to the change in the surface charge of zeolite. The  $\text{pH}_{\text{pzc}}$  of the zeolite was found to be 6.47 and thus, around pH 6 the surface of the zeolite reaches the negative character which is highly favourable for the adsorption of REEs. Hence, the adsorption capacity increased with pH. Thus, when zeolite is used to remove REEs from wastewaters at highly acidic regions, the water should first be neutralised for maximum efficiency. The adsorption of the elements by bentonite showed a different trend (Fig. 5b). A low adsorption capacity was observed only at pH 2 and beyond that adsorption increased. The adsorption efficiency at pH 2 was ~16% less. There was no

**Fig. 4** The effect of dosage on the adsorption of REEs using **a** zeolite and **b** bentonite ( $n = 3$ ,  $RSD < 5\%$ ,  $\text{conc} = 2 \text{ mg L}^{-1}$ ,  $\text{temp} = 25^\circ\text{C}$ ,  $\text{time} = 3 \text{ h}$ ,  $\text{pH} 6.2$  for zeolite and  $\text{pH} 3.2$  for bentonite)



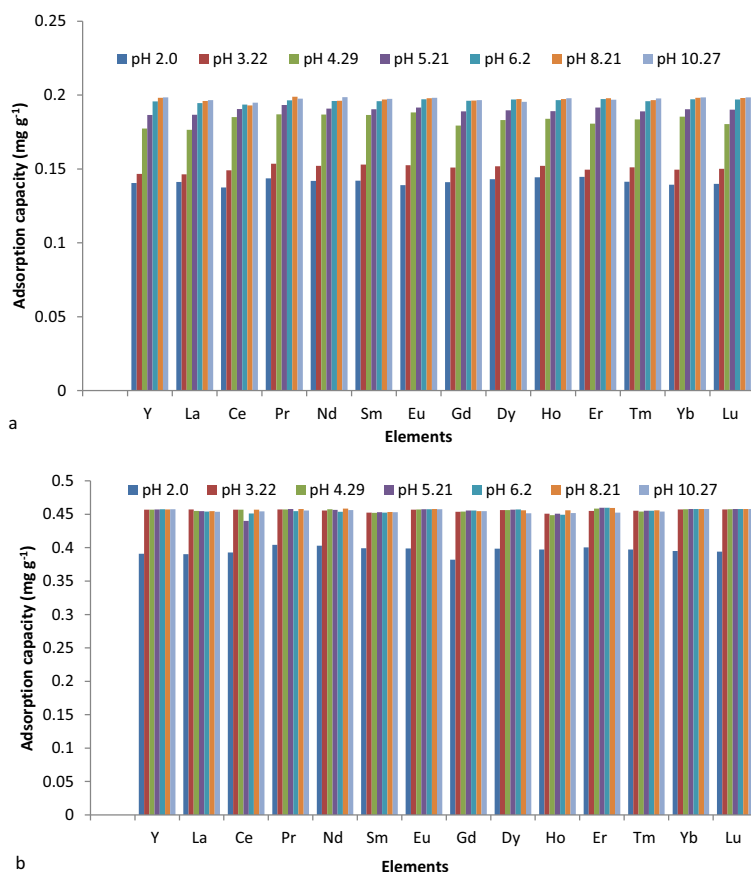
significant difference of the adsorption capacity at different pH values beyond pH 2 and this can be due to the fact that the adsorption of the elements was not driven so much by the adsorbent charge but, by the different active sites. Thus, bentonite can effectively remove REEs from wastewaters in acidic conditions. This makes bentonite a better adsorbent than zeolite in this case since it has a sustained adsorption capability in different conditions. For maximum recovery of REEs from industrial wastewaters with zeolite and bentonite, the pH of 6.2 and 3.2 should be used, respectively. These same pH values were used for subsequent experiments in this study.

### 3.2.3 Effect of Initial Concentration

The effect of initial concentration on the adsorption of REEs by zeolite and bentonite was studied as some studies have indicated that different initial concentrations can affect the adsorption capacity of elements (Bakatula et al. 2015; Mosai et al. 2018). The adsorption capacities of all elements increased with concentration for both zeolite and bentonite (Fig. 6a and b). However,

the adsorption capacity was not increased significantly when zeolite was used and this can be attributed to the limited adsorption sites. The limited sites meant that only a specific amount of the elements can be captured by the adsorbent, leading to a decrease in adsorption efficiency with concentration. Therefore, at higher concentrations, only small amounts of the elements could be removed from the solutions to occupy active sites. The adsorption efficiencies of REEs when zeolite was used were approximately 91, 96, 89, 40, and 20% at 0.5, 1.0, 2.0, 5.0, and 10 mg L<sup>-1</sup>. It is apparent here that zeolite will work best at very low concentrations. Since the amount of Fe and Al was low in the zeolite than in bentonite, they could be playing a major role on the adsorption of the elements under study. Some studies have indicated that some elements can interact with adsorbents through the adsorbent-Fe-element synergistic effect (Baak and Hornyak 1961; Mosai et al. 2018). The bentonite adsorption efficiencies were > 98% for all elements at all concentrations due to the availability of binding sites and high surface area (Bakatula et al. 2015). Thus, it is possible to effectively recover REEs at elevated concentrations using bentonite.

**Fig. 5** The effect of pH on the adsorption of REEs using **a** zeolite and **b** bentonite ( $n = 3$ ,  $RSD < 5\%$ ,  $\text{conc} = 2 \text{ mg L}^{-1}$ ,  $\text{temp} = 25^\circ\text{C}$ ,  $\text{time} = 3 \text{ h}$ ,  $\text{mass} = 100 \text{ mg}$  for zeolite and  $50 \text{ mg}$  for bentonite)



### 3.2.4 Adsorption Isotherms

The Langmuir, Freundlich, and Dubinin-Radushkevich adsorption isotherms were used to fit the initial concentration data and the results are shown in Tables 3 and 4 for zeolite and bentonite, respectively. The Freundlich and Dubinin-Radushkevich isotherms, both of which precisely fit data that corresponds to adsorption of elements on different active sites of the adsorbent, poorly described the adsorption data of all elements adsorbed by the zeolite. The adsorption energy ( $E_s$ ) as determined from the Dubinin-Radushkevich isotherm model indicated that the adsorption of the elements by zeolite was through chemical adsorption as the mean free energy of adsorption of the elements was between 18 and  $40 \text{ kJ mol}^{-1}$  (Table 3) (Mahmoud 2015; Ghasemi et al. 2016). The coefficient of determination ( $R^2$ ) values for zeolite indicated that the Langmuir isotherm fitted the concentration data better than other isotherm models as the values were  $> 0.96$  for all elements. This means that the adsorption of the elements onto zeolite was through

monolayer adsorption onto a homogenous surface (Ghasemi et al. 2016). The declining adsorption capacity with high concentration could be due to the limited active sites that are swiftly occupied.

The results from the isotherm adsorption models with bentonite were significantly different from those for zeolite (Table 4). The adsorption of most elements (Y, Pr, Nb, Eu, Dy, Ho, Yb, and Lu) was better described by Langmuir isotherm. However, the coefficients of determination for the Freundlich and Dubinin-Radushkevich isotherms were also significant for the same elements. This indicated that these elements could also be interacting with different active sites of bentonite. The  $E_s$  was between 8 and  $16 \text{ kJ mol}^{-1}$  for most elements, when bentonite was used, which signifies that the stronger chemical ion exchange interaction is highly plausible (Ghasemi et al. 2016; Mahmoud 2015). The results also indicated that the lower the mean free energy, the higher the adsorption capacity. The adsorption intensity ( $n$ ) for both adsorbents was  $> 1$ , indicating chemical adsorption (Njoku et al. 2014). The bentonite adsorption

**Fig. 6** The effect of concentration on the adsorption of REEs using (a) zeolite and (b) bentonite ( $n = 3$ ,  $RSD < 5\%$ ,  $\text{temp} = 25^\circ\text{C}$ ,  $\text{time} = 3\text{ h}$ ,  $\text{mass} = 100\text{ mg}$  for zeolite and  $50\text{ mg}$  for bentonite,  $\text{pH } 6.2$  for zeolite and  $\text{pH } 3.2$  for bentonite)

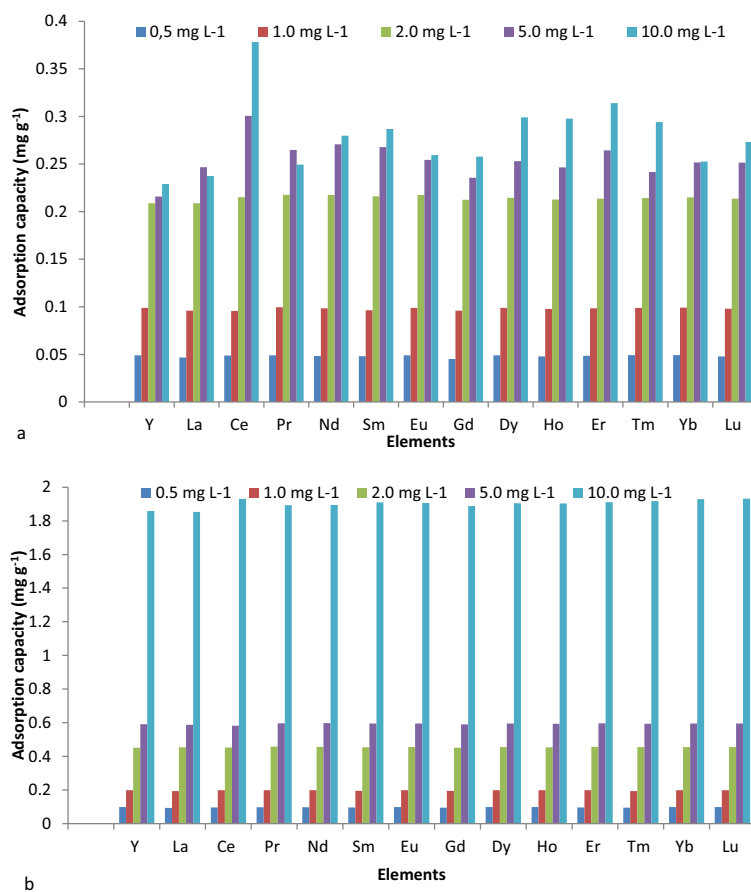


**Table 3** The Langmuir, Freundlich and Dubinin-Radushkevich adsorption isotherm data of REE adsorbed by zeolite

| Element | Langmuir                     |                               |       | Freundlich                                               |     |       | Dubinin-Radushkevich         |                                |       |
|---------|------------------------------|-------------------------------|-------|----------------------------------------------------------|-----|-------|------------------------------|--------------------------------|-------|
|         | $q_m$ ( $\text{mg g}^{-1}$ ) | $K_L$ ( $\text{L mol}^{-1}$ ) | $R^2$ | $K_F$ ( $(\text{mg g}^{-1})/(\text{mol L}^{-1})^{1/n}$ ) | $n$ | $R^2$ | $X_m$ ( $\text{mg g}^{-1}$ ) | $E_s$ ( $\text{kJ mol}^{-1}$ ) | $R^2$ |
| Y       | 0.09                         | $2.7 \times 10^5$             | 0.96  | 0.37                                                     | 9.9 | 0.16  | 0.22                         | 26.0                           | 0.20  |
| La      | 0.24                         | $3.7 \times 10^8$             | 0.97  | 2.76                                                     | 4.4 | 0.19  | 0.70                         | 18.5                           | 0.22  |
| Ce      | 0.22                         | $3.7 \times 10^8$             | 0.99  | 2.76                                                     | 4.3 | 0.80  | 0.69                         | 18.5                           | 0.85  |
| Pr      | 0.13                         | $6.7 \times 10^5$             | 0.97  | 0.71                                                     | 7.5 | 0.25  | 0.32                         | 23.9                           | 0.29  |
| Nb      | 0.14                         | $5.0 \times 10^5$             | 0.98  | 0.84                                                     | 6.5 | 0.41  | 0.35                         | 21.6                           | 0.46  |
| Sm      | 0.11                         | $5.8 \times 10^5$             | 0.98  | 0.47                                                     | 9.6 | 0.46  | 0.26                         | 27.0                           | 0.51  |
| Eu      | 0.11                         | $6.6 \times 10^5$             | 0.97  | 0.49                                                     | 8.7 | 0.32  | 0.24                         | 25.1                           | 0.36  |
| Gd      | 0.16                         | $1.1 \times 10^6$             | 0.98  | 0.80                                                     | 7.2 | 0.24  | 0.35                         | 23.7                           | 0.27  |
| Dy      | 0.15                         | $1.3 \times 10^6$             | 0.99  | 0.86                                                     | 6.7 | 0.55  | 0.36                         | 22.7                           | 0.59  |
| Ho      | 0.17                         | $1.5 \times 10^6$             | 0.99  | 1.1                                                      | 6.2 | 0.51  | 0.41                         | 22.0                           | 0.55  |
| Er      | 0.15                         | $1.2 \times 10^6$             | 0.99  | 0.72                                                     | 7.6 | 0.60  | 0.32                         | 24.4                           | 0.64  |
| Tm      | 0.10                         | $6.0 \times 10^5$             | 0.99  | 0.44                                                     | 9.9 | 0.54  | 0.25                         | 27.7                           | 0.59  |
| Yb      | 0.10                         | $6.1 \times 10^5$             | 0.97  | 0.44                                                     | 9.9 | 0.32  | 0.24                         | 27.8                           | 0.37  |
| Lu      | 0.12                         | $8.3 \times 10^5$             | 0.98  | 0.65                                                     | 7.8 | 0.39  | 0.30                         | 24.3                           | 0.43  |

**Table 4** The Langmuir, Freundlich and Dubinin-Radushkevich adsorption isotherm data of REE adsorbed by bentonite

| Element | Langmuir                    |                              |       | Freundlich                                                             |     |       | Dubinin-Radushkevich        |                               |       |
|---------|-----------------------------|------------------------------|-------|------------------------------------------------------------------------|-----|-------|-----------------------------|-------------------------------|-------|
|         | $q_m$ (mg g <sup>-1</sup> ) | $K_L$ (L mol <sup>-1</sup> ) | $R^2$ | $K_f$ ((mg g <sup>-1</sup> ) / (mol L <sup>-1</sup> ) <sup>1/n</sup> ) | $n$ | $R^2$ | $X_m$ (mg g <sup>-1</sup> ) | $E_s$ (kJ mol <sup>-1</sup> ) | $R^2$ |
| Y       | 1.07                        | $8.1 \times 10^5$            | 0.96  | 774                                                                    | 1.8 | 0.85  | 16.4                        | 12.5                          | 0.86  |
| La      | 1.49                        | $3.1 \times 10^5$            | 0.47  | 4791                                                                   | 1.5 | 0.63  | 46.6                        | 11.0                          | 0.64  |
| Ce      | 1.86                        | $4.5 \times 10^5$            | 0.39  | 7099                                                                   | 1.5 | 0.81  | 41.0                        | 11.6                          | 0.79  |
| Pr      | 1.11                        | $1.6 \times 10^5$            | 0.97  | 753                                                                    | 1.9 | 0.60  | 19.0                        | 12.9                          | 0.61  |
| Nb      | 1.12                        | $9.7 \times 10^5$            | 0.90  | 518                                                                    | 1.9 | 0.56  | 15.6                        | 12.9                          | 0.57  |
| Sm      | 1.58                        | $5.3 \times 10^5$            | 0.53  | 7421                                                                   | 1.4 | 0.60  | 59.5                        | 11.2                          | 0.61  |
| Eu      | 1.14                        | $1.6 \times 10^6$            | 0.95  | 2801                                                                   | 1.6 | 0.77  | 36.1                        | 12.1                          | 0.79  |
| Gd      | 1.70                        | $3.6 \times 10^5$            | 0.48  | 24736                                                                  | 1.3 | 0.72  | 110                         | 10.4                          | 0.74  |
| Dy      | 1.11                        | $2.3 \times 10^6$            | 0.98  | 1957                                                                   | 1.7 | 0.81  | 28.8                        | 22.5                          | 0.84  |
| Ho      | 1.12                        | $1.8 \times 10^6$            | 0.96  | 2044                                                                   | 1.7 | 0.79  | 28.2                        | 12.5                          | 0.83  |
| Er      | 1.3                         | $1.2 \times 10^6$            | 0.67  | 1358                                                                   | 1.8 | 0.55  | 24.2                        | 12.7                          | 0.56  |
| Tm      | 2.87                        | $2.2 \times 10^5$            | 0.31  | 90378                                                                  | 1.2 | 0.83  | 209                         | 9.9                           | 0.83  |
| Yb      | 1.2                         | $2.1 \times 10^6$            | 0.98  | 5172                                                                   | 1.6 | 0.90  | 47.3                        | 12.1                          | 0.92  |
| Lu      | 1.3                         | $1.5 \times 10^6$            | 0.92  | 8414                                                                   | 1.5 | 0.88  | 60.8                        | 11.7                          | 0.89  |

capacities ( $X_m$ ) of the elements determined from the Dubinin-Radushkevich isotherm model were higher than those of zeolite due to a higher amount of active sites. Moreover, the bentonite maximum adsorption capacities ( $q_m$ ) of the elements determined from the Langmuir isotherm were > 10 times better than those of zeolite; hence, the observed trends between the two adsorbents. The separation factor ( $R_L$ ) values of bentonite and zeolite were between 0 and 1 for all elements, indicating that adsorption was favourable.

### 3.2.5 The Effect of Contact Time

The effect of contact time on the adsorption of REEs by zeolite and bentonite was determined and the results are presented in Fig. 7. The maximum adsorption of the elements was reached within 1 h of contact with the zeolite (Fig. 7a). Equilibrium was reached beyond this time as observed in the constant adsorption capacity. The phase where the adsorption capacity is increasing with time can be attributed to the availability of binding sites which decrease with time. The extent of adsorption of the elements was different. The adsorption of all the elements was faster (within 5 min) when in contact with bentonite than with zeolite due to high availability of active sites. From the results, adsorption of the elements for

zeolite and bentonite was in the order: La > Y > Lu > Gd > Eu > Er > Sm > Pr > Tm > Yb > Ho > Ce > Nd > Dy > Sc.

The pseudo first- and second-order adsorption kinetics were used to determine the adsorption controlling mechanisms of the elements onto zeolite or bentonite and the results are presented in Tables 5 and 6 for zeolite and bentonite, respectively. The kinetic data for both adsorbents were best described by pseudo second-order as observed from the coefficients of determination ( $R^2$ ) that were > 0.99 for all the elements. Consequently, the experimental adsorption capacity ( $q_{e(\text{exp})}$ ) was close to the calculated adsorption capacity ( $q_{e(\text{cal})}$ ) for the pseudo second-order model for all elements adsorbed by either adsorbent. The pseudo first-order  $R^2$  values of the elements adsorbed by zeolite were higher than those adsorbed by bentonite and this could mean that though they were all described by pseudo second-order, the extent of adsorption may be different. This can be substantiated by the zeolite pseudo first-order rate constants and adsorption capacity ( $q_e$ ) of the elements which were higher than those of bentonite. Moreover, the bentonite pseudo second-order rate constants of the elements were more than ten times higher than those of zeolite, indicating favourable adsorption with bentonite than with zeolite. This means that a small amount of bentonite would effectively remove high concentrations of the

**Fig. 7** The effect of contact time on the adsorption of REEs using **a** zeolite and **b** bentonite ( $n = 3$ ,  $RSD < 5\%$ ,  $temp = 25\text{ }^{\circ}\text{C}$ ,  $conc = 2\text{ mg L}^{-1}$ ,  $mass = 100\text{ mg}$  for zeolite and  $50\text{ mg}$  for bentonite,  $pH\ 6.2$  for zeolite and  $pH\ 3.2$  for bentonite)

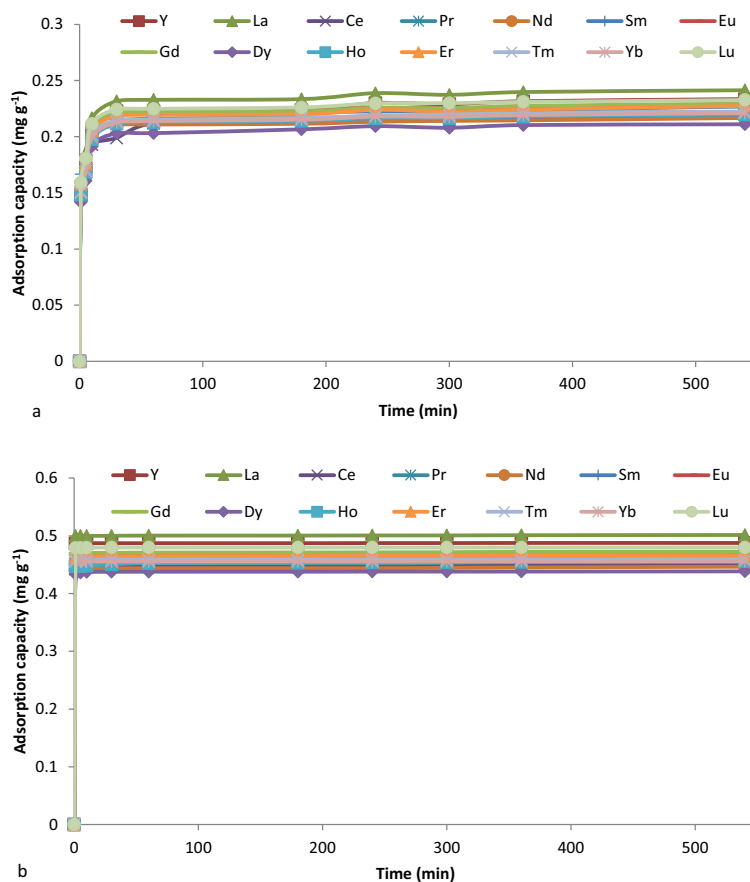


**Table 5** Adsorption kinetics of REEs adsorbed by zeolite

| Metal | Pseudo first-order                     |                                              |                                        |       | Pseudo-second order                             |                                        |       |
|-------|----------------------------------------|----------------------------------------------|----------------------------------------|-------|-------------------------------------------------|----------------------------------------|-------|
|       | $q_{e(exp)}\text{ (mg g}^{-1}\text{)}$ | $k_1\text{ (min}^{-1}\text{)} \cdot 10^{-3}$ | $q_{e(cal)}\text{ (mg g}^{-1}\text{)}$ | $R^2$ | $k_2\text{ (g mg}^{-1}\text{ min}^{-1}\text{)}$ | $q_{e(cal)}\text{ (mg g}^{-1}\text{)}$ | $R^2$ |
| Y     | 0.38                                   | 5.80                                         | 0.13                                   | 0.50  | 1.56                                            | 0.46                                   | 0.99  |
| La    | 0.40                                   | 5.80                                         | 0.12                                   | 0.48  | 1.84                                            | 0.47                                   | 0.99  |
| Ce    | 0.36                                   | 6.77                                         | 0.11                                   | 0.56  | 1.78                                            | 0.43                                   | 0.99  |
| Pr    | 0.37                                   | 6.18                                         | 0.090                                  | 0.44  | 3.54                                            | 0.44                                   | 0.99  |
| Nb    | 0.36                                   | 6.26                                         | 0.090                                  | 0.45  | 2.71                                            | 0.43                                   | 0.99  |
| Sm    | 0.38                                   | 6.16                                         | 0.090                                  | 0.45  | 3.01                                            | 0.45                                   | 0.99  |
| Eu    | 0.38                                   | 6.79                                         | 0.087                                  | 0.47  | 2.77                                            | 0.45                                   | 0.99  |
| Gd    | 0.38                                   | 5.84                                         | 0.011                                  | 0.45  | 2.42                                            | 0.45                                   | 0.99  |
| Dy    | 0.35                                   | 6.14                                         | 0.011                                  | 0.50  | 2.17                                            | 0.42                                   | 0.99  |
| Ho    | 0.36                                   | 6.10                                         | 0.11                                   | 0.48  | 2.21                                            | 0.43                                   | 0.99  |
| Er    | 0.38                                   | 6.68                                         | 0.096                                  | 0.49  | 2.11                                            | 0.45                                   | 0.99  |
| Tm    | 0.37                                   | 6.02                                         | 0.11                                   | 0.48  | 2.12                                            | 0.44                                   | 0.99  |
| Yb    | 0.37                                   | 6.41                                         | 0.10                                   | 0.49  | 2.15                                            | 0.44                                   | 0.99  |
| Lu    | 0.39                                   | 6.44                                         | 0.11                                   | 0.50  | 1.95                                            | 0.46                                   | 0.99  |

**Table 6** Adsorption kinetics of REEs adsorbed by bentonite

| Metal | Pseudo first-order                        |                                             |                                           |       | Pseudo-second order                           |                                           |       |
|-------|-------------------------------------------|---------------------------------------------|-------------------------------------------|-------|-----------------------------------------------|-------------------------------------------|-------|
|       | $q_{e(\text{exp})}$ (mg g <sup>-1</sup> ) | $k_1$ (min <sup>-1</sup> ) 10 <sup>-3</sup> | $q_{e(\text{cal})}$ (mg g <sup>-1</sup> ) | $R^2$ | $k_2$ (g mg <sup>-1</sup> min <sup>-1</sup> ) | $q_{e(\text{cal})}$ (mg g <sup>-1</sup> ) | $R^2$ |
| Y     | 0.44                                      | 4.73                                        | 0.008                                     | 0.11  | 162                                           | 0.49                                      | 0.99  |
| La    | 0.45                                      | 4.20                                        | 0.014                                     | 0.11  | 98.4                                          | 0.50                                      | 0.99  |
| Ce    | 0.40                                      | 6.20                                        | 0.014                                     | 0.22  | 23.9                                          | 0.45                                      | 0.99  |
| Pr    | 0.41                                      | 5.70                                        | 0.009                                     | 0.15  | 36.0                                          | 0.45                                      | 0.99  |
| Nb    | 0.40                                      | 5.27                                        | 0.011                                     | 0.15  | 56.4                                          | 0.44                                      | 0.99  |
| Sm    | 0.41                                      | 0.11                                        | 0.69                                      | 0.14  | 48.1                                          | 0.46                                      | 0.99  |
| Eu    | 0.42                                      | 4.64                                        | 0.007                                     | 0.096 | 3126                                          | 0.47                                      | 0.99  |
| Gd    | 0.42                                      | 4.41                                        | 0.016                                     | 0.13  | 49.8                                          | 0.47                                      | 0.99  |
| Dy    | 0.39                                      | 5.25                                        | 0.011                                     | 0.15  | 98.1                                          | 0.44                                      | 0.99  |
| Ho    | 0.41                                      | 6.40                                        | 0.018                                     | 0.26  | 18.3                                          | 0.45                                      | 0.99  |
| Er    | 0.42                                      | 11.2                                        | 0.003                                     | 0.31  | 83.7                                          | 0.46                                      | 0.99  |
| Tm    | 0.46                                      | 4.07                                        | 0.012                                     | 0.10  | 221.6                                         | 0.46                                      | 0.99  |
| Yb    | 0.41                                      | 4.84                                        | 0.007                                     | 0.10  | 1234                                          | 0.46                                      | 0.99  |
| Lu    | 0.43                                      | 4.95                                        | 0.007                                     | 0.11  | 963.8                                         | 0.48                                      | 0.99  |

elements from aqueous solutions as observed previously. In other words, the amount of active sites on bentonite exceeds those of zeolite for the same mass of adsorbent.

### 3.2.6 Effect of Competing Ions

The adsorption of REEs in the presence of Fe, Co, Ni, Ca, Mg, K, and Zn was studied and the results are shown

**Fig. 8** The adsorption of REEs using **a** zeolite and **b** bentonite in the presence of competing ions (Fe, Co, Ni, Ca, Mg, K, and Zn) ( $n = 3$ , RSD < 5%, temp = 25 °C, time = 3 h, mass = 100 mg for zeolite and 50 mg for bentonite, pH 6.2 for zeolite and pH 3.2 for bentonite)

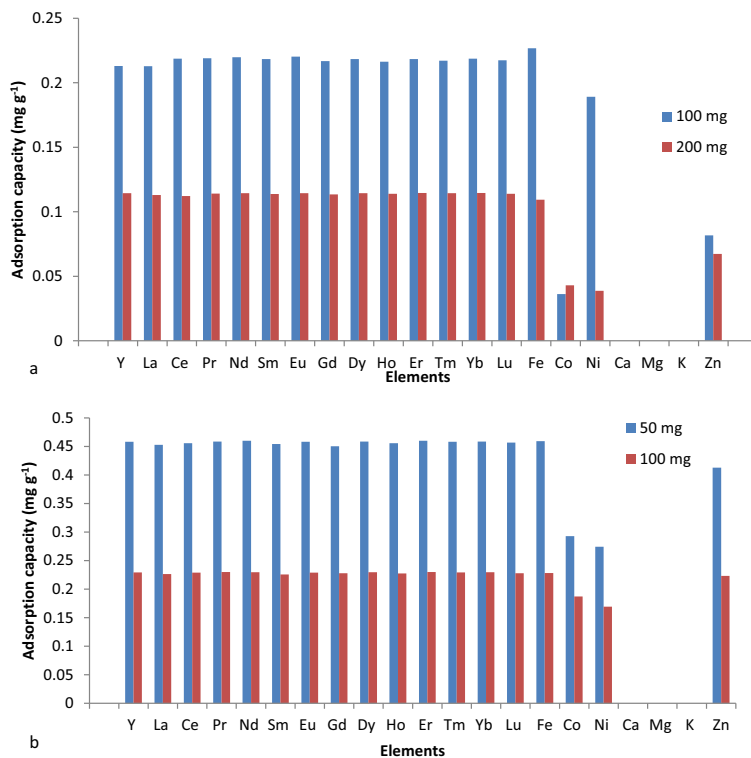
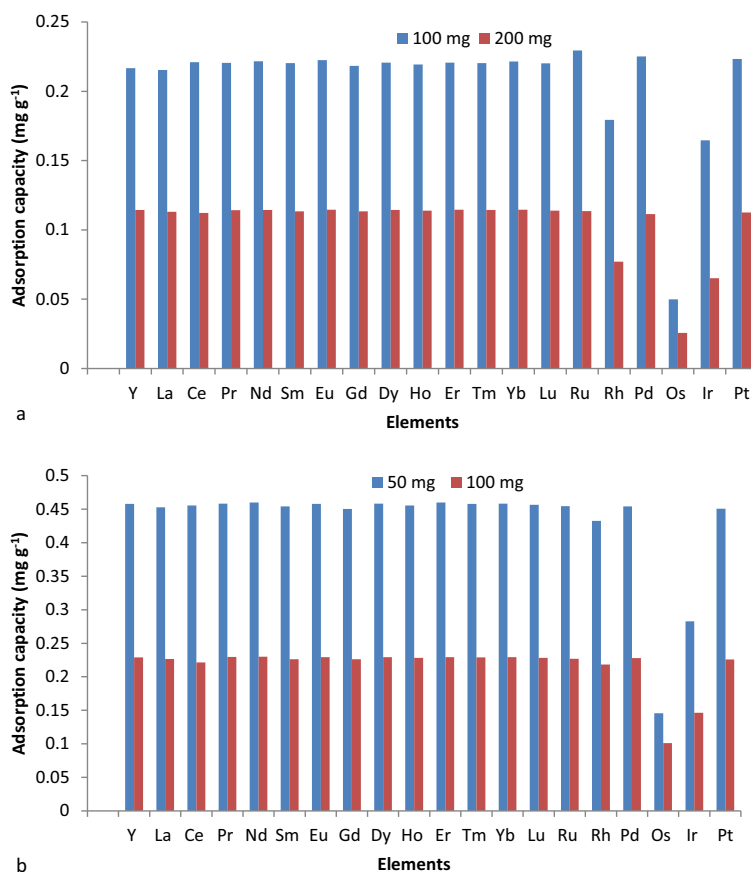


**Fig. 9** The adsorption of REEs using **a** zeolite and **b** bentonite in the presence of competing ions (Ru, Rh, Pd, Os, Ir, and Pt) ( $n = 3$ , RSD < 5%, temp = 25 °C, time = 3 h, mass = 100 mg for zeolite and 50 mg for bentonite, pH 6.2 for zeolite and pH 3.2 for bentonite)



in Fig. 8a and b. Both adsorbents maintained notable adsorption of all REEs in the presence of competing elements. The ability of zeolite to effectively adsorb Fe and Ni even though the adsorption sites were limited can be attributed to the ability of these elements to be adsorbed in a different mechanism from the REEs. A study by Qui et al. (2015) indicated that Fe was occupied in the interior of montmorillonite, making it possible to embed it in the pores of zeolite. The low adsorption capacity of elements such as Co and Zn appears to be dependent on the pH as some studies have indicated that their adsorption is prevalent at pH > 4 (Abollino et al. 2003; do Carmo Ramos et al. 2016). Other elements (Ca, Mg, and K) were not adsorbed by the adsorbents; but their concentrations were more than the initial used meaning that some were actually being detached from the adsorbents as they are constituents.

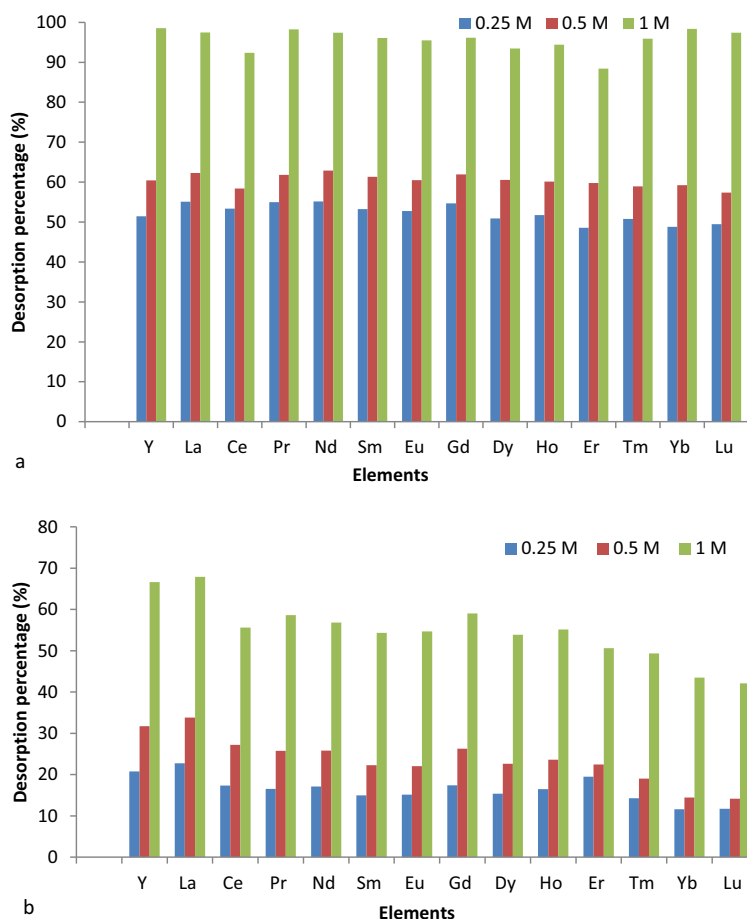
The REEs were also combined with platinum group elements (PGEs) (Ru, Rh, Pd, Os, Ir, and Pt) as their co-existence has been highlighted in some studies (Bechtel et al. 2001; Gutiérrez-Gutiérrez et al. 2015). Again, the adsorption of REEs was not affected by the presence of

PGEs (Fig. 9a and b). Rather, the PGEs were found to be strongly co-adsorbed by both adsorbents. The adsorption of PGEs in the absence of REEs (results not shown) was done and the results indicated that the adsorbents had no affinity for the elements. Thus, PGEs could be adsorbed through a synergistic effect on the surface. This would likely be a bridge-type of adsorption: adsorbent-REE-PGE. A study by Bakatula et al. (2014) showed this phenomenon with Fe acting as a bridge between the adsorbent and the generally non-adsorbing elements. For all the elements, the higher adsorbent mass used the lower the adsorption capacity. Moreover, the bentonite adsorption capacities of the REEs when 100 mg was used were approximately twice as much of the zeolite and thus, bentonite has more active sites than the zeolite counterpart.

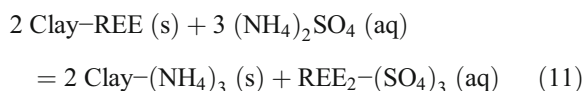
### 3.2.7 Desorption of REEs

The desorption of REEs from zeolite and bentonite using ammonium sulphate was studied and the results are shown in Fig. 10a and b. The elements were

**Fig. 10** The desorption of REEs for zeolite **a** and bentonite **b** using ammonium sulphate at different concentrations ( $n = 3$ ,  $RSD < 5\%$ , temp = 25 °C, time = 3 h, mass = 100 mg for zeolite and 50 mg for bentonite, pH 6.2 for zeolite and pH 3.2 for bentonite)

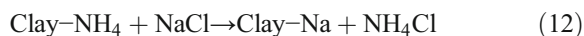


significantly desorbed from zeolite and the desorption increased with the concentration of ammonium sulphate. The desorption of REEs was in the range 48.6–55.2%, 57.3–62.9%, and 88.4–98.5% at 0.25, 0.5 and 1.0 M ammonium sulphate, respectively. Thus, 1.0 M would be best for maximum recovery of REEs from zeolite. Similar results were observed with bentonite, but the desorption percentages were lower. The percentage desorption of the elements from bentonite was in the range 11.6–22.7%, 14.2–33.8%, and 42.1–67.9% at 0.25, 0.5, and 1.0 M ammonium sulphate. The lesser extent of desorption can be attributed to the strong interactions of the elements with bentonite and implies that the desorbing solution has to be applied a few times more for complete desorption. The solutions containing the recovered REEs can then be further treated to recover the elements. The desorbed adsorbents can be reused for further recovery of the REEs from wastewaters. The desorption occurred through ion exchange according to the following equation:



where clay represents zeolite or bentonite in this case,  $s$  is the solid phase and  $aq$  is the aqueous phase (Yanfei et al. 2015). Thus, REEs in sulphate form can be removed from the ammonium-modified zeolite. Owing to the strong adsorption of ammonium to zeolite, the resulting aqueous solution will have a very small concentration of ammonium, making any further treatment of the REE-sulphate solutions to remove ammonium unnecessary. The desorption of REEs is proportional to increasing concentrations of ammonium sulphate. Thus, at low concentrations the ammonium ions are not enough for efficient ion exchange. A study by Bakatula et al. (2015) indicated that uranium can be effectively removed from aqueous solutions using ammonium-modified zeolite. This would make it possible to use the ammonium-modified zeolite from REE

recovery to recover other elements such as uranium in other wastewaters. The adsorbents can also be freed from the ammonium through exposure to NaCl according to the following reaction (Widiastuti et al. 2011):



The Na-rich zeolite and bentonite can be used to recover more REEs from aqueous solutions, providing a cyclic process of recovery and reuse.

#### 4 Conclusion

The recovery of REEs by natural zeolite and bentonite was studied. The characterisation of the adsorbents with X-ray fluorescence (XRF) indicated that silica ( $\text{SiO}_2$ ) and alumina ( $\text{Al}_2\text{O}_3$ ) were dominant on both adsorbents with bentonite having a higher amount of alumina than zeolite. The zeolite adsorption capacities and efficiencies of the elements were generally lower than those of bentonite and this was attributed to the superior surface area (and active sites) and alumina content of the latter. This made it possible to use a lower dosage of bentonite ( $5 \text{ g L}^{-1}$ ) than zeolite ( $10 \text{ g L}^{-1}$ ) for metal recovery. Zeolite was found to be effective at higher solution pH whilst bentonite was effective at both low and high solution pH. The effect of contact time indicated that 30 min and 1 min were enough to reach equilibrium for zeolite and bentonite, respectively. Therefore the adsorbents do not have to be in contact with wastewaters for too long and this is good for a sufficient process. The ability to effectively remove REEs in the presence of competing ions (Fe, Co, Ni, Ca, Mg, K, Zn, and PGEs (Ru, Rh, Pd, Os, Ir, and Pt)) makes zeolite and bentonite excellent potential adsorbents for REE-containing wastewaters. It was quite easy to desorb REEs from zeolite than bentonite with the latter requiring higher concentrations of ammonium sulphate. Natural zeolite and bentonite are potential cost-effective adsorbents for the recovery of REEs from industrial wastewaters, with bentonite offering more advantageous properties. The optimal conditions and parameters established in this study provide a platform for conducting column-based studies in the future to assess the practical applicability of these adsorbents.

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**SECTION 4.4:**  
**RECOVERY OF**  
**PRECIOUS**  
**ELEMENTS USING**  
**FLOW-THROUGH**  
**COLUMN STUDIES**

# PAPER I

**This paper included both batch and flow-through column adsorption studies for the recovery of Pt(IV) from aqueous solutions by APDEMS-functionalised zeolite.**

**The paper is published in Environment, Development and Sustainability.**

**Impact Factor: 2.121.**

**Contribution:** lead author, conducted experimental work and data modelling, conceptualization, methodology, software validation, formal analysis, investigation, writing - original draft and visualization.



# Batch and flow-through column adsorption study: recovery of Pt<sup>4+</sup> from aqueous solutions by 3-aminopropyl(diethoxy)methylsilane functionalised zeolite (APDEMSFZ)

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## Abstract

The recovery of platinum from waste is of high importance since significant concentrations are lost during processing, but the current methods are not economically effective. The removal of Pt<sup>4+</sup> from aqueous solutions at different conditions using zeolite functionalised with 3-aminopropyl(diethoxy)methylsilane (APDEMS) was investigated. The adsorbent was used to assess the effect of adsorbent mass, pH, concentration, time and competing ions on the removal of Pt<sup>4+</sup> so that optimum working conditions could be determined. The two- and three-parameter isotherm models as well as kinetic models were fitted using the experimental data. Effect of adsorbent bed height (2 and 5 cm), pH (2–7) and initial concentration (2 and 5 mg L<sup>-1</sup>) was determined with column experiments. Significant adsorption capacity was achieved with 100 mg adsorbent at pH 2, within 180 min. Adsorption capacity of Pt<sup>4+</sup> significantly decreased at pH > 2. Higher bed depth increased the exhaustion and breakthrough times. The adsorption capacity of Pt<sup>4+</sup> increased as bed height and concentration increased. The highest breakthrough and exhaustion times were achieved at pH 2. Strong Pt<sup>4+</sup>-adsorbent interaction concluded from the experiments, adsorption kinetics and isotherms models indicates that APDEMSFZ is suitable for Pt<sup>4+</sup> recovery from mining wastewater.

**Keywords** Platinum<sup>4+</sup> · Adsorption capacity · Recovery · Column · Adsorption models

## 1 Introduction

Platinum which is one of the platinum group elements (PGEs) is a very important precious element which is used in different industries such as automobiles where it acts as a catalytic converter, jewellery, chemical, electrical and medical where it is used in chemotherapy in forms such as cisplatin and carboplatin (Chassari et al. 2005; Han and Kim 2006). Statista (2017) indicated that in the year 2017, most of the platinum was used in jewellery (28.37%)

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and autocatalyst (41.9%). Johnson Matthey, (2016) also indicated that the consumption of platinum due to automobiles was very strong in 2015. Moreover, most of the platinum was mined in 2017 worldwide and this is due to the demand (Statista 2017). Thus, the demand for platinum worldwide is high and has been increasing over the years. This demand led to more platinum supplies which meant that more platinum was mined (Alonso et al. 2009; Johnson Matthey 2016). The production of platinum goes along with a large amount of waste discharged from the mining plants into the environment (Lottermoser 2003). Therefore, a number of waste streams exist due to platinum mining and may contain significant concentrations of platinum and other PGEs which would add value to mining industries when recovered (Xiao and Laplante 2004; Wang et al. 2017). The economy of many countries where platinum is widely used and produced can be improved through the recovery of this element from waste which includes mine tailings, slag, electronic and waste catalysts (Wang et al. 2017). This is particularly important since the mineral stocks have been decreasing with years (Ramesh et al. 2008).

The adsorption method has been found to be more effective economically, as it is simple in design, cheap and highly efficient (Hua et al. 2012; Ramesh et al. 2008; Sountharajah et al. 2017). The adsorption process has been used to remove precious elements from solutions because of its ability to capture very low concentrations. Low-cost adsorbents such as bentonite (Cantuaria et al. 2016), zeolite (Bakatula et al. 2015), chitosan (Roosen et al. 2016) and activated carbon (Karnib et al. 2014) have been used to remove elements from solutions. Research has shown that the modification or functionalisation of these adsorbents can increase their selectivity and adsorption capabilities (Bakatula et al. 2015; Kyzas and Bikiaris 2015; Ren et al. 2016).

Zeolites are clay minerals which are widely available in nature. There are different types of zeolites out of which, clinoptilolite is the most abundant (Can et al. 2010). Zeolite contains tetrahedral silica ( $\text{SiO}_4^{4-}$ ) and tetrahedral alumina ( $\text{AlO}_4^{4-}$ ) which are linked by oxygen atoms and arranged in a three-dimensional lattice (Huang et al. 2014). The substitution of  $\text{Si}^{4+}$  by  $\text{Al}^{3+}$  or with other elements such as  $\text{Mg}^{2+}$  leads to the negative character of zeolites (Malamis and Katsou 2013; Wen et al. 2016).

The 3-aminopropyl(diethoxy)methylsilane (APDEMS) was used to functionalise zeolite so that  $\text{Pt}^{4+}$  can be recovered from aqueous solutions. Since zeolite was found to poorly attract  $\text{Pt}^{4+}$  (adsorption efficiency  $< 0.5\%$ ), APDEMS was chosen as a ligand because it contains an amine group which has been found to interact strongly with platinum (Gorle et al. 2019). Moreover, the silane group on APDEMS will make it easy and possible for APDEMS to attach to zeolite. Batch and column experiments were used in this study. The batch studies are an extension of a conference paper (Mosai et al. 2018).

## 2 Materials and methods

### 2.1 Chemicals and reagents

Analytical grade reagents purchased from Sigma-Aldrich, South Africa, were used. 10 mg  $\text{L}^{-1}$  stock solution of  $\text{Pt}^{4+}$  was prepared from the standard solution and deionised water. The stock solution was used to prepare working solutions, and the pH was adjusted using 0.01 mol  $\text{L}^{-1}$  HCl and NaOH. The 3-aminopropyl(diethoxy)methylsilane (97%) (MW: 191.34 g  $\text{mol}^{-1}$ ) with a boiling point between 85 and 88 °C was used.

The raw zeolite was purchased from Sigma-Aldrich, (Steinheim, Germany).

## 2.2 Instrumentation

Monowave 450 (Anton Paar, South Africa) was used to react zeolite and 3-aminopropyl(diethoxy)methylsilane. Deionised water used was prepared with Millipore (Massachusetts, USA). Mettler Toledo pH metre (Columbus, USA) was used to determine pH. Masterflex peristaltic pump was used to add the solutions in the columns and to control the flow rate (Cole-Palmer, USA). The  $\text{Pt}^{4+}$  aqueous solutions were brought to equilibrium with elliptical benchtop shaker (Labcon, South Africa). The samples were analysed with inductively coupled plasma optical emission spectroscopy (ICP-OES) from Spector Genesis, Germany. The mineralogy and chemical composition of zeolite was determined using powder X-ray diffraction (PXRD) D2 Phaser (Bruker, Germany) and X-ray fluorescence (XRF) (PAnalytical, Netherlands), respectively. Fourier transform infrared (FTIR) spectra of the raw and functionalised zeolite were obtained using FTIR spectrometer (Tensor 27, Bruker, Germany) with mid-IR source ( $4000\text{--}400\text{ cm}^{-1}$ ). The amount of C, H and N was determined with varioELcube V4.0.13 (Elementar, Germany). Textural properties of zeolite were determined with Micromeritics Flow Prep 060 instrument (Aachen, Germany), and Brunauer–Emmett–Teller isotherm (BET) was used for specific surface area of the adsorbent.

## 2.3 Functionalisation

The raw zeolite (5 g) was added to 10 mL of 3-aminopropyl(diethoxy)methylsilane (APDEMS) in a glass vial and reacted for 30 min at  $180\text{ }^{\circ}\text{C}$ . The contents were cooled to  $\pm 25\text{ }^{\circ}\text{C}$  and filtered before washing with ethanol. The functionalised zeolite was at  $100\text{ }^{\circ}\text{C}$  for 24 h. The APDEMS was chosen as it contains nitrogen groups which have been found to react with platinum (Ramesh et al. 2008). The negative character of zeolite allows for the chemical adsorption of the silicon in APDEMS.

## 2.4 Batch adsorption studies

The batch adsorption experiments were carried out by placing APDEMS-functionalised zeolite (APDEMSFZ) and 10 mL  $\text{Pt}^{4+}$  solution at various conditions in 50 mL polypropylene containers. The contents were reacted through shaking with an elliptical benchtop shaker at room temperature and filtered. The concentrations of the elements at equilibrium were determined using ICP-OES.

Effect of adsorbent dosage (50–500 mg in 10 mL  $\text{Pt}^{4+}$  solution at pH 2) on the removal of  $\text{Pt}^{4+}$  using APDEMSFZ was determined at  $25\text{ }^{\circ}\text{C}$  since studies have indicated that the uptake of elements can be influenced by the amount of the adsorbent used (Mosai et al. 2019). The pH of a solution has been found to play an important role on the adsorption of elements as some elements have been found to be significantly recovered at low solution pH whilst others at high solution pH; hence, the influence of pH (2–9) on the recovery of  $\text{Pt}^{4+}$  was investigated (Li et al. 2018). The initial concentration of  $\text{Pt}^{4+}$  ( $0.5\text{--}5\text{ mg L}^{-1}$ ) was also investigated because some adsorbents can operate well only at high analyte concentrations; therefore, the optimum concentration for the adsorption  $\text{Pt}^{4+}$  by APDEMSFZ had to be known because platinum is in low concentrations in real wastewater solutions (Huang et al. 2018; Mosai et al. 2019). The time required to get the maximum adsorption capacity of  $\text{Pt}^{4+}$  onto the APDEMSFZ was assessed using the contact time study (Lu et al. 2017). The effect of temperature ( $15\text{ to }60\text{ }^{\circ}\text{C}$ ) on the adsorption of  $\text{Pt}^{4+}$  was determined. Since

platinum exists with a host of other elements in real wastewater solutions, a mixture of competing ions (rhodium, palladium, iridium, ruthenium, osmium, iron, calcium, magnesium, potassium, cobalt, nickel, hafnium, zinc and gold) was prepared together with  $\text{Pt}^{4+}$  and exposed to APDEMSFZ to determine the selectivity for the analyte in the mixture of elements.

## 2.5 Data treatment

The amount adsorbed per unit mass,  $q_e$  ( $\text{mg g}^{-1}$ ), was calculated using Eq. 1, and the efficiency was determined with Eq. 2.

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (1)$$

$$\text{Adsorption efficiency} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

where  $C_0$  and  $C_e$  are starting and equilibrium concentrations of elements, respectively,  $V$  (L) is the volume of the  $\text{Pt}^{4+}$  solution used, and  $M$  (g) represents the adsorbent mass.

## 2.6 Adsorption isotherms

The two (Langmuir, Freundlich and Dubinin–Radushkevich (D–R) and Temkin) and three (Sips, Redlich–Peterson and Toth) parameter isotherm models were used to determine the relationship between  $\text{Pt}^{4+}$  and APDEMSFZ. Langmuir isotherm describes the monolayer adsorption between adsorbents and elements (Mushtaq et al. 2016). The reversible interaction between adsorbents and adsorbates on a heterogeneous surface with the possibility of multilayer adsorption can be described by Freundlich isotherm (Chen 2015; Mushtaq et al. 2016). The D–R adsorption isotherm which expresses the adsorption mechanism with Gaussian energy distribution was also used (Chen 2015). Temkin isotherm assumes that there is a linear decrease in the heat of adsorption with coverage which is a result of adsorbent-adsorbate interaction and there is uniform distribution of adsorption energies (Chieng et al. 2015). The Langmuir, Freundlich, D–R adsorption and Temkin isotherm models can be expressed as, respectively:

$$\frac{C_e}{q_e} = \left( \frac{1}{q_m} \right) C_e + \left( \frac{1}{K_L q_m} \right) \quad (3)$$

$$q_e = K_F C_e^{\frac{1}{n}} \quad (4)$$

$$\ln q_e = \ln X_m - K_{\text{ad}} \epsilon^2 \quad (5)$$

$$q_e = \frac{RT}{b_T} \ln K_T C_e \quad (6)$$

where  $q_m$  ( $\text{mg g}^{-1}$ ) is the saturation monolayer coverage,  $K_L$  ( $\text{L mol}^{-1}$ ) and  $K_F$  ( $(\text{mg g}^{-1})/(\text{mol L}^{-1})^{1/n}$ ) are constants,  $1/n$  is the heterogeneity factor,  $K_{\text{ad}}$  ( $\text{mol}^2 (\text{kJ}^2)^{-1}$ ) is the D–R constant,  $X_m$  ( $\text{mg g}^{-1}$ ) is the D–R monolayer coverage,  $\varepsilon$  is the Polanyi constant,  $R$  is the gas constant ( $8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}$ ),  $T$  (K) is temperature,  $b_T$  ( $\text{J mol}^{-1}$ ) is related to the heat of adsorption, and  $K_T$  ( $\text{L mol}^{-1}$ ) is the Temkin binding isotherm constant.

The Sips isotherm model is a three-parameter isotherm which has characteristics of both the Langmuir and Freundlich isotherms. This isotherm behaves more like Freundlich at low concentrations and like Langmuir at high concentrations (Sips 1948). Another three-parameter isotherm is known as the Redlich–Peterson which combines the Langmuir and Freundlich isotherm equations whereby the mechanism of adsorption is basically a hybrid which does not follow ideal monolayer adsorption. Contrary to Sips model, the equation reduces to Freundlich at high concentrations and to Henry's law at low concentrations (Redlich and Peterson 1959). Toth isotherm model was also used as it was found to accurately fit many systems with sub-monolayer coverage (Terzyk et al. 2003). The isotherm describes well the adsorbates that form multilayer adsorption and those that adsorb onto heterogeneous surfaces. It assumes an asymmetrical quasi-Gaussian energy distribution. Unlike other isotherms, the Toth isotherm considers both low and high adsorbate concentrations. The Sips, Redlich–Peterson and Toth isotherm models can be expressed as follows, respectively:

$$q_e = \frac{q_m (K_s C_e)^{n_s}}{1 + (K_s C_e)^{n_s}} \quad (7)$$

$$q_e = \frac{k_R C_e}{1 + a_R C_e^\beta} \quad (8)$$

$$q_e = \frac{q_m b_T C_e}{(1 + (b_T C_e)^{nT})^{\frac{1}{nT}}} \quad (9)$$

where  $K_S$  ( $\text{L mg}^{-1}$ ) is the Langmuir isotherm constant,  $n_s$  is the Freundlich heterogeneity factor,  $K_R$  ( $\text{mg g}^{-1}$ ) is the R–P adsorption isotherm constant,  $\alpha_R$  ( $\text{mg L}^{-1}$ ) is the R–P isotherm constant,  $\beta$  is the R–P isotherm constant which should be between 0 and 1,  $b_T$  is the Toth isotherm constant, and  $nT$  is the Toth isotherm exponent.

An extended Langmuir isotherm which is temperature dependent was used to evaluate the effect of temperature on the adsorption of  $\text{Pt}^{4+}$  using APDEMSFZ (Karimi et al. 2016). The  $C_e$  values were found at 15, 20, 25, 30, 40, 50 and 60 °C, and from these, the  $q_e$  values were determined using Eq. 10. The Langmuir and Freundlich isotherm parameters were also determined at these temperatures.

$$q_e = \frac{k_1 k_2 \exp\left(\frac{k_3}{T}\right) C_e}{1 + k_2 \exp\left(\frac{k_3}{T}\right) C_e} \quad (10)$$

where  $k_1$  is the maximum adsorption coverage ( $q_m$ ),  $k_2$  is the Langmuir isotherm constant, and  $k_3$  is  $\Delta H/R$ .  $\Delta H$  is enthalpy change, and  $R$  is a gas constant.

## 2.7 Kinetic models

The adsorption process controlling mechanism between  $\text{Pt}^{4+}$  and APDEMSFZ was determined with pseudo-first- and second-order, Elovich and Weber–Morris intraparticle diffusion kinetic models represented by Eqs. 11, 12, 13 and 14, respectively (Bakatula et al. 2015). The correlation coefficient ( $R^2$ ) and the closeness of  $q_{e,\text{exp}}$  to  $q_{e,\text{cal}}$  were used to determine the kinetic model that fits the data.

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (11)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (12)$$

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (13)$$

$$q_t = k_{ld} t^{\frac{1}{2}} + C \quad (14)$$

where  $q_t$  ( $\text{mg g}^{-1}$ ) is the amount adsorbed at a particular time  $t$ ,  $C$  ( $\text{mg g}^{-1} \text{ min}^{-1}$ ) is the thickness of a boundary layer,  $\alpha$  ( $\text{mg g}^{-1} \text{ min}^{-1}$ ) is the chemisorption rate and available adsorption surface,  $\beta$  ( $\text{mg g}^{-1}$ ) is related to surface coverage, and  $k_l$  ( $\text{min}^{-1}$ ),  $k_2$  ( $\text{g mg}^{-1} \text{ min}^{-1}$ ) and  $k_{ld}$  ( $\text{mg g}^{-1} \text{ min}^{1/2}$ ) are rate constants.

## 2.8 Flow-through column experiments

The flow-through column experiments were carried out at  $25^\circ\text{C} \pm 2$ , using a glass column that is 30 cm long and 1.2 cm wide. The column had a glass wool at the bottom to support the adsorbent. The role of initial concentration (2, 5 and  $10 \text{ mg L}^{-1}$ ), pH (2, 5 and 8) and bed depth (1, 3 and 5 cm) on the adsorption of  $\text{Pt}^{4+}$  by APDEMSFZ was determined. The column studies experimental setup is presented in Fig. 1 which can also be used in real wastewater applications.

The breakthrough and adsorption capacity were calculated to determine the performance of the column using Eq. 8 (Biswas and Mishra 2015):

$$q_B = Q_v \left( C_o - \frac{C_B}{2} \right) \frac{t_B}{m_{\text{adsorbent}}} \quad (15)$$

where  $q_B$  ( $\text{mg g}^{-1}$ ) is the amount captured at 50% breakthrough concentration,  $C_B$  ( $\text{mg L}^{-1}$ ) is the  $\text{Pt}^{4+}$  concentration at breakthrough,  $Q_v$  ( $\text{mL min}^{-1}$ ) is flow rate,  $t_B$  (min) is the time it takes from breakthrough to occur, and  $m_{\text{adsorbent}}$  (g) is the mass of APDEMSFZ.

## 2.9 Data analysis

The column experimental data were analysed with Bohart–Adams, Thomas and Yoon–Nelson models to investigate the efficiency of the column on recovery. The Bohart–Adams model

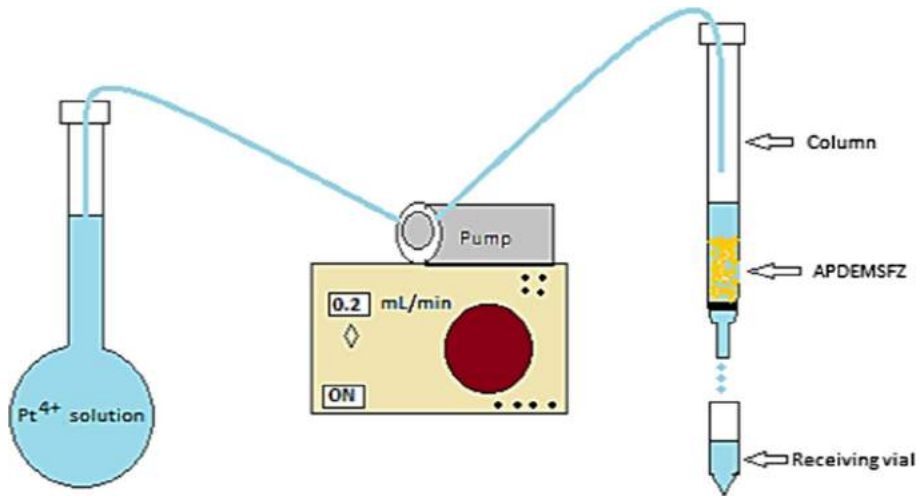


Fig. 1 Column study experimental setup

describes surface reactions of elements and assumes that equilibrium is not attained instantaneously (Muraleedharan et al. 1994; Kiran and Kaushik 2008). The Bohart–Adams model can be represented by:

$$\ln \left( \frac{C_t}{C_o} \right) = k_{AB} C_o t - \frac{k_{AB} N_o Z}{V} \quad (16)$$

where  $C_o$  is the influent concentration,  $N_o$  ( $\text{mg L}^{-1}$ ) is sorption capacity of APDEMSFZ,  $Z$  (cm) is column bed height,  $V$  ( $\text{cm min}^{-1}$ ) is superficial velocity, and  $k_{AB}$  ( $\text{L mg}^{-1} \text{min}^{-1}$ ) is kinetic rate constant. The  $R^2$ ,  $N_o$  and  $k_{AB}$  values were obtained from the resulting equation of the plot of  $\ln \left( \frac{C_t}{C_o} \right)$  versus  $t$ .

Thomas model has been used model to determine the performance of the flow-through column. The adsorption data that conform to this model are assumed to be limited by mass transfer and not by chemical interactions (Foo et al. 2013; Wang et al. 2015). The linearised Thomas model equation could be expressed as:

$$\ln \left( \frac{C_o}{C_t} - 1 \right) = \frac{k_{Th} q_o m_{\text{adsorbent}}}{Q_v} - k_{Th} C_o t \quad (17)$$

where  $k_{Th}$  ( $\text{L min}^{-1} \text{mg}^{-1}$ ) is rate constant and  $q_o$  ( $\text{mg g}^{-1}$ ) is the maximum concentration of  $\text{Pt}^{4+}$  on the adsorbent which were obtained from the plot of  $\ln \left( \frac{C_o}{C_t} - 1 \right)$  versus  $t$ .

Yoon–Nelson adsorption isotherm is a simple model that does not require physicochemical properties of adsorbents (Wang et al. 2015). An assumption with this isotherm is that the reduction in adsorption probability of substances is directly proportional to the adsorption of that particular substance and breakthrough of the substance (Biswas and Mishra 2015; Han et al. 2009). The Yoon–Nelson equation can be expressed as:

$$\ln \left( \frac{C_t}{C_o - C_t} \right) = k_{YN} t - \tau k_{YN} \quad (18)$$

where  $k_{YN}$  ( $\text{min}^{-1}$ ) is the proportionality constant and  $\tau$  is time needed for the adsorbate or substance to reach 50% breakthrough (min). These constants were determined for the plot of  $\ln\left(\frac{C_i}{C_o - C_i}\right)$  versus  $t$ .

The correlation coefficient ( $R^2$ ) was used to select the model that best describes the experimental data.

### 3 Results and discussion

#### 3.1 Characterisation

The chemical composition of the raw zeolite was determined with XRF, and the results indicated that silica ( $\text{SiO}_2$ ) (68.49%) and alumina ( $\text{Al}_2\text{O}_3$ ) (11.48%) were the main components of the adsorbent. Other chemical components were  $\text{K}_2\text{O}$  (3.79%),  $\text{Na}_2\text{O}$  (1.47%),  $\text{CaO}$  (1.22%),  $\text{Fe}_2\text{O}_3$  (1.09%) and loss on ignition of 11.03%. The mineral composition of the zeolite was determined with PXRD, and the results are shown in Fig. 2. The main minerals of the zeolite were: clinoptilolite, quartz and sanidine which contain a high amount of Si and O or Al for some. The functional groups of the raw and functionalised zeolite were determined using FTIR (Fig. 3). The peaks observed at 695 and 964  $\text{cm}^{-1}$  which were present in both the raw and functionalised zeolite can be attributed to the presence of Si–O, Al–O–Si and Si–OH groups (Guaya et al. 2015). The peaks beyond 3300  $\text{cm}^{-1}$  can be attributed to the presence of hydroxyl groups of the zeolite. The peak at 1644  $\text{cm}^{-1}$  was due to the deformation vibration of water molecules. The observed peaks at 790 and 765  $\text{cm}^{-1}$  indicated the success of functionalisation of the zeolite with APDEMS since they were indicative of the Si–O–Si bonds resulting from the interaction of zeolite and APDEMS. The distinct bands at 2925 and 2872  $\text{cm}^{-1}$  observed on the functionalised zeolite were due to  $-\text{CH}_2$  and  $-\text{CH}$  stretching vibrations of

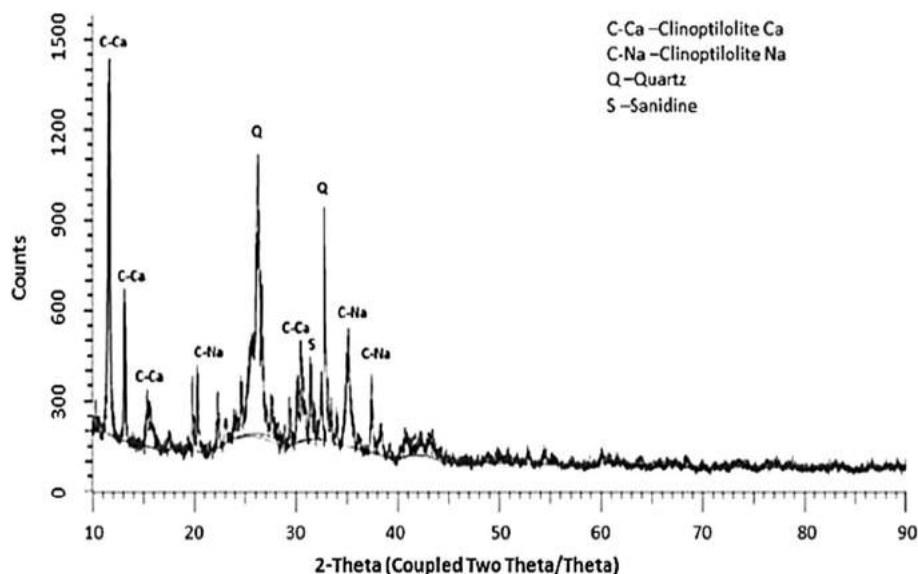


Fig. 2 Powder X-ray diffraction pattern of the raw zeolite

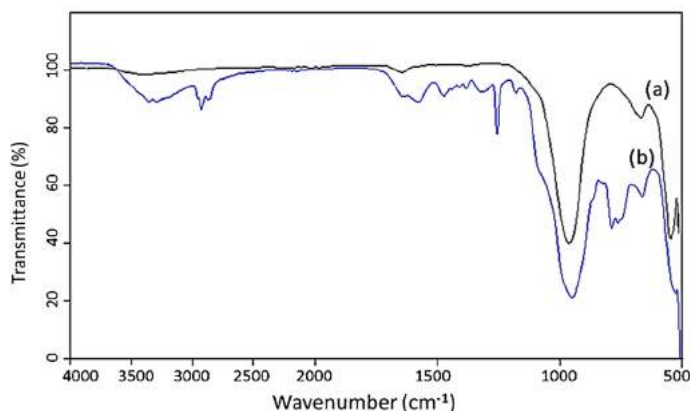


**Fig. 3** FTIR spectra of raw zeolite (a) and APDEMSFZ (b)

APDEMS, respectively. The observed peaks at 1182 and 1257  $\text{cm}^{-1}$  on the functionalised zeolite can be attributed to  $\text{Si-CH}_2$  and  $\text{Si-CH}_3$ , respectively. The presence of the nitrogen groups was represented by the peaks at 1575  $\text{cm}^{-1}$  ( $-\text{NH}$  vibration) and 3366  $\text{cm}^{-1}$  (primary amines). The elemental analysis showed that the amount of C, H and N were high on the functionalised zeolite, thus further confirming the addition of APDEMS on the raw zeolite (Table 1). The specific surface area and pore characteristics of the raw zeolite and APDEMSFZ were determined by BET method from  $\text{N}_2(\text{g})$  adsorption isotherm. The surface area of the raw zeolite decreased from 16.28 to 2.17  $\text{m}^2 \text{g}^{-1}$  due to the addition of APDEMS. The reduction can be attributed to the smothering of the pores by APDEMS, since the pore size and pore volume also decreased from 12.97 to 4.50 nm and 0.052 to 0.0045  $\text{cm}^3$ , respectively. The  $\text{N}_2$  adsorption isotherms for the raw zeolite and APDEMSFS are presented in Fig. 4. The raw zeolite  $\text{N}_2$  uptake was generally higher than that of APDEMSFZ. The  $\text{N}_2$  uptake with APDEMSFZ started around 0.13  $\text{cm}^3 \text{g}^{-1}$  and increased slowly before reaching saturated pressure (Teo et al. 2017). Furthermore, the uptake increased to about 2.9  $\text{cm}^3 \text{g}^{-1}$  of APDEMSFZ.

## 3.2 Batch adsorption studies

### 3.2.1 Effect of adsorbent dosage

The sufficient amount of APDEMSFZ required for significant adsorption or recovery of  $\text{Pt}^{4+}$  was investigated. The adsorption efficiency was observed to increase with increase in amount of adsorbent due to the escalating amount of active sites (Fig. 5). Thus, more  $\text{Pt}^{4+}$  could be captured by the adsorbent. The adsorption capacity, however, decreased with the increase in dosage. For subsequent experiments, 10  $\text{g L}^{-1}$  adsorbent dosage was used since the adsorption capacity and the efficiency were momentous.

**Table 1** The amount of C, H and N in raw and functionalised zeolite

|             | C (%) | H (%) | N (%) |
|-------------|-------|-------|-------|
| Raw zeolite | 0.20  | 1.18  | 0.06  |
| APDEMSFZ    | 9.22  | 2.81  | 2.32  |

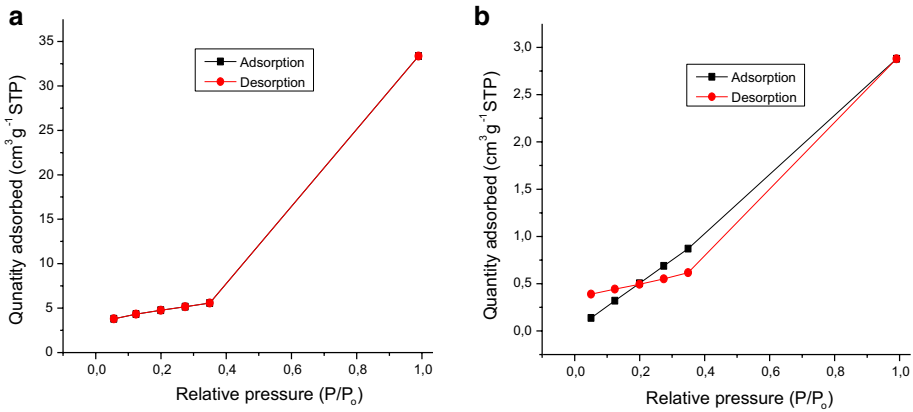


**Fig. 4**  $N_2$  adsorption-desorption isotherm for **a** raw zeolite and **b** APDEMSFZ

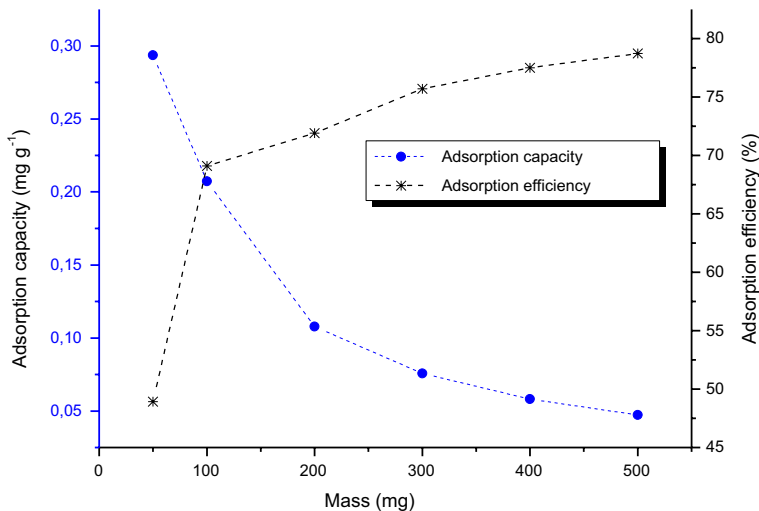


**Fig. 5** Effect of mass on the recovery of  $\text{Pt}^{4+}$  by APDEMSFZ (pH=2, temp=25 °C, concentration=2  $\text{mg L}^{-1}$ , volume=10 mL, time=180 min,  $n=3$  and  $\text{RSD}<5\%$ )

### 3.2.2 Effect of pH

Research has indicated that pH can affect the behaviour and hence the adsorption efficiency of adsorbents; thus, the role of pH was investigated (Bakatula et al. 2015; Ren et al. 2016). The amount of  $\text{Pt}^{4+}$  adsorbed by APDEMSFZ decreased with increase in solution pH due to the changing speciation of  $\text{Pt}^{4+}$  and the surface charge (Fig. 6). At acidic pH, the surface groups were protonated due to high concentration of hydronium ions, and thus, the amine groups of APDEMS were positively charged (i.e.  $-\text{NH}_3^+$ ). These groups had a high affinity for the anionic  $\text{Pt}^{4+}$  species ( $\text{PtCl}_6^{2-}$ ). The anionic chloride species of  $\text{Pt}^{4+}$  were more prevalent at acidic pH since HCl was used to control the acidic pH. During the processing of

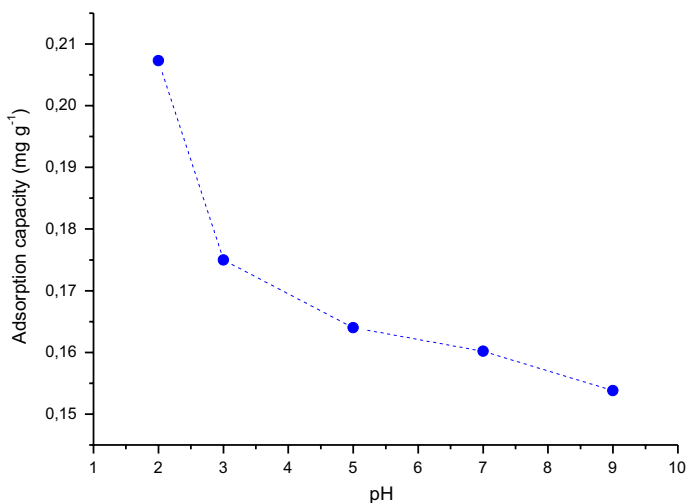


**Fig. 6** Role of pH on the recovery of  $\text{Pt}^{4+}$  by APDEMSFZ (mass=100 mg, temp=25 °C, concentration=2 mg L<sup>-1</sup>, volume=10 mL, time=180 min,  $n=3$  and RSD < 5%)

PGEs, concentrated acids are used for extraction, and thus, the discharged water is highly acidic (Nguyen et al. 2016). Therefore, APDEMSFZ will work well and significantly recover  $\text{Pt}^{4+}$  from mining wastewaters which are highly acidic. The PZC was found to be 5.3. The adsorption capacity decreased significantly beyond pH 2 due to the low amount of chloride species of  $\text{Pt}^{4+}$  as well as electrostatic repulsion, since the surface groups were no longer positively charged due to high hydroxide concentration.

### 3.2.3 Role of initial concentration

The role of initial concentration on the recovery of  $\text{Pt}^{4+}$  by APDEMSFZ was investigated. The adsorption capacity of  $\text{Pt}^{4+}$  at pH 2 increased with concentration up to 2 mg L<sup>-1</sup>, and this was due to the availability of APDEMS active sites ( $-\text{NH}_3^+$ ) (Fig. 7). The adsorption efficiencies were: 75.6% at 0.5 mg L<sup>-1</sup>, 79.7% at 1 mg L<sup>-1</sup>, 78.3% at 2 mg L<sup>-1</sup>, 57.7% at 3 mg L<sup>-1</sup> and 40.4% at 5 mg L<sup>-1</sup>. The reduction in adsorption efficiency beyond 2 mg L<sup>-1</sup> was due to the exhaustion of active sites which are quickly occupied at high concentrations. Since the adsorbent can efficiently remove  $\text{Pt}^{4+}$  in very low concentrations from aqueous solutions, it can be suitable for PGEs wastewater which contains low concentrations of PGEs (Hunt et al. 2015). This also means that the interaction between  $\text{Pt}^{4+}$  and the adsorbent is strong enough. Based on the two- and three-parameter isotherm results (Table 2), the interaction of  $\text{Pt}^{4+}$  onto APDEMSFZ was best described by Langmuir isotherm ( $R^2 > 0.98$ ). This indicated that the interaction between  $\text{Pt}^{4+}$  and APDEMSFZ was through monolayer adsorption. The  $n_T$  from the Toth isotherm model was very close to 1, and this means that the equation was tending to Langmuir isotherm, thus confirming the above results. The Sips ( $R^2 > 0.94$ ) and the Toth ( $R^2 > 0.95$ ) isotherm models had better correlation for the experimental data after Langmuir (Tanzifi et al. 2018). The free energy change as determined from the D-R isotherm was found to be 12.42 kJ mol<sup>-1</sup>, indicating chemical ion exchange (Bakatula et al. 2015).

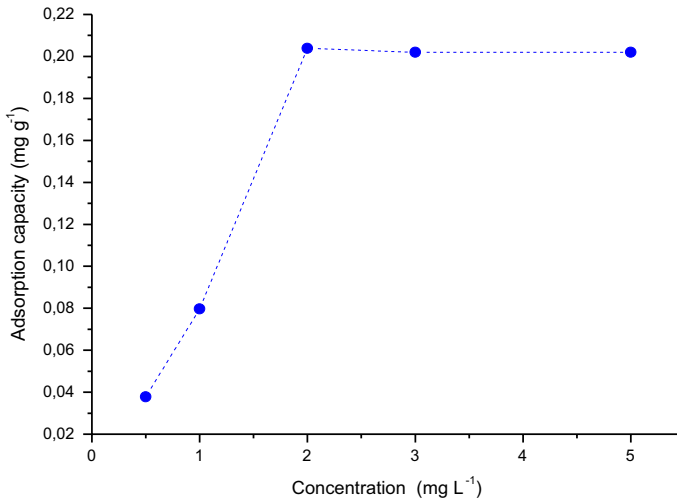


**Fig. 7** The role of concentration on the recovery of  $\text{Pt}^{4+}$  by APDEMSFZ (pH=2, mass=100 mg, temp=25 °C, volume=10 mL, time=180 min,  $n=3$  and RSD < 5%)

**Table 2** Adsorption isotherm data of  $\text{Pt}^{4+}$  adsorption by APDEMSFZ

| Isotherm model       | Isotherm parameters                                                  | Parameter values   |
|----------------------|----------------------------------------------------------------------|--------------------|
| Langmuir             | $q_m$ (mg g <sup>-1</sup> )                                          | 0.122              |
|                      | $K_L$ (L mol <sup>-1</sup> )                                         | $3.5 \times 10^5$  |
|                      | $R^2$                                                                | 0.98               |
| Freundlich           | $n$                                                                  | 32.29              |
|                      | $K_F$ ((mg g <sup>-1</sup> )/(mol L <sup>-1</sup> ) <sup>1/n</sup> ) | 1.99               |
|                      | $R^2$                                                                | 0.91               |
| Dubinin–Radushkevich | $E_s$ (kJ mol <sup>-1</sup> )                                        | 12.42              |
|                      | $X_m$ (mg g <sup>-1</sup> )                                          | 1.37               |
|                      | $R^2$                                                                | 0.92               |
| Temkin               | $b_T$ (J mol <sup>-1</sup> )                                         | $2.01 \times 10^7$ |
|                      | $K_T$ (L mol <sup>-1</sup> )                                         | $3.7 \times 10^6$  |
|                      | $R^2$                                                                | 0.84               |
| Sips                 | $q_m$ (mg g <sup>-1</sup> )                                          | 0.21               |
|                      | $n_s$                                                                | 0.47               |
|                      | $K_s$ (L mg <sup>-1</sup> )                                          | 19.21              |
| Redlich–Peterson     | $R^2$                                                                | 0.94               |
|                      | $\alpha_R$ (mg L <sup>-1</sup> )                                     | 1.97               |
|                      | $\beta$                                                              | 0.33               |
| Toth                 | $k_R$ (mg g <sup>-1</sup> )                                          | 0.68               |
|                      | $R^2$                                                                | 0.82               |
|                      | $q_m$ (mg g <sup>-1</sup> )                                          | 0.29               |
|                      | $b_T$                                                                | 0.85               |
|                      | $n_T$                                                                | 0.93               |
|                      | $R^2$                                                                | 0.95               |

### 3.2.4 Effect of contact time

A rapid uptake of  $\text{Pt}^{4+}$  by APDEMSFZ was observed between 0 and 30 min after which a slow uptake was observed until 180 min (Fig. 8). The fast uptake was due to the availability of amine sites. A steady state was observed beyond 180 min, where the adsorption was controlled by diffusion. For this study, 180 min was selected for the experiments to ensure maximum adsorption. However, 30 min was found to be enough for APDEMSFZ to be in contact with the  $\text{Pt}^{4+}$  solution as sufficient recovery of  $\text{Pt}^{4+}$  was observed between 0 and 30 min. The kinetic data were best described by pseudo-second-order ( $R^2 > 0.99$ ), indicating that chemisorption was the rate controlling mechanism (Table 3) (Karimi et al. 2019). This was also supported by the calculated adsorption capacity ( $q_{e, \text{calc}}$ ) ( $0.102 \text{ mg g}^{-1}$ ) which was very similar to the experimental adsorption capacity ( $0.103 \text{ mg g}^{-1}$ ). The pseudo-first-order experimental  $q_e$  was found to be  $0.0061 \text{ mg g}^{-1}$  which was significantly ( $p < 0.05$ ) different from  $q_{e, \text{calc}}$ , further confirming that the data do not correlate with first-order kinetics. Moreover, the Elovich and intraparticle diffusion models did not describe the kinetic data well.

### 3.2.5 Effect of temperature

The role of temperature on the adsorption of  $\text{Pt}^{4+}$  was investigated since temperature can affect the efficiency of adsorbents. The Langmuir and Freundlich isotherm parameters for the adsorption of  $\text{Pt}^{4+}$  by APDEMSFZ were determined at different temperatures (Table 4). The results indicated that the Langmuir isotherm took precedence over Freundlich at all temperatures; however, the correlation coefficient decreased beyond 303 K. Moreover, the maximum monolayer coverage on the surface of APDEMSFZ decreased beyond this temperature, indicating that the adsorbent will not be too efficient at higher temperatures. This is good since industrial adsorption processes are desirable at lower temperatures (Karimi

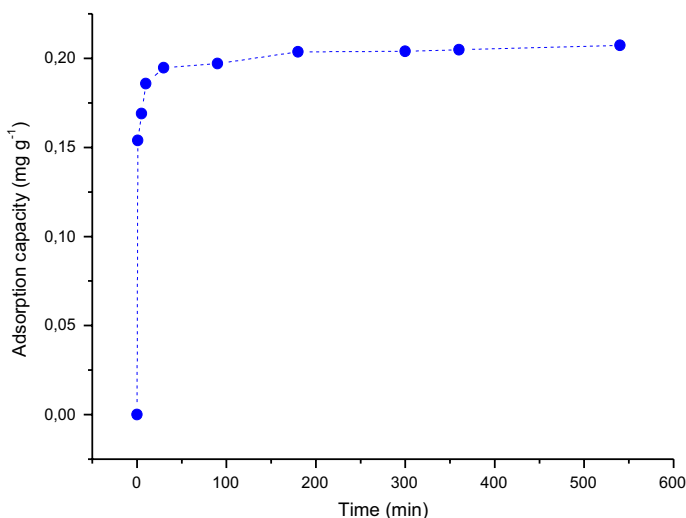


**Fig. 8** Effect of contact time on the adsorption of  $\text{Pt}^{4+}$  by APDEMSFZ (pH=2, mass=100 mg, temp=25 °C, concentration=2 mg L<sup>-1</sup>, volume=10 mL,  $n=3$  and RSD < 5%)

**Table 3** Kinetic parameters for  $\text{Pt}^{4+}$  adsorption by APDEMSFZ

| Kinetic model           | Model parameters                                       | Values             |
|-------------------------|--------------------------------------------------------|--------------------|
| Pseudo-first order      | $q_{e^{\text{calc}}}$                                  | 0.102              |
|                         | $k_1$ ( $\text{min}^{-1}$ )                            | 0.0088             |
|                         | $q_{\text{exp}}$ ( $\text{mg g}^{-1}$ )                | 0.0061             |
|                         | $R^2$                                                  | 0.71               |
| Pseudo-second order     | $k_2$ ( $\text{mg g}^{-1} \text{min}^{-1}$ )           | 6.71               |
|                         | $q_{\text{exp}}$ ( $\text{mg g}^{-1}$ )                | 0.103              |
|                         | $R^2$                                                  | >0.99              |
| Elovich                 | $\alpha$ ( $\text{mg g}^{-1} \text{min}^{-1}$ )        | $6.20 \times 10^5$ |
|                         | $\beta$ ( $\text{mg g}^{-1}$ )                         | $9.01 \times 10^6$ |
|                         | $R^2$                                                  | 0.93               |
| Intraparticle diffusion | $C$                                                    | 0.00043            |
|                         | $k_{\text{id}}$ ( $\text{mg g}^{-1} \text{min}^{-1}$ ) | 0.0011             |
|                         | $R^2$                                                  | 0.36               |

**Table 4** Langmuir and Freundlich isotherm parameters for the adsorption of  $\text{Pt}^{4+}$  by APDEMSFZ at different temperatures

| Temperature (K) | Langmuir                                  |                              |       | Freundlich                                               |      |       |
|-----------------|-------------------------------------------|------------------------------|-------|----------------------------------------------------------|------|-------|
|                 | $K_L \times 10^5$ ( $\text{L mol}^{-1}$ ) | $q_m$ ( $\text{mg g}^{-1}$ ) | $R^2$ | $K_F$ ( $(\text{mg g}^{-1})/(\text{mol L}^{-1})^{1/n}$ ) | $n$  | $R^2$ |
| 288             | 3.78                                      | 0.122                        | 0.96  | 33.96                                                    | 1.98 | 0.88  |
| 293             | 3.65                                      | 0.123                        | 0.97  | 32.61                                                    | 1.99 | 0.91  |
| 298             | 3.51                                      | 0.122                        | 0.98  | 32.29                                                    | 1.99 | 0.92  |
| 303             | 3.43                                      | 0.122                        | 0.98  | 33.27                                                    | 1.97 | 0.91  |
| 313             | 3.27                                      | 0.116                        | 0.96  | 37.85                                                    | 1.91 | 0.86  |
| 323             | 2.84                                      | 0.0968                       | 0.93  | 25.77                                                    | 1.96 | 0.79  |
| 333             | 4.13                                      | 0.0734                       | 0.92  | 15.41                                                    | 2.08 | 0.73  |

et al. 2016). The temperature-dependent extended Langmuir isotherm model was plotted and showed that the uptake of  $\text{Pt}^{4+}$  decreases with increase in temperature (Fig. 9).

### 3.2.6 Effect of competing ions

A mixture consisting of  $2 \text{ mg L}^{-1}$  of  $\text{Pt}^{4+}$  and other competing ions at pH 2 was exposed to APDEMSFZ, and the results are reported in Fig. 10. The adsorption capacity of  $\text{Pt}^{4+}$  was insignificantly ( $p > 0.05$ ) affected by the presence of other ions, some of which were PGEs. Moreover, these PGEs and other cations except Ca and Mg were adsorbed by the adsorbent due to their ability to adsorb on different active sites of APDEMSFZ. A study by Chantawong (2004) indicated that elements such as Zn and Pd can be adsorbed by raw montmorillonite clay mineral, and thus, it is possible that some elements adsorbed on non-functionalised sites. The ability of the adsorbent to capture PGEs and contaminants makes APDEMSFZ a dual efficacy adsorbent. The significant adsorption of  $\text{Pt}^{4+}$  in the presence of other ions makes the adsorbent suitable for mining wastewater which contains a cocktail of elements.

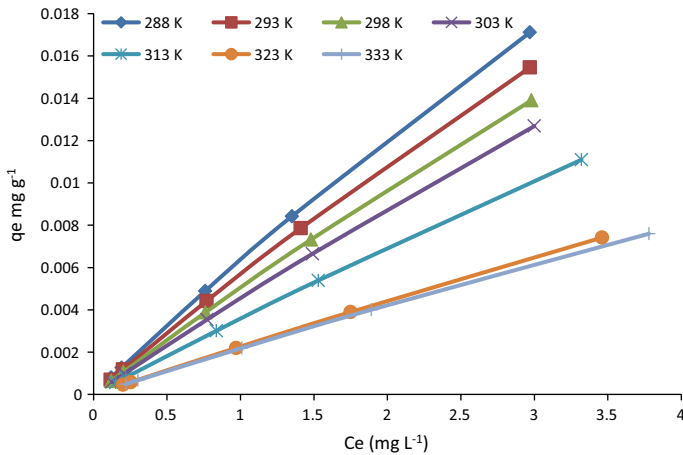


**Fig. 9** Extended Langmuir isotherm for the adsorption of  $\text{Pt}^{4+}$  by APDEMSFZ at different temperatures (pH=2, concentration=2 mg L<sup>-1</sup>, volume=10 mL, time=180 min,  $n=3$  and RSD<5%)

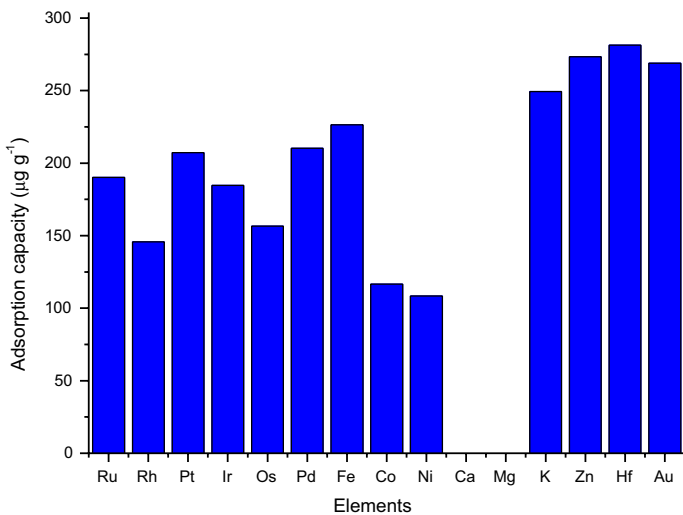


**Fig. 10** Effect of competing ions on the adsorption of  $\text{Pt}^{4+}$  by APDEMSFZ (pH=2, temp=25 °C, concentration=2 mg L<sup>-1</sup>, volume=10 mL, time=180 min,  $n=3$  and RSD<5%)

### 3.3 Column studies

#### 3.3.1 Effect of bed height

The adsorption of  $\text{Pt}^{4+}$  by APDEMSFZ was also assessed using column experiments at 25 °C. Exhaustion and breakthrough times were observed to increase with bed height (Fig. 11). The adsorption column data were determined and showed that  $q_B$  of  $\text{Pt}^{4+}$  increased with bed height and this could be due to the presence of more active sites

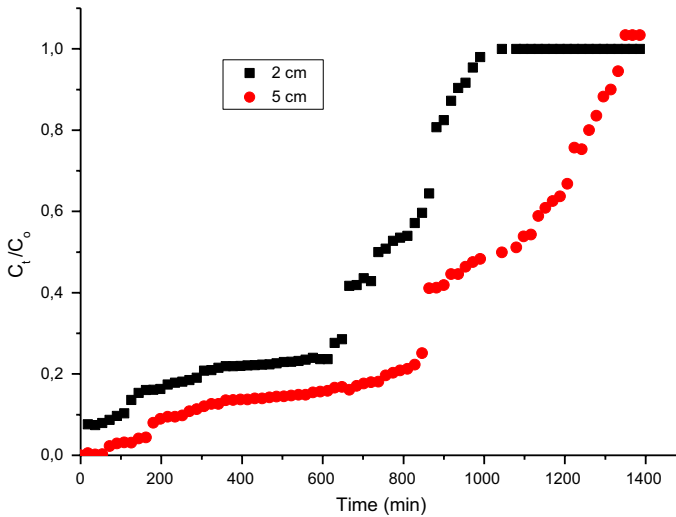


**Fig. 11** Effect of bed height on the adsorption of  $\text{Pt}^{4+}$  by APDEMSFZ (pH=2, temp=25 °C, concentration=2 mg  $\text{L}^{-1}$ ,  $n=3$  and RSD < 5%)

**Table 5** Column adsorption data of  $\text{Pt}^{4+}$  adsorption by APDEMSFZ

| $C_0$ | $Q_v$ | $Z$ | PH | $m_{\text{adsorbent}}$ | $V$ | $T$  | $C_B$ | $Q_B$    |
|-------|-------|-----|----|------------------------|-----|------|-------|----------|
| 2     | 0.28  | 2   | 2  | 2.11                   | 240 | 864  | 1.29  | 0.155356 |
| 2     | 0.28  | 5   | 2  | 2.08                   | 320 | 1152 | 1.22  | 0.215557 |
| 2     | 0.28  | 2   | 5  | 2.09                   | 80  | 288  | 1.38  | 0.050545 |
| 2     | 0.28  | 2   | 7  | 2.11                   | 75  | 270  | 1.43  | 0.046041 |
| 5     | 0.28  | 2   | 2  | 2.11                   | 155 | 558  | 2.53  | 0.276567 |

(Table 5). Thus, longer bed depths provide high amount of N active sites which will lead to high  $\text{Pt}^{4+}$  capture. Biswas and Mishra (2015) also reported similar results.

### 3.3.2 Effect of pH

The pH of the influent solution was varied, whilst bed height and concentration were fixed. The lowest pH (pH 2) had higher breakthrough and exhaustion times due to the dominant  $\text{PtCl}_6^-$  species which were favourable for adsorption by the protonated APDEMS ( $\text{CH}_3\text{Si}(\text{OC}_2\text{H}_5)_2(\text{CH}_2)_3\text{NH}_3^+$ ) (Fig. 12). Thus,  $\text{Pt}^{4+}$  reacted with the adsorbent through electrostatic interactions (Mosai et al. 2019). The amount of chloride and hydronium ions decreased as pH increased, and thus,  $\text{Pt}^{4+}$  was no longer in a favourable state for adsorption; hence, the breakthrough and exhaustion times were reached quicker at pH 5 and 7. The  $q_B$  decreased as pH was increased (Table 5). Therefore, the adsorbent will work best at lower pH values and this is good since the wastewater from refinery processes are highly acidic due to the amount of acids used (Jones 1999; Mosai et al. 2019).

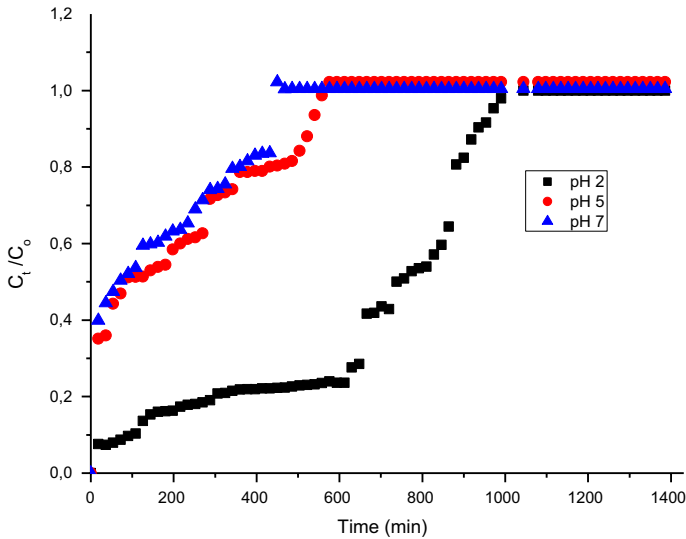


**Fig. 12** The role of pH on the adsorption of  $\text{Pt}^{4+}$  by APDEMSFZ (bed height = 2 cm, temp = 25 °C, concentration = 2 mg L<sup>-1</sup>,  $n = 3$  and RSD < 5%)

### 3.3.3 Effect of concentration

The role of initial concentration on the capturing and recovery of  $\text{Pt}^{4+}$  by APDEMSFZ was determined at pH 2 (Fig. 13). The breakthrough and exhaustion times increased with concentration. Fast exhaustion of active sites was observed at the higher concentration

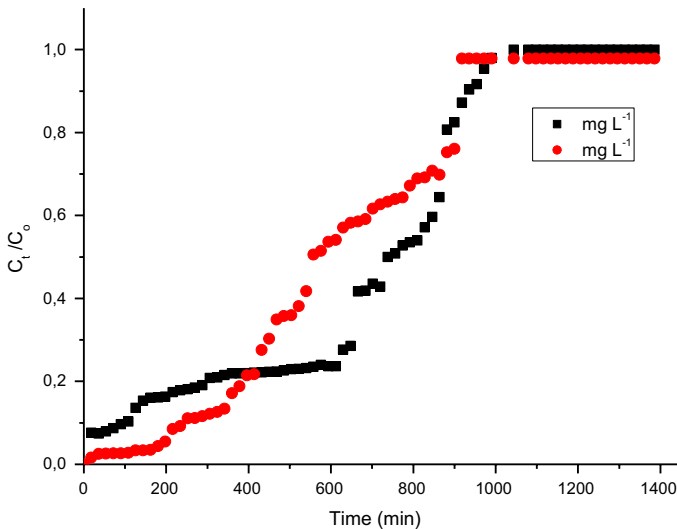


**Fig. 13** The role of influent concentration on the adsorption of  $\text{Pt}^{4+}$  by APDEMSFZ (pH = 2, bed height = 2 cm, temp = 25 °C,  $n = 3$  and RSD < 5%)

(5 mg L<sup>-1</sup>). The fast Pt<sup>4+</sup> breakthrough time could be due to limited APDEMSFZ sites. The breakthrough time was higher with 2 mg L<sup>-1</sup> due to slow transport of Pt<sup>4+</sup> on the adsorbent. Thus, lower concentration gradient may have led to lower mass transfer coefficient (Aziz et al. 2014). The adsorption capacity was, however, observed to increase with initial concentration (Table 5).

### 3.3.4 Column adsorption models

The Bohart–Adams model was applied to determine the behaviour of the flow-through column on the adsorption of Pt<sup>4+</sup> by APDEMSFZ. The kinetic constant ( $k_{AB}$ ) increased slightly with increase in adsorbent dosage but decreased significantly at pH values > 2 which can be attributed to the low adsorption capacity at high pH (Table 6). The highest kinetic constant was achieved with high initial concentration of Pt<sup>4+</sup>. The saturation concentration ( $N_0$ ) decreased as the adsorbent dosage and pH increased. The highest saturation concentration was achieved at pH 2 with 2 mg L<sup>-1</sup> of the Pt<sup>4+</sup> solution. The  $R^2$  values when the Bohart–Adams model was used were between 0.80 and 0.97.

The experimental results were also fitted using the Thomas model and the results as shown in Table 6 indicated that bed height and influent concentration will affect the Thomas kinetic coefficient ( $k_{TH}$ ) and  $q_0$ . As pH increased, the adsorption capacity decreased and this shows that the Pt<sup>4+</sup> capture was not limited by mass transfer but chemical interactions with APDEMSFZ (Wang et al. 2015). The highest adsorption capacity according to this model and the column sorption experiments (Table 5) was achieved when 5 mg L<sup>-1</sup> was used. Moreover, the highest  $R^2$  value (> 0.95) was obtained at this concentration.

The Yoon–Nelson model was used and showed that  $k_{YN}$  decreased with increase in bed depth, whilst  $\tau$  increases with bed depth due to high amount of active sites for Pt<sup>4+</sup> adsorption. The adsorption of platinum by the adsorbent was not favoured at high pH.

The correlation coefficient indicated that the Bohart–Adams model fitted the column adsorption data better. Thus, the sorption process of Pt<sup>4+</sup> onto APDEMSFZ may be continuous (Muraleedharan et al. 1994; Kiran and Kaushik 2008).

## 4 Conclusion

3-aminopropyl(diethoxy)methylsilane functionalised zeolite (APDEMSFZ) was synthesised and used to recover Pt<sup>4+</sup> from aqueous solutions. The raw adsorbent could only remove about 0.32% of Pt<sup>4+</sup>, whilst more than 78% of Pt<sup>4+</sup> was removed with APDEMSFZ. This amount will obviously increase as the adsorbent is increased, and the value of the recovered platinum can be very significant. The adsorbent significantly adsorbed platinum at highly acidic pH (pH 2) which makes the adsorbent very suitable for PGM mining wastewater which is highly acidic. The possibility of the removal of platinum was also indicated by the kinetic and isotherm models which indicated that there was strong chemisorptive Pt-adsorbent interaction. Since the Langmuir isotherm described the Pt<sup>4+</sup> adsorption data better than all the isotherms, the adsorption of platinum was through the amine groups of APDEMS. The adsorbent will work effectively at temperatures lower than 303 K. The adsorbent can be used in real wastewater and will perform adequately since the adsorption of Pt<sup>4+</sup> was still significant in the mixture of other ions. The column adsorption results indicated that the adsorbent can be used practically as an ion exchanger for Pt<sup>4+</sup>. To significantly recover platinum, higher bed height leading to more active sites for adsorption

**Table 6** The column adsorption data of the adsorption of  $\text{Pt}^{4+}$  by APDEMSFZ

| $C_o$ (mg $\text{L}^{-1}$ ) | $Q_v$ (mL $\text{min}^{-1}$ ) | $Z$ (cm) | PH | $K_{AB}$ (L $\text{mg}^{-1}$ $\text{min}^{-1}$ ) | $N_o$ (mg $\text{L}^{-1}$ ) | $R^2$ | $K_{Th}$ (L $\text{min}^{-1}$ $\text{mg}^{-1}$ ) | $Q_o$ (mg $\text{g}^{-1}$ ) | $R^2$ | $K_{YN}$ ( $\text{min}^{-1}$ ) | $\tau$ (min) | $R^2$ |
|-----------------------------|-------------------------------|----------|----|--------------------------------------------------|-----------------------------|-------|--------------------------------------------------|-----------------------------|-------|--------------------------------|--------------|-------|
| 2                           | 0.28                          | 2        | 2  | 0.001                                            | 287                         | 0.94  | 0.0045                                           | 0.14                        | 0.83  | 0.010                          | 518          | 0.83  |
| 2                           | 0.28                          | 5        | 2  | 0.0014                                           | 128                         | 0.80  | 0.0023                                           | 0.092                       | 0.82  | 0.0046                         | 932          | 0.82  |
| 2                           | 0.28                          | 2        | 5  | 0.00080                                          | 138                         | 0.94  | 0.0033                                           | 0.038                       | 0.72  | 0.0066                         | 144          | 0.72  |
| 2                           | 0.28                          | 2        | 7  | 0.00085                                          | 119                         | 0.97  | 0.0055                                           | 0.033                       | 0.57  | 0.011                          | 126          | 0.57  |
| 5                           | 0.28                          | 2        | 2  | 0.0022                                           | 203                         | 0.92  | 0.0032                                           | 0.16                        | 0.95  | 0.0063                         | 628          | 0.95  |

should be used at  $\text{pH} \leq 2$ . The APDEMSFZ was found to successfully recover  $\text{Pt}^{4+}$  from aqueous solutions and can thus be used in mining wastewater for the removal of  $\text{Pt}^{4+}$  and other precious elements.

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## Compliance with ethical standards

**Conflict of interest** The authors declare no conflict of interest.

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# PAPER II

**This paper addressed the Recovery of Pt(IV) from aqueous solutions by spent brewer's yeast-functionalized zeolite using batch and column studies.**

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# Recovery of Pt(IV) from aqueous solutions by spent brewer's yeast-functionalized zeolite (SBYFZ): A batch and column study

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## Abstract

Mineral commodities in Earth's crust, such as platinum, palladium, and gold have to be sustained especially since their ore deposits have been dramatically declining, due to intensive mining, motivated by high demand. The mining of these commodities results in large amounts of wastewater containing traces of precious elements. The current study presents on the recovery of Pt(IV) from aqueous solutions using spent brewer's yeast-functionalized zeolite (SBYFZ). Batch and column experiments were conducted at different conditions. Two- and three-parameter isotherm and kinetic models were fitted using adsorption data. Pt(IV) was significantly ( $p < .05$ ) recovered from aqueous solutions within 300 min of contact time, using 10 g/L adsorbent dosage and 2 mg/L at pH 2. The platinum uptake was reduced by 5% when incorporated with adsorption competing ions. Other platinum group elements were successfully removed from aqueous solutions along with Pt(IV). Column studies indicated that breakthrough times were proportional to increasing bed height, highly acidic pH, and low influent concentration. The recovery of Pt(IV) was through mass transfer as concluded from column adsorption models. These results indicated that SBYFZ was excellent for the significant recovery of Pt(IV) from aqueous solutions. Thus, SBYFZ can be used in wastewaters with optimum conditions.

## KEYWORDS

adsorption efficiency, isotherms models, precious elements, spent yeast

## 1 | INTRODUCTION

Platinum-group elements (PGEs) are widely used in car exhaust catalysts, jewelry, electronics, and medical as well as laboratory equipment.<sup>1,2</sup> Due to the declining PGEs reserves and high demand, the rate of scarcity of PGEs especially platinum is alarming hence; ways of their recovery from wastewaters are of high importance. These ways can be very attractive and highly considered by mining and other industries, which rely on their availability. The current methods used to retain precious elements from wastewaters cannot recover low concentrations of PGEs significantly.<sup>3</sup> It is because of this limitation that these elements

continue to be lost along with non-precious elements such as Mg, Ca, and Zn.<sup>4</sup> It will thus be beneficial to recover PGEs from wastewaters since they are already low in the earth's crust.<sup>3,5</sup>

Several methods have been used to recover elements from aqueous solutions, of which adsorption has been found to be the cheapest and most effective method for recovery of elements in low concentrations.<sup>1,6-8</sup> Cheap adsorbents such as zeolite, bentonite, chitosan, and activated carbon have been widely used for the recovery of elements.<sup>4,8-10</sup> Zeolites are aluminosilicates clay minerals, which are formed in nature through volcanic activities.<sup>11</sup> They are negatively charged due to isomorphous exchange of  $\text{Si}^{4+}$  with  $\text{Al}^{3+}$  but, this charge

is neutralized by cations such as  $\text{Na}^+$  and  $\text{K}^+$ .<sup>12</sup> Studies have indicated that the efficiency and selectivity of zeolites can be improved by modifying the surface with ligands that target the analytes of interest.<sup>8,10</sup>

Spent brewer's yeast is the second-largest by-product of the brewing industry and has been used for animal feed or disposed of as waste.<sup>13</sup> It contains high amounts of proteins, amino acids, and vitamins.<sup>14</sup> The amino acids include glutamine, aspartic acid, glutamic acid, arginine, threonine, alanine, and valine, which contain amine ( $-\text{NH}_2$ ) and carboxyl ( $-\text{COOH}$ ) groups.<sup>13</sup> The amine groups have been found to interact strongly with PGEs.<sup>2,4,15</sup> This idea was then incorporated in this study, and the zeolite was modified with spent brewer's yeast for the recovery of Pt(IV) from aqueous solutions.

## 2 | MATERIALS AND METHODS

### 2.1 | Reagents and standards

A 10 mg/L stock solution of Pt(IV) was prepared from 1,000 mg/L  $\text{PtCl}_6^{2-}$  standard and deionized water. A 10 mg/L stock solution of a mixture of Pt, Rh, Pd, Ir, Ru, Os, Fe, Ca, Mg, K, Co, Ni, Hf, Zn, and Au was also prepared for this study. These solutions were preserved with drops of concentrated hydrochloric acid and refrigerated at 4°C when not used.

Spent brewer's yeast was a by-product of beer brewing at the Wits Microbreweries from the University of the Witwatersrand, South Africa.

### 2.2 | Functionalization and characterization of zeolite

The collected spent yeast (40 ml) was mixed with 10 g zeolite and allowed to react for 24 hr at 25°C using an elliptical benchtop shaker (Labcon). The contents were then filtered using suction, and the unreacted spent yeast was removed by shaking the zeolite with deionized water for 10 min. The contents were filtered again, and the spent brewer's yeast-functionalized zeolite (SBYFZ) was dried at room temperature for 24 hr before used.

The zeolite was characterized by X-ray fluorescence (XRF) (PANalytical, Netherlands), powder X-ray diffraction (PXRD) (Bruker D2 Phaser, Germany), and Fourier transform infrared (FTIR) spectroscopy (Tensor 27, Bruker, Germany). The varioELcube V4.0.13 (Elementar, Germany) was used to determine the amount of C, H, and N on the raw zeolite and SBYFZ. The SBYFZ point of zero charges (pHpzc) was also determined. The surface area, pore volume, and pore size of the raw and functionalized zeolite were determined using Micromeritics Flow Prep 060 instrument (Aachen, Germany).

### 2.3 | Batch adsorption studies

Batch adsorption experiments were conducted in triplicates ( $n = 3$ ) and relative standard deviation (% RSD) was used to determine the

reliability of the obtained data. The raw zeolite, yeast, and the functionalized zeolite were used as adsorbents and compared with each other. The impact of the adsorbent dosage (5–50 g/L) on the removal of Pt(IV) was investigated. The adsorbent dosage would give an indication of how much adsorbent is needed to significantly recover Pt(IV) in a particular volume of water, without wasting the adsorbent. Most elements can be better recovered at specific pH ranges hence; the influence of pH (2–9) on the recovery of Pt(IV) was investigated.<sup>4</sup> Some adsorbents can be efficient when the concentration of the analyte is very low, while others can work well even at high concentrations.<sup>8,10</sup> It is for this reason that the role of initial concentration (0.5–10 mg/L) of Pt(IV) was investigated. The time it takes for the adsorbent to significantly remove and recover Pt(IV) from aqueous solutions was studied between 0 and 540 min. Since real wastewaters also contain a host of other elements, the role of competing ions (Rh (III), Pd(II), Ir(III), Ru(III), Os(III), Fe(II), Ca(II), Mg(II), K(I), Co(II), Ni(II), Hf (IV), Zn(II), and Au(I)) on the adsorption of Pt(IV) was investigated.<sup>4</sup>

The adsorbed amount,  $q_e$  (mg/g) of Pt(IV), and other elements were determined using Equation (1) while the adsorption efficiency was determined using Equation (2).

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (1)$$

$$\text{adsorption efficiency} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

where  $C_0$  and  $C_e$  (mg/L) are starting and equilibrium concentrations of Pt(IV), respectively,  $V$  (L) is the volume of the solutions in and  $M$  (g) is the mass of SBYFZ.

### 2.4 | Isotherm models

To determine how Pt(IV) interacts with the adsorbent, adsorption isotherms (Langmuir, Freundlich, and Dubinin-Radushkevich [D-R]) were considered.<sup>16</sup> The Langmuir isotherm (Equation (3)) fits the experimental data where the adsorbate is bound on specific similar sites of the adsorbent.<sup>17</sup>

$$\frac{C_e}{q_e} = \left( \frac{1}{q_m} \right) C_e + \left( \frac{1}{K_L q_m} \right) \quad (3)$$

where  $q_m$  (mg/g) is the maximum monolayer coverage and  $K_L$  (L/mol) is the isotherm constant.

The Freundlich isotherm (Equation (4)) better describes data where the adsorbate is bound by different sites of the adsorbent and thus, a heterogeneous surface is considered. Moreover, multilayer adsorption of the analyte is possible.<sup>18</sup>

$$q_e = K_f C_e^{\frac{1}{n}} \quad (4)$$

where  $K_f$  ((mg/g)/(mol/L)<sup>1/n</sup>) is the isotherm constant and  $n$  is the adsorption intensity.

The Dubinin-Radushkevich isotherm, which assumes that the adsorbate can be described using Gaussian energy distribution that is, Polanyi potential.<sup>19</sup> The D-R adsorption model and the Polanyi potential ( $\epsilon$ ) are expressed in Equations (5) and (6), respectively.

$$\ln q_e = \ln X_m - K_{DR} \epsilon^2 \quad (5)$$

$$\epsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \quad (6)$$

where  $K_{ad}$  ( $\text{mol}^2 [\text{kJ}^2]^{-1}$ ) is isotherm constant,  $X_m$  ( $\text{mg/g}^{-1}$ ) is the theoretical isotherm saturation capacity,  $R$  is the universal gas constant ( $\text{J} [\text{mol} \cdot \text{K}]^{-1}$ ), and  $T$  is the temperature (K). The energy of adsorption ( $E_s$ ) was determined using the following equation:

$$E_s = \frac{1}{\sqrt{2K_{DR}}} \quad (7)$$

The model that best fits the experimental data was determined by using the coefficient of determination ( $R^2$ ).

The separation factor ( $R_L$ ) (Equation (8)) that can be determined from the Langmuir isotherm constant ( $K_L$ ) was used to determine whether the adsorption of Pt(IV) by the adsorbent is favorable ( $0 < R_L < 1$ ), unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), or irreversible ( $R_L = 0$ ).<sup>20</sup>

$$R_L = \frac{1}{1 + C_0 K_L} \quad (8)$$

The experimental adsorption data were also used to fit Redlich-Peterson, Sips and Toth isotherm models. These isotherms are more complicated than the ones stated above as they have three parameters that have to be determined.<sup>21</sup> The solver found in excel was used to determine the unknowns. The Redlich-Peterson empirical isotherm has elements from the Langmuir and the Freundlich isotherm equations (Equation (9)).<sup>22</sup>

$$\ln \left( k_R \frac{C_e}{q_e} - 1 \right) = \beta \ln C_e + \ln \alpha_R \quad (9)$$

where  $K_R$  ( $\text{mg/g}$ ) and  $\alpha_R$  ( $\text{mg/L}$ ) are isotherm constants and  $\beta$  is the exponent, which should lie between 0 and 1.

The Sips model (Equation (10)) also has characteristics of the Langmuir and Freundlich isotherm models, and reduces to the Langmuir isotherm at high concentrations of elements, but turns to behave more like the Freundlich isotherm at low concentrations of elements.<sup>21,23</sup>

$$q_e = \frac{q_m (K_S C_e)^{n_S}}{1 + (K_S C_e)^{n_S}} \quad (10)$$

where  $K_S$  ( $\text{L/mg}$ ) is the Sips equilibrium constant and  $n_S$  is the heterogeneity factor, which is dimensionless.

The Toth isotherm model, which takes into consideration both high and low analyte concentrations were used. It is an empirical modification of the Langmuir isotherm and describes systems that undergo heterogeneous adsorption.<sup>24</sup> The Toth isotherm model can be expressed as:

$$q_e = \frac{q_m b_T C_e}{\left( 1 + (b_T C_e)^{n_T} \right)^{\frac{1}{n_T}}} \quad (11)$$

where  $b_T$  is the Toth isotherm constant and  $n_T$  is the Toth isotherm exponent.

## 2.5 | Kinetic models

The mechanism of adsorption of Pt(IV) onto the SBYFZ and rate constants were determined using pseudo-first- and second-order kinetic models and are expressed in Equations (12) and (13), respectively.<sup>4,8,10</sup>

$$\log(q_e - q_t) = -\frac{k_1 t}{2.303} + \log q_e \quad (12)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (13)$$

where  $q_t$  ( $\text{mg/g}$ ) represents the amount of Pt(IV) at time  $t$ ,  $k_1$  ( $\text{min}^{-1}$ ) and  $k_2$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ) are equilibrium rate constants.

The Elovich model has been applied to chemisorptive processes thus; it is used for the mechanism of adsorption and can be expressed as:

$$\frac{dq_t}{dt} = a \cdot \exp(-b \cdot q_t) \quad (14)$$

where  $a$  ( $\text{mg g}^{-1} \text{min}^{-1}$ ) is the initial adsorption rate and  $b$  ( $\text{g/mg}$ ) is the extent of surface coverage, which is related to the activation energy for chemisorption.

The intra-particle diffusion model describes the adsorption process that is controlled by diffusion and can be expressed as:

$$q_t = k_{id} t^{\frac{1}{2}} + C \quad (15)$$

where  $k_{id}$  is the intra-particle diffusion rate constant ( $\text{mg g}^{-1} \text{min}^{1/2}$ ) and  $C$  gives an idea about the boundary layer thickness.

## 2.6 | Column adsorption studies

The efficiency of the adsorbent on the removal of Pt(IV) from mining wastewaters was investigated using dynamic fixed-bed column adsorption studies. The 1.2 by 30 cm column was used. The effect of

bed depth (1, 2, and 5 cm), starting concentration (2 and 5 mg/L), and pH (2, 5, and 8.3) were investigated.

Continuous fixed-bed column adsorption studies were also conducted to get a better representation of how the adsorbent will behave in mining wastewaters. Breakthrough curves showing breakthrough points, which are due to the detected adsorbate concentrations in the receiving container were used to determine the efficiency of the SBYFZ. In this study, a breakthrough time when 50% of the initial adsorbate concentration has been reached was used.<sup>25</sup> The breakthrough capacity was calculated using Equation (16).

$$Q_{50\%} = Q_v \left( C_0 - \frac{C_{50\%}}{2} \right) \frac{t_{50\%}}{m_{\text{adsorbent}}} \quad (16)$$

where  $Q_{50\%}$  (mg/g) is the adsorption capacity at 50% breakthrough concentration of Pt(IV),  $C_0$  (mg/L) is the initial concentration of Pt(IV),  $C_{50\%}$  (mg/L) is the effluent concentration of Pt(IV) that has reached 50% of the feed concentration,  $Q_v$  is the flow rate (ml/min),  $t_{50\%}$  is the time it takes for 50% breakthrough concentration to occur, and  $m_{\text{adsorbent}}$  is the mass of the adsorbent used (g).

## 2.7 | Column adsorption models

The Adams-Bohart, Thomas, and the Yoon-Nelson column adsorption models were used to determine the dynamic behavior of the column when Pt(IV) is introduced.<sup>26</sup> The Adams-Bohart model, which focuses mainly on the initial stages of breakthrough points assumes that the

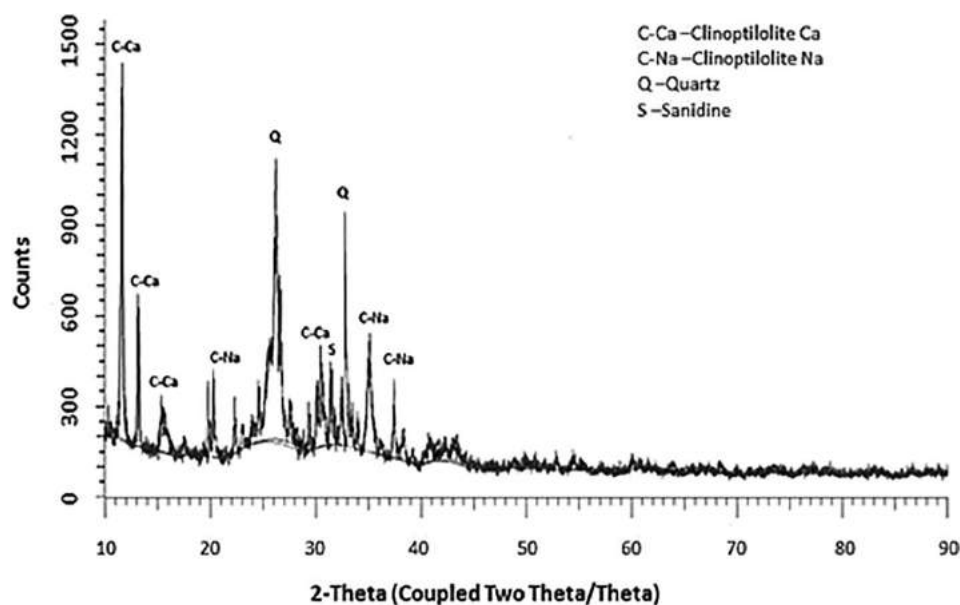


**FIGURE 1** PXRD pattern of the natural zeolite. PXRD, powder X-ray diffraction

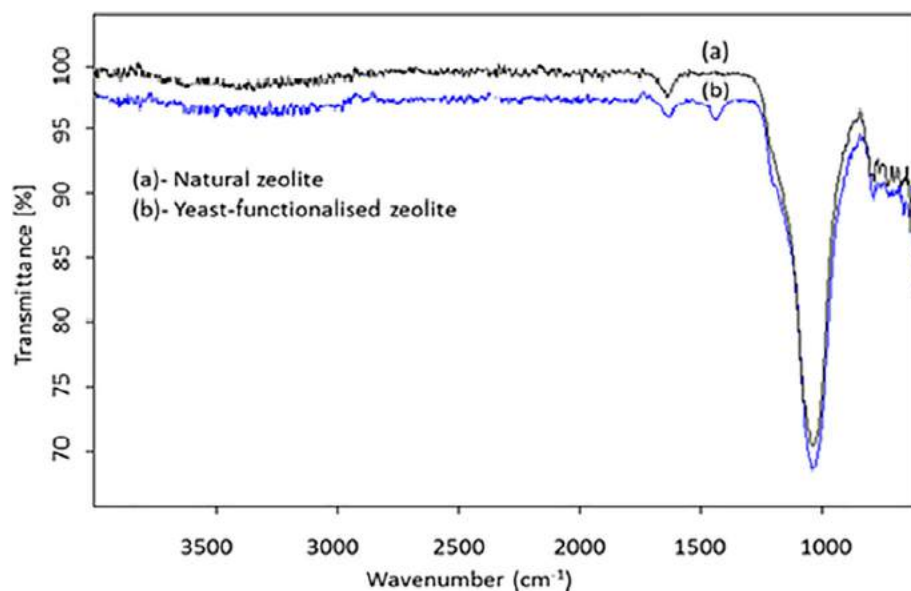


**FIGURE 2** FTIR spectra of the natural zeolite (a) and SBYFZ (b). SBYFZ, spent brewer's yeast-functionalized zeolite [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

rate of adsorption of analytes is controlled by external mass transfer and that equilibrium is not attained in an instant.<sup>27,28</sup> The linear form of the Adams-Bohart model can be expressed as:

$$\ln\left(\frac{C_t}{C_o}\right) = k_{AB}C_o t - \frac{k_{AB}N_o Z}{U_o} \quad (17)$$

where  $k_{AB}$  ( $L \text{ mg}^{-1} \text{ min}^{-1}$ ) is the kinetic constant,  $N_o$  (mg/L) is the saturation concentration,  $Z$  is bed depth (cm), and  $U_o$  (cm/min) is the superficial velocity. The plot of  $\ln\left(\frac{C_t}{C_o}\right)$  versus  $t$  was used to determine the values of  $N_o$  and  $k_{AB}$ .

The Thomas model (Equation (18)) assumes that the adsorption of analytes is limited by mass transfer at the interface and not through chemical interactions.<sup>27,29</sup>

$$\ln\left(\frac{C_o}{C_t} - 1\right) = \frac{k_{Th}q_o m_{adsorbent}}{Q_v} - k_{Th}C_o t \quad (18)$$

**TABLE 1** The elemental analysis of the natural and yeast-functionalized zeolite (per 10 mg adsorbent)

| Sample                       | C (%) | H (%) | N (%) |
|------------------------------|-------|-------|-------|
| Natural zeolite              | 0.20  | 1.18  | 0.06  |
| Yeast-functionalized zeolite | 2.68  | 1.51  | 0.78  |

**TABLE 2** Textural properties of the natural zeolite and SBYFZ

| Sample                       | Pore size (nm) | Pore volume ( $\text{cm}^3/\text{g}$ ) | Surface area ( $\text{m}^2/\text{g}$ ) |
|------------------------------|----------------|----------------------------------------|----------------------------------------|
| Natural zeolite              | 12.97          | 0.052                                  | 16.28                                  |
| Yeast-functionalized zeolite | 5.45           | 0.053                                  | 5.31                                   |

where  $k_{Th}$  ( $L \text{ min}^{-1} \text{ mg}^{-1}$ ) is the Thomas model kinetic constant and  $q_o$  (mg/g) is the equilibrium adsorption capacity and was determined from the plot of  $\ln\left(\frac{C_o}{C_t} - 1\right)$  versus  $t$ .

The Yoon-Nelson model (Equation (19)), which assumes that there is proportionality in the rate of the probability of the decrease in adsorption, and the probability of adsorption of the analyte was used.<sup>30</sup>

$$\ln\left(\frac{C_t}{C_o - C_t}\right) = k_{YN}t - \tau k_{YN} \quad (19)$$

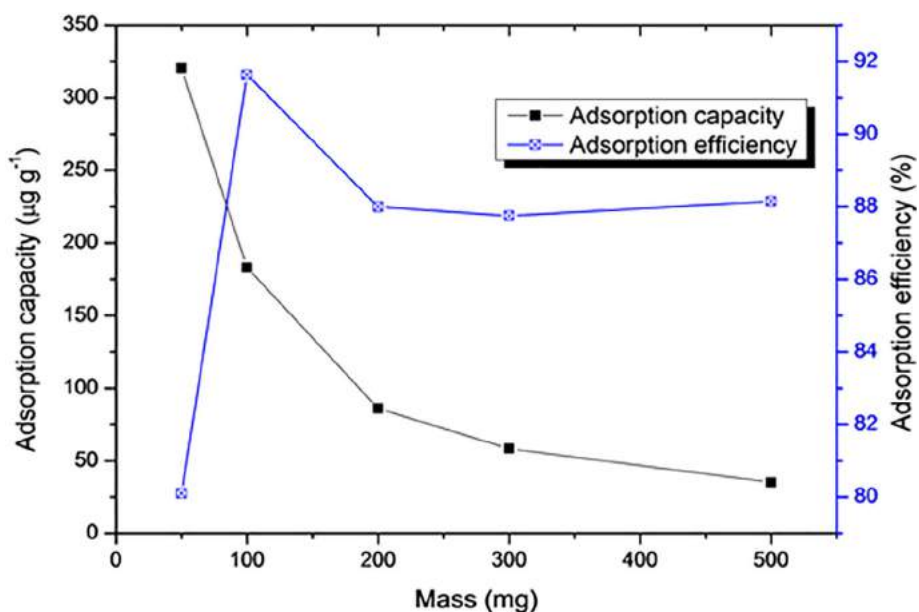
where  $k_{YN}$  ( $\text{min}^{-1}$ ) is the rate constant and  $\tau$  (min) is the time it takes for 50% of the analyte to breakthrough. These constants were determined for the plot of  $\ln\left(\frac{C_t}{C_o - C_t}\right)$  versus  $t$ .

### 3 | RESULTS AND DISCUSSION

#### 3.1 | Characterization

The XRF results indicated that the zeolite was highly composed of  $\text{SiO}_2$  (64.5%) and  $\text{Al}_2\text{O}_3$  (11.6%), however, other minerals such as  $\text{K}_2\text{O}$  (3.8%),  $\text{Na}_2\text{O}$  (1.5%),  $\text{CaO}$  (1.2%), and  $\text{Fe}_2\text{O}_3$  (1.1%) were also in significant amounts. The PXRD pattern (Figure 1), indicated that the adsorbent material used was a clinoptilolite zeolite. The silica ( $\text{SiO}_2$ ) observed from XRF was a quartz type, as concluded by the PXRD results. The Fourier transform infrared spectroscopy (FTIR) results complemented those observed with XRF and PXRD since they all

**FIGURE 3** The consequence of adsorbent dosage on the adsorption of Pt (IV) by SBYFZ (pH 2, concentration = 2 mg/L, time = 300 min, temp = 25°C,  $n = 3$ , variance = 11,183, RSD <5%). RSD, relative standard deviation; SBYFZ, spent brewer's yeast-functionalized zeolite [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]



indicated the presence of silica in high amounts. The Si-O and Al-O interactions were represented by the peak at  $1036\text{ cm}^{-1}$  as indicated by FTIR (Figure 2).<sup>4</sup> The peak at  $1482\text{ cm}^{-1}$  on the functionalized zeolite was due to N-H stretch, which indicated that the zeolite was successfully functionalized. The N-H band observed could have been

due to the amino acids in the yeast, and thus the interaction of the yeast could have been through the oxide minerals of the zeolite. This is a good attribute of the adsorbent since studies have indicated that the amine groups can form strong interactions with PGEs.<sup>2,15</sup> The presence of amine groups was also evidenced by elemental analysis

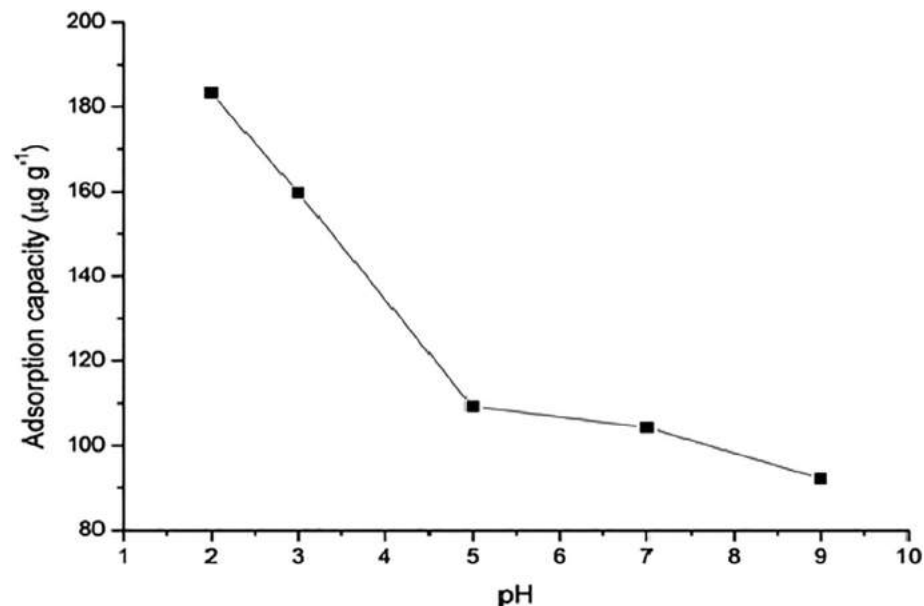


**FIGURE 4** Role of pH on the adsorption of Pt(IV) by SBYFZ (mass = 100 mg, concentration = 2 mg/L, time = 300 min, temp = 25°C,  $n = 3$ , variance = 1,258, RSD <5%). RSD, relative standard deviation; SBYFZ, spent brewer's yeast-functionalized zeolite

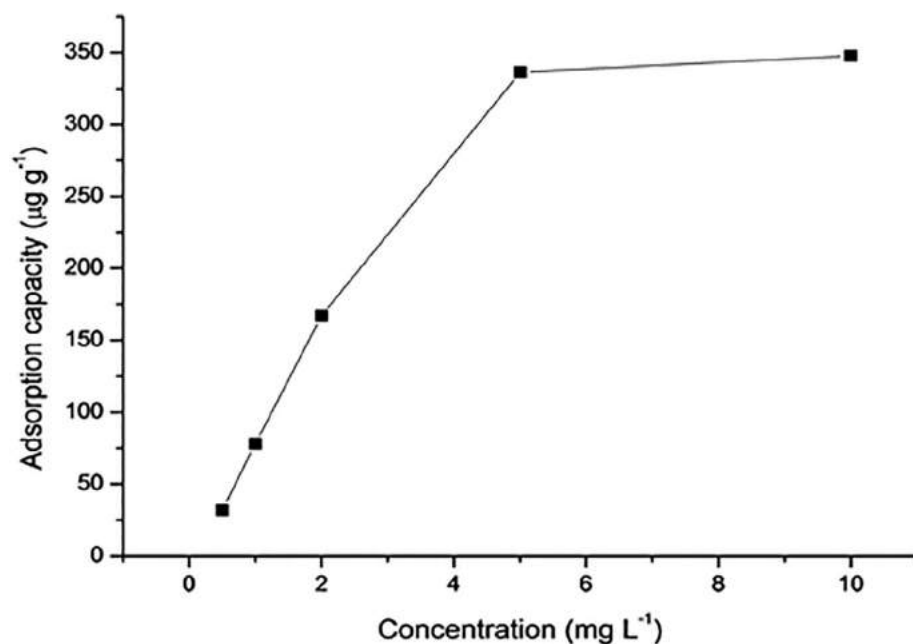


**FIGURE 5** Role of initial concentration on the capturing of Pt(IV) by SBYFZ (mass = 100 mg, pH 2, time = 300 min, temp = 25°C,  $n = 3$ , variance = 16,272, RSD <5%). RSD, relative standard deviation; SBYFZ, spent brewer's yeast-functionalized zeolite

**TABLE 3** Adsorption isotherms data for the adsorption of Pt(IV) by SBYFZ

| Langmuir   |                    |       | Freundlich                                                      |     |       | Dubinin-Radushkevich |              |       |
|------------|--------------------|-------|-----------------------------------------------------------------|-----|-------|----------------------|--------------|-------|
| $q_m$ mg/g | $K_L$ L/Mol        | $R^2$ | $K_F$ (mgg <sup>-1</sup> )/(molL <sup>-1</sup> ) <sup>1/n</sup> | $n$ | $R^2$ | $X_m$ mg/g           | $E_s$ kJ/Mol | $R^2$ |
| 0.41       | $1.92 \times 10^5$ | 0.98  | 162                                                             | 1.8 | 0.92  | 5.97                 | 11.4         | 0.93  |

(Table 1). The pore size and the surface area decreased upon functionalization due to the smothering of the pores by spent yeast, and this also confirms the success of functionalization (Table 2).

### 3.2 | Batch adsorption studies

The adsorption of Pt(IV) using raw zeolite was conducted, but the results indicated that the adsorption was very poor (0.01% adsorption efficiency), therefore, the results were not considered for this study. The yeast was also used by itself to recover Pt(IV) from aqueous solutions, and the adsorption efficiency was found to be less than 43% for all variables. These results were not included in this study as they were not significant ( $p > .05$ ). The zeolite functionalized with spent yeast (SBYFZ) was used for subsequent experiments.

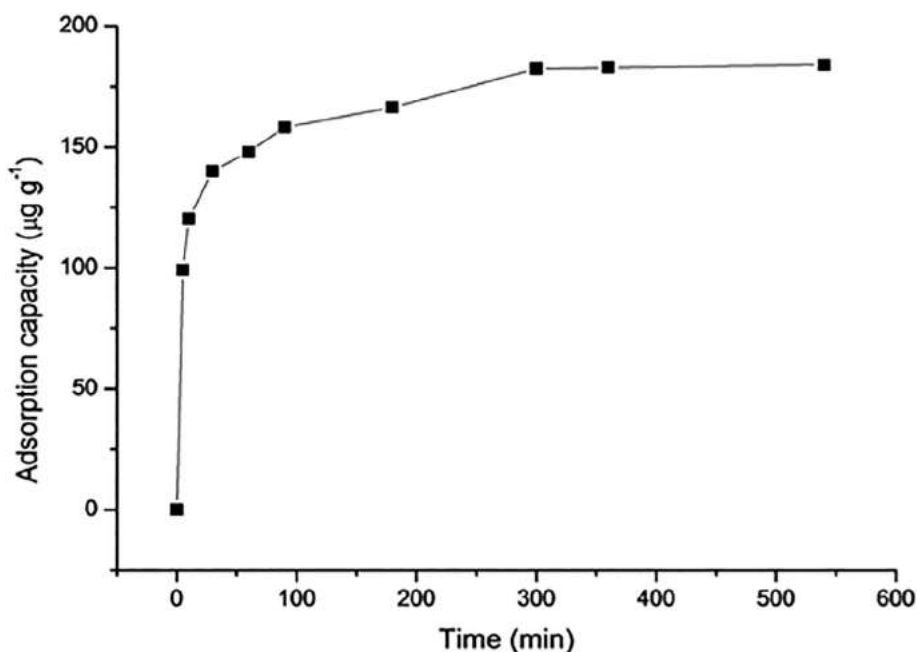
**TABLE 4** Separation factor for the adsorption of Pt(IV) at different concentration

| Concentration (mg/L) | $R_L$     |
|----------------------|-----------|
| 0.5                  | 0,670,684 |
| 1.0                  | 0,504,534 |
| 2.0                  | 0,337,375 |
| 5.0                  | 0,169,201 |
| 10.0                 | 0,092,419 |

**TABLE 5** Three-parameter adsorption isotherms for the adsorption of Pt(IV) by SBYFZ

| Sips  |            |            |       | Redlich-Peterson   |         |            |       | Toth       |       |            |       |
|-------|------------|------------|-------|--------------------|---------|------------|-------|------------|-------|------------|-------|
| $n_s$ | $K_s$ L/mg | $q_m$ mg/g | $R^2$ | $\alpha_R$ mg/L    | $\beta$ | $k_R$ mg/g | $R^2$ | $q_m$ mg/g | $n_T$ | $b_T$ mg/g | $R^2$ |
| 0.26  | 96.19      | 0.34       | 0.73  | $2.32 \times 10^3$ | 0.44    | 399        | 0.61  | 0.65       | 0.89  | 0.93       | 0.73  |

**FIGURE 6** Role of contact time on the adsorption of Pt(IV) by SBYFZ (pH 2, concentration = 2 mg/L, mass = 100 mg, temp = 25°C,  $n = 3$ , variance = 2,616, RSD <5%). RSD, relative standard deviation; SBYFZ, spent brewer's yeast-functionalized zeolite



### 3.3 | Effect of adsorbent dosage

The adsorption capacity of Pt(IV) was inversely proportional to the SBYFZ dosage. The volume of the samples was fixed at 10 ml, therefore, the adsorption capacity was only affected by changing the mass of the adsorbent (Figure 3). The adsorption efficiency increased with an adsorbent dosage between 5 and 10 g/L due to an increasing amount of active sites. Beyond 10 g/L, the efficiency decreased and remained fairly similar at ~88%. The maximum efficiency (~91%) was attained at 100 mg SBYFZ, and thus the adsorbent dosage of 10 g/L should be considered in industrial wastewaters containing Pt(IV). This dosage was used for subsequent experiments. Since the adsorption of Pt(IV) was high when yeast was used but very low when only the zeolite was used, it was clear that the uptake of Pt(IV) was due to affinity for the spent yeast. Therefore, zeolite was only used as bed support for the yeast.

### 3.4 | Effect of pH

The pH of solutions has been found to affect the adsorption capacity of elements hence the role of pH was studied.<sup>4,8</sup> The recovery of Pt(IV) by SBYFZ decreased with increasing pH, due to the changing speciation of Pt(IV) and the adsorbent surface charge (Figure 4). At pH 2–3, where the HCl concentration is high, the dominating platinum species of Pt(IV) is  $\text{PtCl}_6^{2-}$ , which was electrostatically

attracted to the positively charged adsorbent surface influenced by a high concentration of hydronium ions ( $\text{H}_3\text{O}^+$ ). These ions protonated the amino acids of the yeast leading to  $\text{R}-\text{NH}_3^+$  groups (where

R represents the amino acid chains), which interacted with the negatively charged species.<sup>4</sup> The adsorption capacity decreased beyond pH 2 even though the solution was still acidic, and this was

**TABLE 6** Kinetic models parameters for the adsorption of Pt(IV) by SBYFZ

| $q_e$ (exp) mg/g | Pseudo-first-order             |                    |       | Pseudo-second-order                      |                    |       | Elovich                                |                  |       |
|------------------|--------------------------------|--------------------|-------|------------------------------------------|--------------------|-------|----------------------------------------|------------------|-------|
|                  | $k_1 \text{ min}^{-1} 10^{-3}$ | $q_e \text{ mg/g}$ | $R^2$ | $k_2 \text{ g mg}^{-1} \text{ min}^{-1}$ | $q_e \text{ mg/g}$ | $R^2$ | $a \text{ mg g}^{-1} \text{ min}^{-1}$ | $b \text{ g/mg}$ | $R^2$ |
| 0.20             | 5.4                            | 0.09               | 0.82  | 2.04                                     | 0.19               | 0.99  | 3,900                                  | 0.019            | 0.98  |

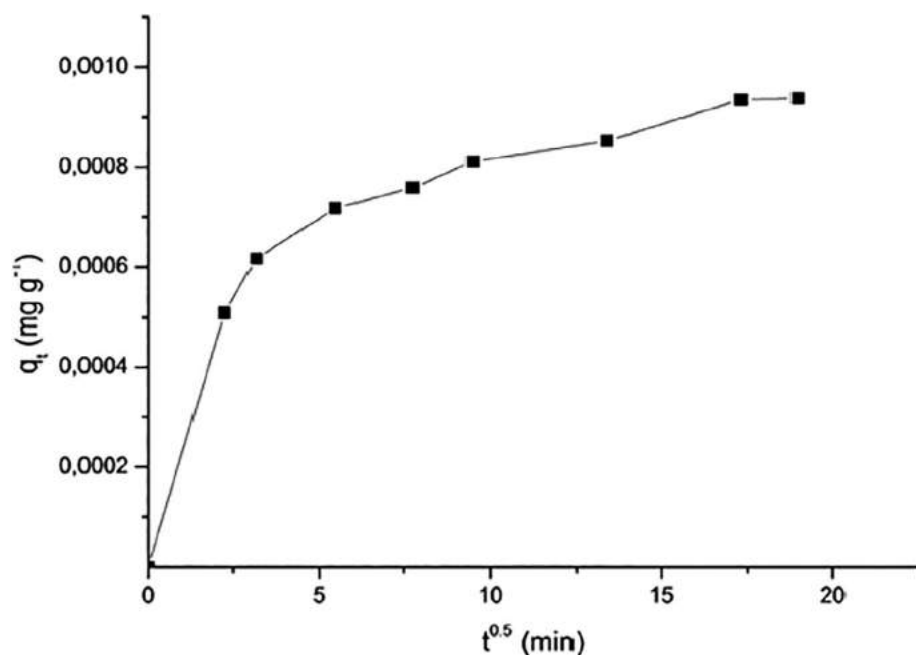


**FIGURE 7** Intra-particle diffusion model for the capturing of Pt(IV) by SBYFZ. SBYFZ, spent brewer's yeast-functionalized zeolite

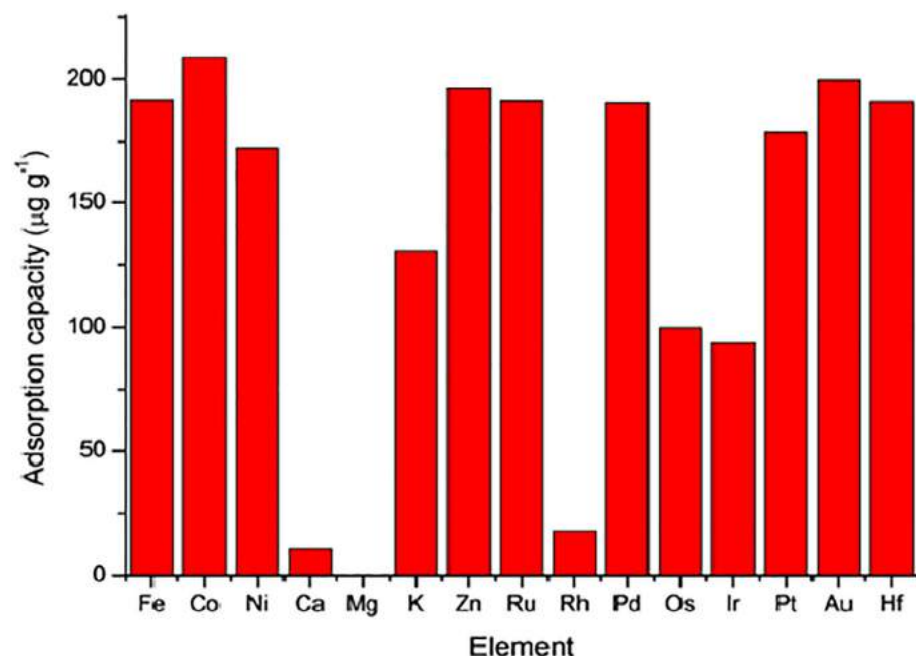


**FIGURE 8** Effect of competing ions on the adsorption of Pt(IV) by SBYFZ (pH 2, concentration = 2 mg/L, time = 300 min, mass = 100 mg, temp = 25°C,  $n = 3$ , RSD < 5%). RSD, relative standard deviation; SBYFZ, spent brewer's yeast-functionalized zeolite [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

attributed to decreasing chloride ions due to reduced concentration of HCl. The reduction in adsorption capacity beyond pH 3 was significant ( $p < .05$ ), and this was ascribed to the possible electrostatic repulsions between the negatively charged hydroxide species of Pt(IV) and the adsorbent surface since the hydroxide concentration was high. Thus, Pt(IV) will be significantly recovered by the SBYFZ when the pH of mining wastewater is highly acidic. This is a good attribute of the adsorbent since, acids such as HCl are constantly used during PGEs processing, therefore, the wastewater is normally highly acidic, and the Pt(IV) species are highly likely to be found in the  $\text{PtCl}_6^{2-}$  form.<sup>31</sup> The PZC of the functionalized adsorbent was found to be 6.3; however, the positive character decreased as pH increased hence the observed effect.

### 3.5 | Effect of initial concentration

The amount of the analyte adsorbed increased significantly with an initial concentration of Pt(IV) due to the accessibility of active sites but this was up to 5 mg/L after which saturation of the adsorbent was

observed (Figure 5).<sup>32</sup> The adsorption efficiency was found to be 64, 78, 91, 67, and 35% at 0.5, 1, 2, 5, and 10 mg/L, respectively. Thus, the adsorbent will be more efficient at concentrations lower than 5 mg/L. This makes the SBYFZ a good adsorbent for Pt(IV) recovery since the concentrations in wastewaters are very low. The decrease in efficiency was ascribed to the exhaustion of active sites with the given amount (100 mg) of the adsorbent.

The Langmuir isotherm described the adsorption data better ( $R^2 > 0.98$ ). Meaning that Pt(IV) was likely bound only to amine groups in a monolayer fashion where the active sites are identical and have similar adsorption energies.<sup>8</sup> The mean free energy was found to be 11.4 kJ/mol, meaning that the adsorption of Pt(IV) is likely due to the strong chemical ion-exchange (Table 3).<sup>20</sup>

The separation factor (Table 4) was found to be between 0 and 1, indicating that the adsorption of Pt(IV) by SBYFZ was favorable hence suitable to capture Pt(IV) from mining wastewaters.

The Sips model fitted the data better than the Redlich-Peterson model. However, since the coefficient of determination is lower than that of the Langmuir isotherm, it was discarded as a possible empirical model for the adsorption of Pt(IV) by SBYFZ (Table 5).

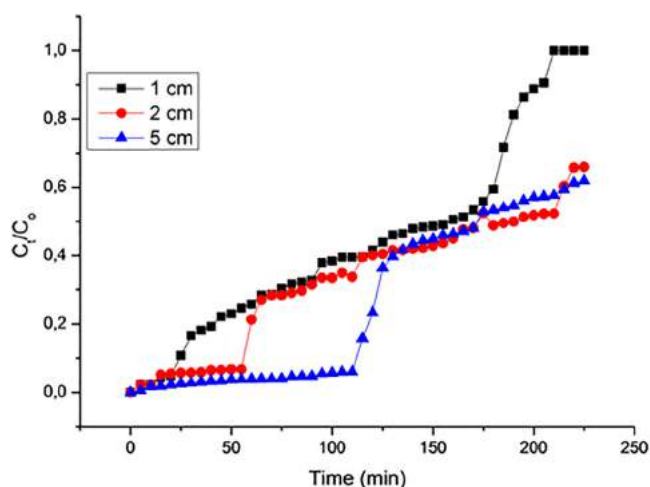


**FIGURE 9** Role of SBYFZ bed height on the adsorption of Pt(IV) (pH 2, concentration = 2 mg/L, temp = 25°C,  $n = 3$ , variance = 0.15, 0.15, 0.25 for 1, 2 and 5 cm, respectively, RSD < 5%). RSD, relative standard deviation; SBYFZ, spent brewer's yeast-functionalized zeolite [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

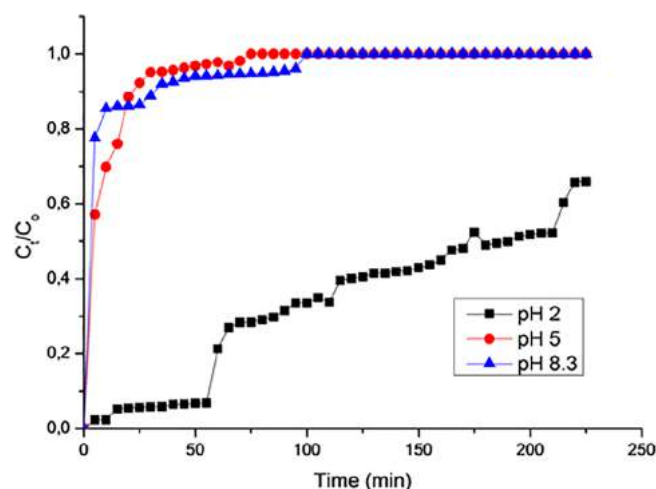


**FIGURE 10** Role of pH on the adsorption of Pt(IV) by SBYFZ (concentration = 2 mg/L, temp = 25°C,  $n = 3$ , variance = 0.15, 0.051, 0.014 for pH 2, 5, and 8, respectively, RSD < 5%). RSD, relative standard deviation; SBYFZ, spent brewer's yeast-functionalized zeolite [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

**TABLE 7** The column adsorption parameters for the adsorption of Pt(IV) by SBYFZ

| $C_0$ mg/L | $Q_v$ ml/min | Z cm | pH   | $m_{\text{adsorbent}}$ g | $V_{\text{eff}}$ ml | $t_B$ min | $C_B$ mg/L | $Q_B$ mg/g |
|------------|--------------|------|------|--------------------------|---------------------|-----------|------------|------------|
| 2.1        | 1.11         | 1    | 2.01 | 1.24                     | 911                 | 125       | 0.97       | 0.19       |
| 2.1        | 1.11         | 2    | 2.01 | 1.84                     | 911                 | 165       | 1.0        | 0.17       |
| 2.1        | 1.11         | 5    | 2.01 | 3.11                     | 830                 | 180       | 1.0        | 0.10       |
| 5.0        | 1.11         | 2    | 2.01 | 1.84                     | 75                  | 125       | 1.0        | 0.20       |
| 2.1        | 1.11         | 2    | 5.02 | 1.83                     | 911                 | 5         | 1.0        | 0.015      |
| 2.1        | 1.11         | 2    | 8.3  | 1.84                     | 911                 | 5         | 1.0        | 0.0038     |

### 3.6 | Effect of contact time

The adsorption capacity was significant within the first 30 min because of the availability of amine active sites. Beyond 30 min, the adsorption capacity increased slowly until 300 min, after which the adsorption of Pt(IV) reached equilibrium (Figure 6).

The coefficient of determination of pseudo-second-order was higher ( $R^2 > 0.99$ ) than that of other models, indicating that it describes the kinetic data better (Table 6). Thus, the interaction of Pt(IV) with SBYFZ was strong and possibly chemical adsorption rather than physical adsorption was responsible for the interaction.<sup>8</sup> The Elovich model, which better describes adsorption processes that are chemisorptive in nature also significantly described the kinetic data, further confirming that the adsorption of Pt(IV) is possibly through chemisorption.<sup>33</sup>

The adsorption mechanism was also determined by the intra-particle diffusion model (Figure 7). The adsorption of Pt(IV) by SBYFZ was in two phases. The first phase was observed during the

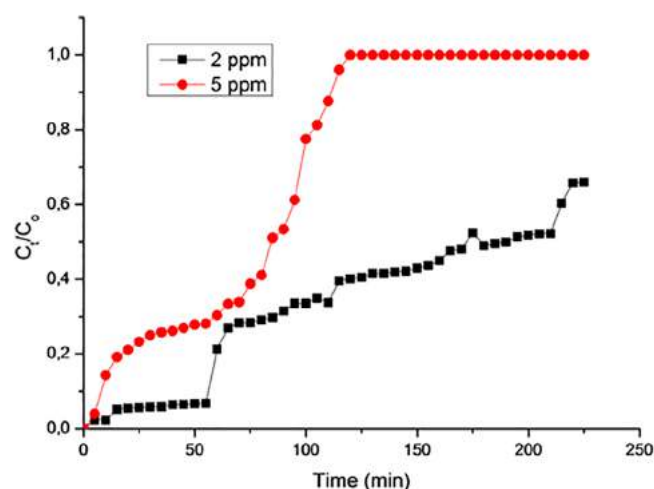


**FIGURE 11** Role of influent concentration on the adsorption of Pt(IV) by SBYFZ (pH 2, concentration = 2 mg/L, temp = 25°C,  $n = 3$ , variance = 0.15 and 0.73 for 2 and 5 ppm, respectively, RSD <5%). RSD, relative standard deviation; SBYFZ, spent brewer's yeast-functionalized zeolite [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

initial stages of uptake where the adsorption was through mass transfer, and the second one was through intra-particle diffusion.

### 3.7 | Effect of competing ions

The adsorption efficiency of Pt(IV) went down by 5% in the presence of other ions, but the recovery was still significant (Figure 8). Other precious elements such as Ru(III), Pd(II), Ir(III), Rh(III), and Au(I) were significantly adsorbed. Therefore, the adsorbent can be used for the recovery of these elements. Contaminants such as Fe(II), Co(II), Ni(II), K(I), and Zn(II) were also significantly removed, thus, the adsorbent will recover precious elements while removing unwanted contaminants in wastewater. This will reduce wastewater clean-up costs.

### 3.8 | Column adsorption studies

Different bed depths had a different effect on breakthrough and exhaustion times (Figure 9). Shorter bed depth having a low amount of active sites had the shortest breakthrough and exhaustion times, whereas longer adsorbent depths were associated with longer breakthrough times and higher influent volume. At higher bed depths there are more amine groups that can capture Pt(IV) hence the observed trends. The uptake of Pt(IV) capacity decreased with increasing depth as observed in the column sorption data (Table 7).

The role of pH as determined from column experiments complemented that, which was obtained from batch experiments as they showed that pH 5 and 8.3 significantly decreased the adsorption of Pt(IV) and led to a very small breakthrough and exhaustion times (Figure 10). There was no significant difference ( $p > .05$ ) on the adsorption of Pt(IV) between these pH values. The column experiments indicated that the adsorbent will significantly remove Pt(IV) from wastewaters when the pH is highly acidic.

The role of influent concentration on the adsorption of Pt(IV) by functionalized adsorbent was also assessed, and the results indicated that the breakthrough and exhaustion times will be reached faster with high concentrations (Figure 11). The adsorption capacity increased with concentration probably due to faster transport of Pt(IV) onto the adsorbent surface, which was influenced by diffusion coefficient or mass transfer coefficient.

**TABLE 8** Column models parameters under different conditions

| C <sub>0</sub><br>mg/L | Q <sub>v</sub><br>ml/min | Z<br>cm | pH   | k <sub>AB</sub> L<br>mg <sup>-1</sup> min <sup>-1</sup> | N <sub>0</sub><br>mg/L | R <sup>2</sup> | k <sub>Th</sub> L<br>min <sup>-1</sup> mg <sup>-1</sup> | q <sub>0</sub><br>mg/g | R <sup>2</sup> | K <sub>YN</sub><br>min <sup>-1</sup> | τ<br>min | R <sup>2</sup> |
|------------------------|--------------------------|---------|------|---------------------------------------------------------|------------------------|----------------|---------------------------------------------------------|------------------------|----------------|--------------------------------------|----------|----------------|
| 2                      | 1.11                     | 1       | 2.01 | 0.0091                                                  | 246                    | 0.74           | 0.010                                                   | 0.23                   | 0.84           | 0.019                                | 118      | 0.84           |
| 2                      | 1.11                     | 2       | 2.01 | 0.011                                                   | 153                    | 0.86           | 0.014                                                   | 0.15                   | 0.89           | 0.028                                | 125      | 0.89           |
| 2                      | 1.11                     | 5       | 2.01 | 0.012                                                   | 82                     | 0.83           | 0.014                                                   | 0.12                   | 0.88           | 0.029                                | 166      | 0.88           |
| 5                      | 1.11                     | 2       | 2.01 | 0.0036                                                  | 99                     | 0.80           | 0.010                                                   | 0.079                  | 0.80           | 0.049                                | 27       | 0.80           |
| 2                      | 1.11                     | 2       | 5.03 | 0.0010                                                  | 9.4                    | 0.96           | 0.088                                                   | 0.006                  | 0.95           | 0.18                                 | 4.8      | 0.96           |
| 2                      | 1.11                     | 2       | 8.3  | 0.0007                                                  | 7.3                    | 0.82           | 0.022                                                   | 0.038                  | 0.83           | 0.045                                | 31       | 0.83           |

### 3.9 | Column adsorption models

The Adams-Bohart model (Table 8) indicated that the saturation concentration decreased as the bed depth increased, while the mass transfer coefficient increased. Thus, the adsorption of Pt(IV) by SBYFZ was influenced by mass transfer. At higher concentrations, the transport of Pt(IV) onto the adsorbent through mass transfer was not prevalent. The Thomas model gave a better fit for the experimental data than the Adams-Bohart model since the coefficient of determination ranged between 0.80 and 0.96, therefore, adsorption was limited by mass transfer (Table 8). The  $k_{Th}$  values were higher with longer bed depths and lower concentrations. The value of  $q_0$  decreased with bed depth and significantly decreased with higher concentration. Thus, the adsorbent will work best at lower concentrations. Both  $K_{YN}$  and  $\tau$  from the Yoon-Nelson model were directly proportional to bed depth.

The coefficient of determination ( $R^2$ ) indicated that both the Thomas and the Yoon-Nelson models can be used to explain the adsorption of Pt(IV) onto the SBYFZ in a flow-through column system.

## 4 | CONCLUSION

The recovery of precious elements from wastewaters using cheap and efficient materials is crucial especially now since the ore grades are drastically declining and significant amounts of these elements are generally lost daily as waste. The current methods of recovery are expensive and the efficiency is often less than 75%. In this study, the widely available zeolite clay material was used as a bed for spent yeast waste in order to come up with a cheap adsorbent for the recovery of Pt(IV). The raw zeolite and spent yeast poorly adsorbed Pt(IV) as separated entities, but SBYFZ was efficient. SBYFZ should be considered at a dosage of 10 g/L and at wastewater concentrations lower than 5 mg/L in order to significantly recover Pt(IV). The adsorbent will work best at highly acidic pH solutions hence the adsorbent should be applied before any neutralization. Other elements such as Pd(II) and Rh(III) may slightly decrease the adsorption capacity of Pt(IV) due to competition for amine actives sites; however, this is not a loss as these are still precious elements. The adsorption isotherms indicated that the adsorption of Pt(IV) onto SBYFZ was through identical adsorption sites (amine groups) of the adsorbent, and the interaction was a strong chemical ion-exchange. Breakthrough and exhaustion times were longer at highly acidic pH, low concentration, and high bed depth. The yeast-functionalized zeolite was found to be a cheap and efficient adsorbent that can be used to significantly ( $p < .05$ ) recover Pt(IV) and other PGEs from wastewater.

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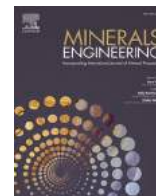
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# PAPER III

**This paper addressed the recovery of Pd(II), Ir(III) and Rh(III) from aqueous solutions by spent brewer's yeast-functionalized zeolite using flow-through column mode.**

**The paper is published in Minerals Engineering.  
Impact Factor: 3.795.**

**Contribution:** lead author, conducted experimental work and data modelling, conceptualization, methodology, software validation, formal analysis, investigation, writing - original draft and visualization.



# Simultaneous recovery of Pd(II), Ir(III) and Rh(III) from aqueous solutions by spent brewer's yeast-functionalised zeolite using flow-through column mode

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Platinum group elements  
Recovery  
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## ABSTRACT

Economies of many countries around the world have been improved by the mining of precious elements such as gold and platinum group elements (PGEs). As such, the demand for these elements has increased over the years, which led to increased rate of mining. However, the resources and reserves of these elements have been reduced as a result. The alarming rate of mining indicates a need for secondary sources for precious elements. This study was aimed at using a cheap and efficient spent brewer's yeast-functionalised zeolite to recover Pd(II), Ir(III) and Rh(III) from aqueous solutions. The solutions represent industrial wastewaters which normally contain PGEs which were lost during processing. The adsorbent bed height, solution pH, initial concentration and flow rate were optimised to obtain the best working conditions of the adsorbent. The bed depth service time, Adams-Bohart, Thomas, Yoon-Nelson, Clark column, Wolborska and modified dose response models were used to evaluate the dynamic behaviour of the column. The maximum recovery was achieved at longer bed height, low concentration ( $2 \text{ mg L}^{-1}$ ) and low flow rate ( $2 \text{ mL min}^{-1}$ ). The speciation of the elements at different conditions motivated the recovery outcome. For example, the dominant species Pd(II) and Ir(III) were negatively charged at highly acidic pH hence, their uptake was favoured by the positively charged surface but, the uptake of Rh(III) was not favoured at these conditions since,  $[\text{RhCl}(\text{H}_2\text{O})_5]^{2+}$  and  $[\text{RhCl}_2(\text{H}_2\text{O})_4]^+$  were dominant and thus, repelled by the adsorbent. The success of the recovery of Pd(II), Ir(III) and Rh(III) from aqueous solutions makes the adsorbent a potential recovery agent in the PGEs mining industrial wastewater.

## 1. Introduction

Precious elements including platinum group elements (PGEs), rare earth elements and gold are widely used in machinery (Wang et al., 2017), phosphors (Unruh and McShane, 2016), thin film solar cells (Xue et al., 2017), medicine (Lazarević et al., 2017) and catalytic converters (Lee et al., 2017), due to their unique physical and chemical properties (Ding et al., 2019). Improvements and the discoveries of many technologies and processes that make life easier are possible due to the availability of these elements. Moreover, the economies of many countries such as South Africa, China, Russia, Canada, India and Brazil have been greatly improved by the mining of precious elements which are also investment commodities (Fujiwara et al., 2007; Ericsson and Löf, 2019). Some of the precious elements such platinum and palladium are forms of currency (Fujiwara et al., 2007). Because of their many uses and demand, precious elements are usually obtained from mineral ores in large quantities thus, their ore deposits have been decreasing over the

years and this poses a serious strain on the sustainability of these elements (Mu et al., 2019; Zhang et al., 2020). Thus, new technologies, methods and innovations designed to recover precious elements from waste solutions are very important especially in this time where many mining companies and other industries using precious elements are closing down due to COVID-19 impact, leading to high rates of unemployment and weak economic growth (McKay, 2020).

Significant concentrations of precious elements have been accumulating in wastewaters over the years but, the current methods are not designed to recover them because of their complex physicochemical characteristics and low concentrations (Ding et al., 2020). The removal of elements from aqueous solutions using conventional methods such as adsorption (Da'na, 2017; Burakov et al., 2018), ion-exchange (Kim and Kwak, 2017), oxidation (Bora and Dutta, 2019), reduction (Sun et al., 2020), solvent extraction (Tanong et al., 2017), membrane separation (Pino et al., 2018) and chemical precipitation (Li et al., 2019) has been reported. Out of all these, the adsorption method has been found to be

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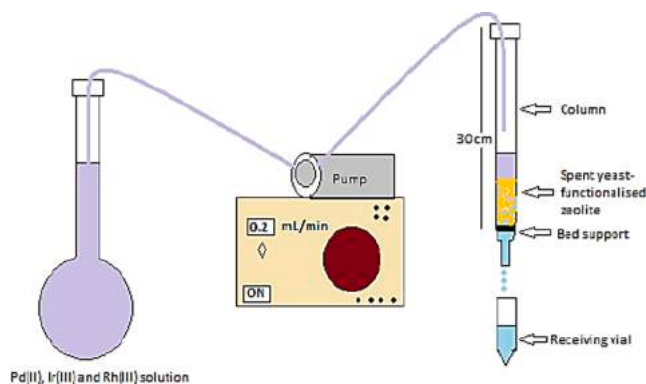


Fig. 1. Column experimental setup for the uptake of Pd(II), Ir(III) and Rh(III) (Mosai et al., 2020).

very efficient and economical. Adsorption entails adhesion of solute particles to a suitable substrate by means of chemical and/or physical interactions (Parlayıcı and Pehlivan 2017). In this study, the adsorption of Pd(II), Ir(III) and Rh(III) was investigated. Studies by Clemente et al. (2018) and Yu et al. (2020) indicated that PGEs can interact with nitrogen or amine ligands. The zeolite clay material was used as a base where amine groups from the spent brewer's yeast could be anchored. The performance of the adsorbent on the recovery of PGEs from aqueous solutions and its applicability in industrial mining wastewaters were assessed using flow through column experiments. The yeast was chosen as a source of nitrogen groups because it is non-toxic, hydrophilic and biocompatible.

Column adsorption experiments are better representations of how adsorbents can behave in real wastewaters (Aichour et al., 2019). The mining and other industries using or producing PGEs can use columns to recover precious elements from wastewaters. This study will provide a benchmark for determining important column parameters such as solution flow rate and adsorbent bed height required for significant recovery of Pd(II), Ir(III) and Rh(III) using spent brewer's yeast-functionalised zeolite in large scale.

## 2. Materials and methods

### 2.1. Functionalisation and characterisation of zeolite

Brewer's spent yeast (40 mL) collected from the microbrewery at the University of the Witwatersrand was mixed with the zeolite clay material (10 g) for 24 h using an elliptical bench-top shaker (Labcon, USA) at room temperature. The functionalised zeolite was filtered and rinsed several times with deionised water. The adsorbent was dried for 24 h at room temperature and stored until required. The collected yeast could have been used without incorporation onto the zeolite but, PGEs-amine complexes would have formed in aqueous solutions. In this case, ultrafiltration method would be required to retrieve the analytes. This would render the recovery process expensive since, ultrafiltration can be costly. This was avoided by using zeolite as a base to hold the amine groups from the yeast tightly so that they do not escape into the solution. The success of functionalisation was tested with Fourier transform infrared spectroscopy (FTIR) (Bruker Tensor 27, Germany) which indicated the functional groups on the zeolite before and after functionalisation. The amount of nitrogen on the zeolite was determined using VarioELcube V4.0.13 (Elementar, Germany). The D2 Phaser powder X-ray diffraction (PXRD) (Bruker, Germany) and X-ray fluorescence (XRF) (PANalytical, Netherlands) were used to determine mineralogy and composition of the zeolite, respectively. The pore size, pore volume and surface area were determined using Flow Prep 060 instrument (Aachen, Germany). The morphology of the natural and functionalised zeolite was determined using scanning electron microscope (SEM) (ThermoFisher Scientific,

USA). The point of zero charge (PZC) was also determined using Surpass 3 electrokinetic analyser (Anton Paar, South Africa).

### 2.2. Column studies

Dynamic flow-through column experiments were conducted using a  $1.2 \times 30$  cm glass column with glass wool at the bottom to provide mechanical support for the adsorbent (Fig. 1) (Hu et al., 2020). The experiments were conducted in triplicates and the percentage relative standard deviation (%RSD) was used to determine the reliability of the data. The flow rate was controlled using Masterflex® peristaltic pump (Cole-Parmer instrument company, USA). The time required to reach 50% of the initial concentration of the analytes was considered to determine the performance of the column. The concentration of PGEs was measured with inductively coupled plasma optical emission spectroscopy (ICP-OES) (Spectro Genesis, Germany). The chemicals used in this study were purchased from Sigma Aldrich, South Africa. HCl and NaOH were used to control the pH which was determined using a pH meter (Mettler Toledo, USA).

The role of bed height (1, 2 and 5 cm) on the recovery of Pd(II), Ir(III) and Rh(III) was studied at pH 2, 2 mL min<sup>-1</sup> flow rate and 2 mg L<sup>-1</sup> initial concentration. The performance of adsorbents can be highly dependent on solution pH hence, the role of pH (2, 5 and 8) on the uptake of Pd(II), Ir(III) and Rh(III) by yeast-functionalised zeolite was investigated (Fujiwara et al., 2007). Industrial wastewaters may contain varying concentrations of elements which may also affect the performance of adsorbents thus; the impact of initial concentration (1, 2 and 10 mg L<sup>-1</sup>) was determined (Mnasri-Ghnnimi and Frini-Srasra, 2019). The role of flow rate (2, 5 and 7 mL min<sup>-1</sup>) was studied since; studies have indicated that flow rate can influence the uptake of elements (Hamdaoui, 2009; Zhang et al., 2019).

The adsorption capacity of the elements at 50% breakthrough was determined using Eq. (1) (Van et al., 2019).

$$Q_{50\%} = Q_v \left( C_0 - \frac{C_{50\%}}{2} \right) \frac{t_{50\%}}{m_{\text{adsorbent}}} \quad (1)$$

where  $Q_v$  (mL min<sup>-1</sup>) is flow rate,  $C_0$  (mg L<sup>-1</sup>) and  $C_{50\%}$  (mg L<sup>-1</sup>) are the initial and breakthrough concentrations, respectively,  $t_{50\%}$  (min) is time at 50% breakthrough and  $m_{\text{adsorbent}}$  (g) is the mass of the adsorbent in the column.

### 2.3. Data analysis

Bed depth service time (BDST) model which considers the relationship between bed height and service time was used to determine the performance of the adsorbent. The model assumes that the column bed depth and service time have a linear relationship due to the impact of inlet concentration and adsorption parameters. Another assumption for this model is that the intra-particle diffusion and external mass transfer resistance forces are negligible (Yakout et al., 2018). The BDST model can be expressed as:

$$t = \left( \frac{N_0 Z}{C_0 V} \right) - \left( \frac{1}{K_0 C_0} \right) \ln \left( \frac{C_0}{C_t} - 1 \right) \quad (2)$$

where  $t$  (min) is the breakthrough time,  $V$  (cm min<sup>-1</sup>) is the influent linear velocity,  $N_0$  (mg L<sup>-1</sup>) is the saturation concentration,  $Z$  (cm) is the bed height and  $K_0$  (L mg<sup>-1</sup> min<sup>-1</sup>) is the rate constant in BDST model.

The Adams-Bohart, Thomas, Yoon-Nelson, Clark column, Wolborska and modified dose response models were used to evaluate the dynamic behaviour of the column. The Adams-Bohart model can describe surface reactions occurring in the initial part of the breakthrough curve. This model assumes that the rate of uptake of elements is directly proportional to the concentration of the elements in the solution and the uptake ability of the adsorbent (Bohart and Adams, 1920). The model can be expressed as:

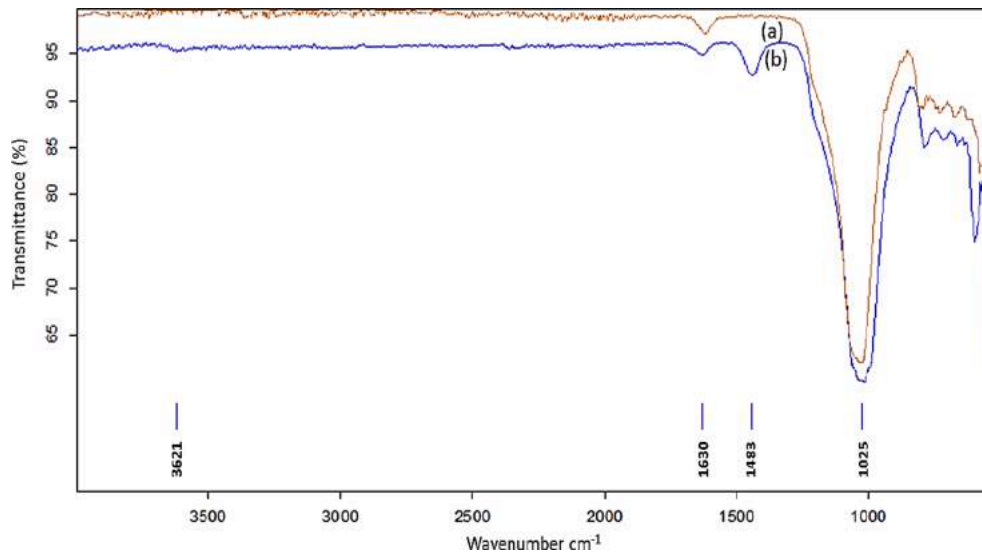


Fig. 2. FTIR spectra of the (a) natural zeolite and (b) spent yeast-functionalised zeolite.

$$\ln\left(\frac{C_o}{C_t} - 1\right) = k_{AB}C_o t - \frac{k_{AB}N_o Z}{V} \quad (3)$$

where  $k_{AB}$  ( $L \text{ mg}^{-1} \text{ min}^{-1}$ ) is the adsorption rate constant, and  $V$  ( $\text{cm}^3$ ) is the superficial velocity.

The Thomas model assumes that the interaction of the elements and the adsorbent at the interface is not due to a chemical reaction but through mass transfer (Thomas, 1944). The Thomas model equation is represented below:

$$\ln\left(\frac{C_o}{C_t} - 1\right) = \frac{k_{Th}q_o m_{adsorbent}}{Q_v} - k_{Th}C_o t \quad (4)$$

where  $k_{Th}$  ( $L \text{ min}^{-1} \text{ mg}^{-1}$ ) is the Thomas rate constant and  $q_o$  ( $\text{mg g}^{-1}$ ) is the equilibrium adsorption capacity.

The breakthrough time of elements can be determined using the Yoon-Nelson model, which assumes that the rate of decrease in the probability of adsorption of analytes is proportional to the probability of adsorption of analytes and the probability of breakthrough of elements (Yoon and Nelson, 1984; Aksu and Gönen, 2004). The model can be expressed as:

$$\ln\left(\frac{C_t}{C_o - C_t}\right) = k_{YN}t - \tau k_{YN} \quad (5)$$

where  $k_{YN}$  ( $\text{min}^{-1}$ ) is the Yoon-Nelson rate constant and  $\tau$  ( $\text{min}$ ) is the time required for an element to reach 50% breakthrough.

The Clark model which describes the adsorption of elements in a fixed-bed system due to the combination of mass transfer concept and the Freundlich isotherm was also used (Hu et al., 2020). This model also describes the plug flow behaviour of a fixed-bed system. The Clark model equation is given in Eq. (6) (Patel, 2019).

$$\frac{C_t}{C_o} = \frac{1}{(1 + Ae^{-rt})^{1/(n-1)}} \quad (6)$$

where  $A$  is a Clark constant,  $r$  ( $\text{min}^{-1}$ ) is Clark or fractal-like Clark constant and  $n$  is Freundlich constant.

Wolborska came up with a model that describes the concentration distribution of elements in a fixed-bed for the low concentration range of the breakthrough using the equations of mass transfer for diffusion mechanisms (Hamdaoui, 2009). This is known as the Wolborska model and can be expressed as:

$$\ln \frac{C_t}{C_o} = \frac{\beta C_o t}{N_o} - \frac{\beta Z}{V} \quad (7)$$

where  $\beta$  ( $\text{h}^{-1}$ ) is the kinetic coefficient of the external mass transfer expressed as:

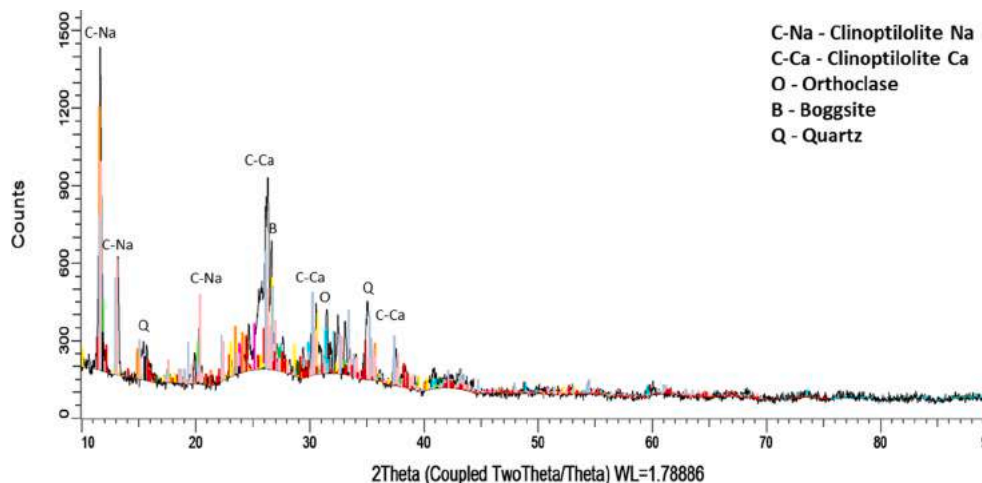


Fig. 3. PXRD pattern of the natural zeolite.

**Table 1**  
Porosity characteristics of the natural and functionalised zeolite.

| Sample                       | Pore size (nm) | Pore volume (cm <sup>3</sup> g <sup>-1</sup> ) | Surface area (m <sup>2</sup> g <sup>-1</sup> ) |
|------------------------------|----------------|------------------------------------------------|------------------------------------------------|
| Natural zeolite              | 12.97          | 0.052                                          | 16.28                                          |
| Yeast-functionalised zeolite | 5.45           | 0.053                                          | 5.31                                           |

$$\beta = \frac{V^2}{2D} \left( \sqrt{1 + \frac{4\beta_o D}{V^2}} - 1 \right) \tag{8}$$

where D (mm<sup>2</sup> h<sup>-1</sup>) is axial diffusion coefficient and β<sub>o</sub> is the external mass transfer coefficient.

Modified dose response model was also used in this study. It has been found to minimise the error from the Thomas model at lower and higher

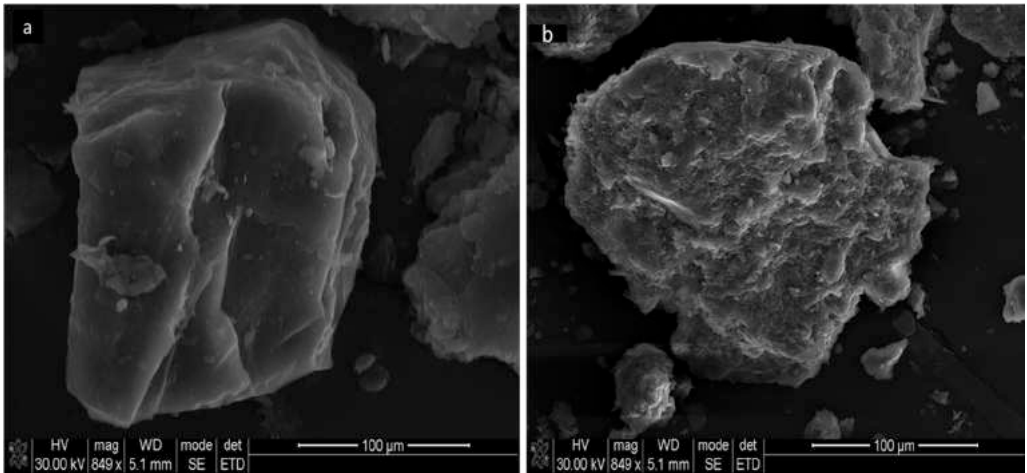


Fig. 4. SEM micrographs of the (a) natural zeolite and (b) yeast-functionalised zeolite.

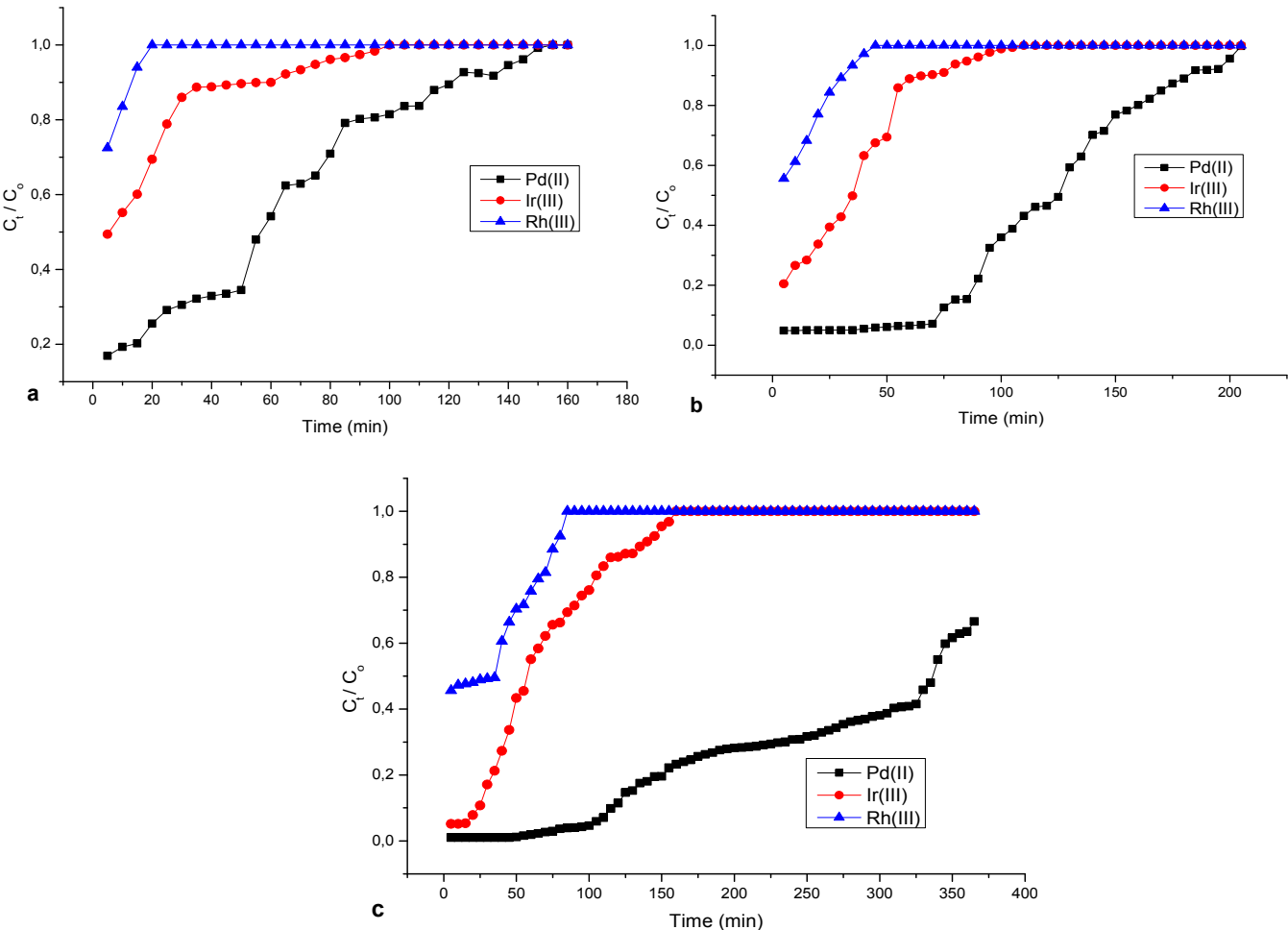


Fig. 5. Role of (a) 1 cm, (b) 2 cm and (c) 5 cm bed height on the adsorption of Pd(II), Ir(III) and Rh(III) by yeast-functionalised zeolite.

**Table 2**

Column parameters of the uptake of Pd(II), Ir(III) and Rh(III) by spent yeast-functionalised zeolite.

| Z (cm) | pH | Q <sub>v</sub> (mL min <sup>-1</sup> ) | C <sub>o</sub> (mg L <sup>-1</sup> ) | Pd(II)<br>t <sub>e</sub> (min) | Q <sub>50%</sub> (mg g <sup>-1</sup> ) | Ir(III)<br>t <sub>e</sub> | Q <sub>50%</sub> | Rh(III)<br>t <sub>e</sub> | Q <sub>50%</sub> |
|--------|----|----------------------------------------|--------------------------------------|--------------------------------|----------------------------------------|---------------------------|------------------|---------------------------|------------------|
| 1      | 2  | 2                                      | 2                                    | 155                            | 0.17                                   | 100                       | 0.015            | 20                        | 0.008            |
| 2      | 2  | 2                                      | 2                                    | 205                            | 0.16                                   | 110                       | 0.025            | 40                        | 0.007            |
| 5      | 2  | 2                                      | 2                                    | 630                            | 0.17                                   | 155                       | 0.026            | 75                        | 0.015            |
| 2      | 2  | 2                                      | 1                                    | 345                            | 0.14                                   | 145                       | 0.035            | 75                        | 0.005            |
| 2      | 2  | 2                                      | 10                                   | 120                            | 0.13                                   | 45                        | 0.054            | 30                        | 0.027            |
| 2      | 5  | 2                                      | 2                                    | 160                            | 0.081                                  | 25                        | 0.005            | 75                        | 0.027            |
| 2      | 8  | 2                                      | 2                                    | 210                            | 0.19                                   | 25                        | 0.005            | 205                       | 0.16             |
| 2      | 2  | 5                                      | 2                                    | 80                             | 0.054                                  | 55                        | 0.027            | 35                        | 0.005            |

time periods of the breakthrough curve (Yan et al., 2001). This model can be expressed as:

$$\ln \frac{C_t}{C_o - C_t} = \alpha \ln(C_o V_{\text{eff}}) - \alpha \ln(q_{\text{mdr}} m) \quad (9)$$

where  $\alpha$  is modified dose response model constant,  $V_{\text{eff}}$  is the volume of the analyte solution passed into the column,  $q_{\text{mdr}}$  (mg g<sup>-1</sup>) is the maximum solid phase concentration of the analyte and  $m$  is the mass of the adsorbent in the column.

### 3. Results and discussion

#### 3.1. Characterisation

Functional groups of the natural and functionalised zeolite materials were characterised using FTIR and the spectra of both materials indicated that there were absorbance peaks at approximately 1025 cm<sup>-1</sup> (Fig. 2). These were due to the Si-O(Si) and Si-O(Al) internal vibrations

whose intensities indicated that they were in high amounts (Mirzaei et al., 2019). The absorbance peaks at 1630 and 3621 cm<sup>-1</sup> on both materials were due to the zeolite water bending mode and hydroxyl groups, respectively (Çalışkan et al., 2019). Berestova et al. (2017) investigated the FTIR spectra of different amino acids and found that absorbance peaks between 1444 and 1588 cm<sup>-1</sup> were due to NH<sub>2</sub> functional groups of the amino acids. Therefore, the 1483 cm<sup>-1</sup> band observed only on the yeast-functionalised zeolite was due to the NH<sub>2</sub> groups of amino acids in the yeast. The CHNS elemental analysis indicated that the amount of nitrogen in the natural zeolite increased from 0.06% to 0.78% after the addition of yeast, further confirming the success of functionalisation. The PXRD results (Fig. 3) indicated that clinoptilolite-Na, clinoptilolite-Ca and quartz were dominating the natural zeolite. There were strong peaks at  $2\theta = 11.5^\circ$ ,  $13^\circ$  and  $26^\circ$  which indicated the zeolite used was clinoptilolite with a formula: (Na, Ca)<sub>6</sub>(Si, Al)<sub>36</sub>O<sub>72</sub>·20H<sub>2</sub>O (Mirzaei et al., 2019). The mineralogy of the zeolite did not change after functionalisation. The chemical composition was determined using XRF which indicated that the zeolite was composed of

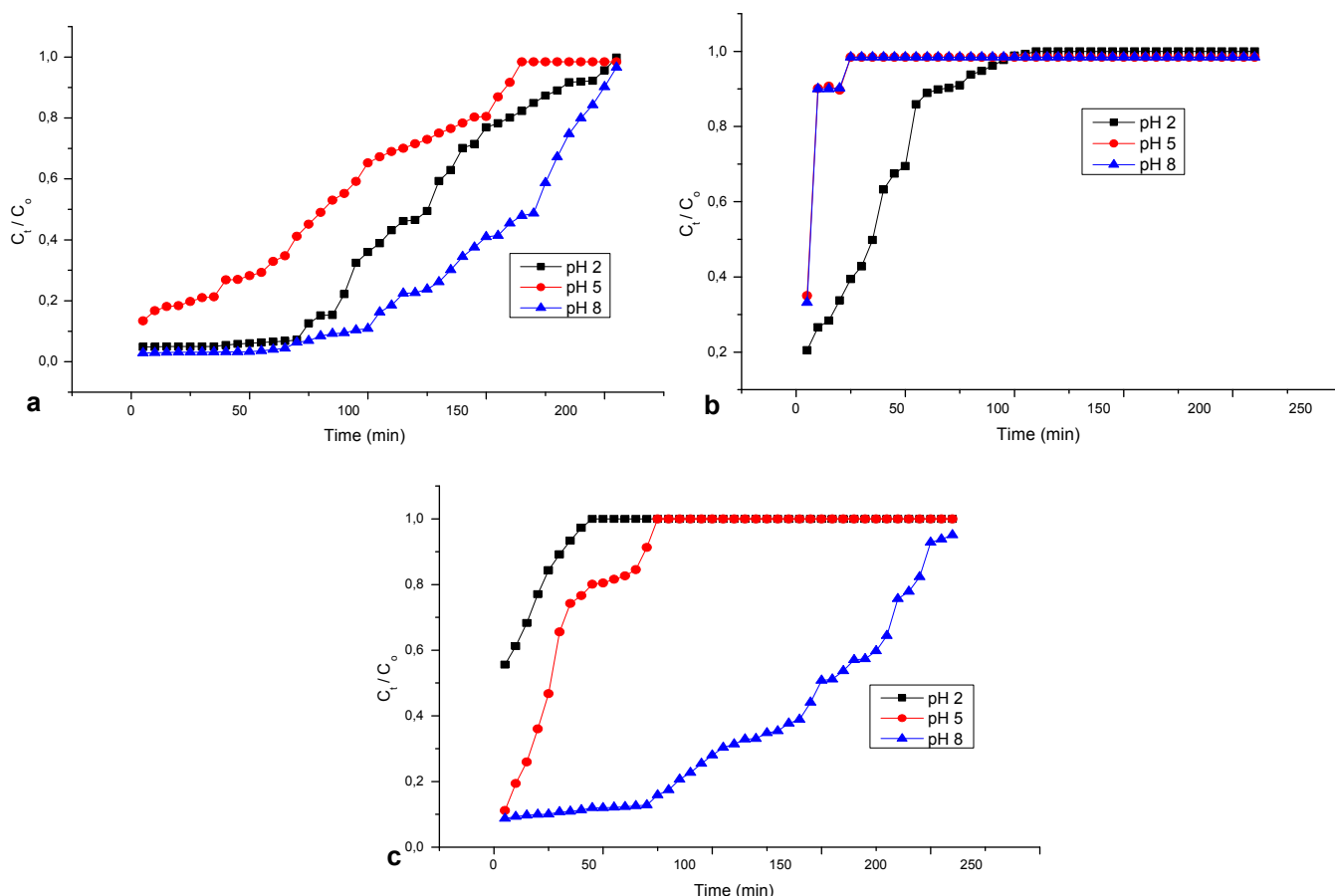


**Fig. 6.** Adsorption of (a) Pd(II), (b) Ir(III) and (c) Rh(III) by yeast-functionalised zeolite at different pH values.

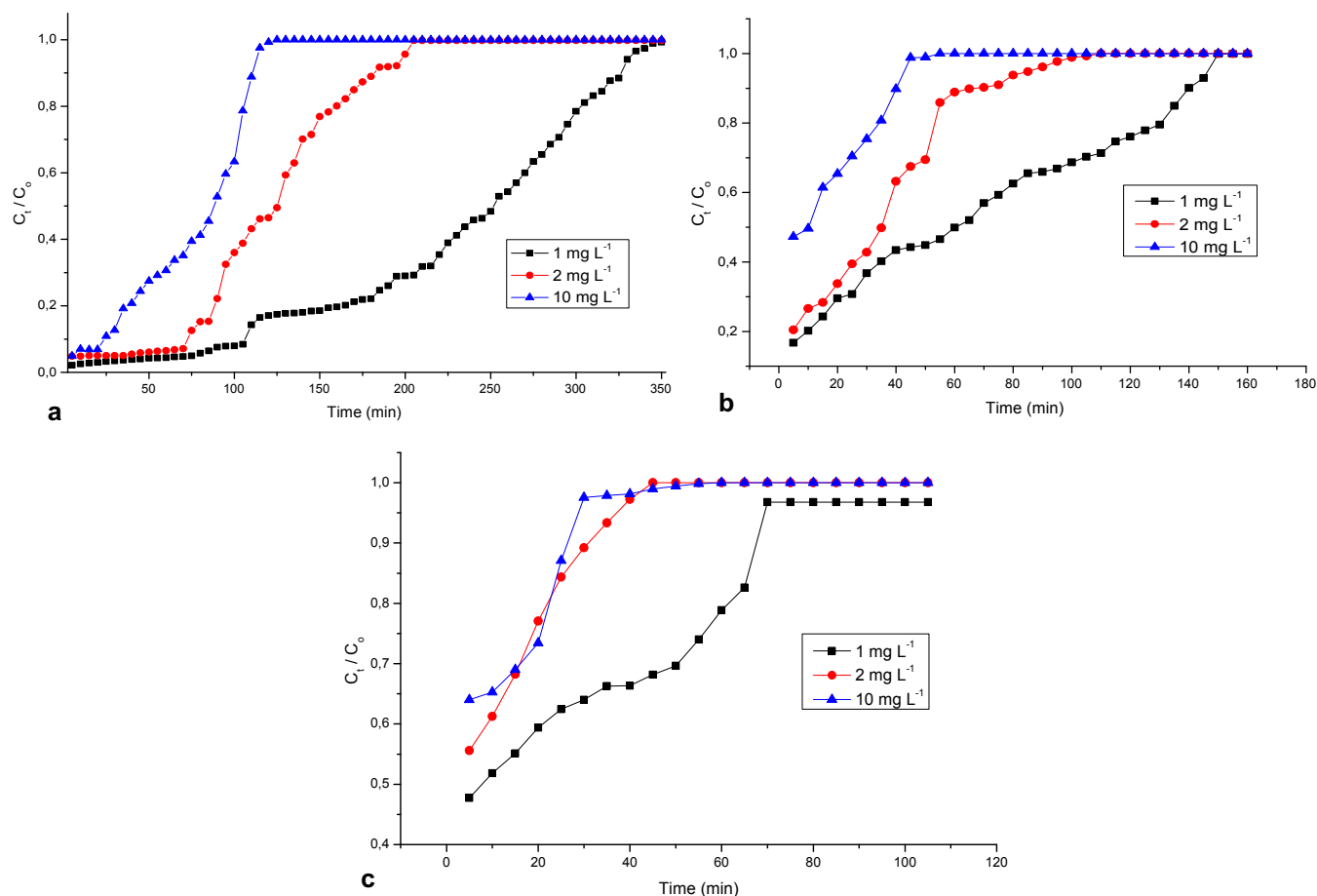


Fig. 7. Role of initial concentration on the uptake of (a) Pd(II), (b) Ir(III) and (c) Rh(III) by yeast-functionalised zeolite.

64.49% SiO<sub>2</sub>, 11.48% Al<sub>2</sub>O<sub>3</sub>, 3.79% K<sub>2</sub>O, 1.47% Na<sub>2</sub>O, 1.22% CaO and 1.09% Fe<sub>2</sub>O<sub>3</sub> with loss on ignition of 11.03%. The surface area and pore size of the natural zeolite decreased after functionalisation as a result of smothered pores by the yeast (Table 1). Based on the decreased pore size and increased pore volume of zeolite after the addition of yeast, it can be concluded that the yeast functional groups are situated on the surface of the zeolite. The SEM micrographs of the natural and functionalised zeolite are shown in Fig. 4. The roughness of natural zeolite increased after the addition of yeast (Golie and Upadhyayula, 2016). This indicated the success of functionalisation with yeast. In essence, zeolite was only a support for amine groups from the yeast.

### 3.2. Role of adsorbent bed height

Adsorbent bed height is one of the most important parameters to investigate when using flow-through columns for recovery (Golie and Upadhyayula, 2016). The adsorption of Pd(II), Ir(III) and Rh(III) was investigated at 1, 2 and 5 cm yeast-functionalised zeolite which contained 1.029, 2.277 and 4.7510 g of the adsorbent, respectively (Fig. 5). The uptake of the elements was different for the different bed heights ( $p < 0.05$ ) at pH 2, 25 °C, 2 mL min<sup>-1</sup> flow rate and 2 mg L<sup>-1</sup> solution concentration. The breakthrough curves indicated that the adsorbent was able to capture Pd(II) for a longer period of time than other elements, and this was attributed to the speciation of the elements at these conditions as well as the affinity of Pd(II) for the adsorbent. The uptake of the elements was proportional to bed height as a result of increasing amount of active sites. This was indicated by breakthrough curves shifting to the right and increasing maximum tolerance time ( $t_e$ ) for each element (Table 2). Similar results were reported by Abdolali et al. (2017) and Yusuf et al. (2020). However, this was more prevalent for Pd(II)

which had high affinity for the yeast-functionalised zeolite. The adsorption was in the order of Pd(II) > Ir(III) > Rh(III) at all bed heights. Since Ir(III) and Rh(III) were poorly adsorbed by the adsorbent when the lower bed height was used at pH 2, a higher bed height would be ideal as indicated in Fig. 5 c.

### 3.3. Role of pH on the uptake of elements

The role of pH on the adsorption of the elements was investigated using 2 cm bed height, 2 mg L<sup>-1</sup> initial concentration and 2 mL min<sup>-1</sup> flow rate. During the processing of PGEs, acids such as HCl are used, leading to acidic wastewaters with high concentration of chloride ions, thus, HCl was used to control the pH (Fujiwara et al., 2007; Khutlane, 2018). PHREEQC geochemical modelling code was used to determine the speciation of the elements at different pH conditions (Parkhurst and Appelo, 1999). The uptake of Pd(II) by yeast-functionalised zeolite was high at pH 2 and 8 hence, later breakthroughs were observed (Fig. 6a). However, PHREEQC showed that palladium becomes supersaturated ( $SI > 0$ ) beyond pH 6 therefore, the later breakthrough observed at pH 8 was not due to Pd(II) uptake by the adsorbent but precipitation. The amine groups of the adsorbent were protonated at pH 2 due to the presence of high concentration of H<sub>3</sub>O<sup>+</sup> ions. The most dominant species of palladium at pH 2 were; Pd(II)Cl<sub>4</sub><sup>2-</sup> and Pd(II)Cl<sub>3</sub><sup>-</sup> which, had high affinity for protonated amine groups. The uptake of Pd(II) decreased at pH 5 due to low amount of active sites hence,  $C_t/C_0$  was seen to increase within the first pore volume (initial time of contact). Moreover, the adsorption capacity and maximum tolerance time of Pd(II) were very low at pH 5 (Table 2). The PZC was found to be 5.3 hence the observed results. Mosai et al. (2020) reported similar results. The Ir(III) uptake by the adsorbent was high at pH 2 but, very poor beyond this pH (Fig. 6b).

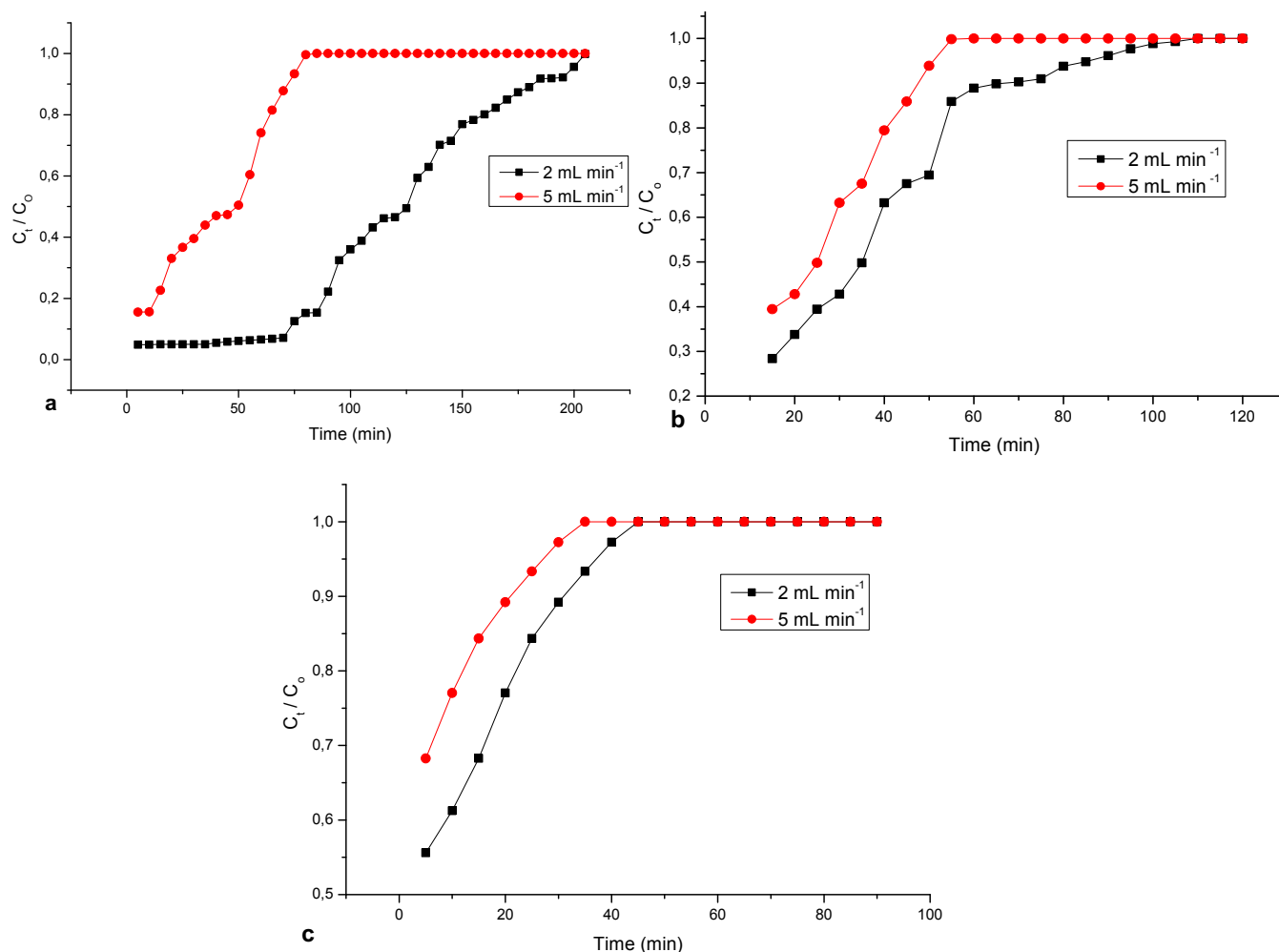


Fig. 8. Role of flow rate on the uptake of (a) Pd(II), (b) Ir(III) and (c) Rh(III) by yeast-functionalised zeolite.

At pH 2, the dominant species of Ir(III) were;  $\text{Ir(III)Cl}_6^{3-}$ ,  $\text{Ir(III)Cl}_4^-$  and  $\text{Ir(III)Cl}_3$ . The protonated adsorbent was able to attract the negatively charged species hence, uptake was possible. At higher pH values, the adsorbent was negatively charged and could not adsorb the dominant Ir(III) species viz  $\text{Ir(III)(OH)}_6^{3-}$  and  $\text{Ir(III)(OH)}_3$ . Contrary to the uptake of The adsorption of Pd(II) and Ir(III), the adsorption of Rh(III) increased with increasing pH (Fig. 6c). The dominant species of Rh(III) at pH 2, 5 and 8 were;  $\text{RhCl}_3(\text{H}_2\text{O})_3$ ,  $[\text{RhCl}_2(\text{H}_2\text{O})_4]^+$  and  $[\text{RhCl}(\text{H}_2\text{O})_5]^{2+}$ , respectively. Similar results were reported by Labib et al. (2018). Therefore, the uptake of Rh(III) can be done after neutralisation of industrial wastewaters.

#### 3.4. Role of concentration on the uptake of elements

The effect of concentration of the uptake of Pd(II), Ir(III) and Rh(III) by yeast-functionalised zeolite was investigated at 2 cm bed height, pH 2 and 2 mL min<sup>-1</sup> flow rate (Fig. 7). The breakthrough times for the uptake of Pd(II) decreased with increasing initial concentration due to fast occupation of active sites at higher concentrations, leading to fast saturation (Van et al., 2019). The quick occupation of active sites at higher concentrations might have been due to concentration gradient and smaller mass transfer resistance (Manirethan and Balakrishnan, 2020). The Pd(II) breakthrough times at 50% of initial concentrations were found to be 240, 120 and 75 min at 1, 2 and 10 mg L<sup>-1</sup>, respectively. Thus, at lower concentrations, the yeast-functionalised zeolite was capable of treating a large volume of the aqueous solution. The adsorption capacity of Pd(II) decreased with increasing concentration

(Table 2). The maximum tolerance for the uptake of Ir(III) was observed at 145, 110 and 45 min for 1, 2 and 10 mg L<sup>-1</sup>, respectively. The uptake of Rh(III) reached equilibrium at 75, 40 and 30 min at 1, 2 and 10 mg L<sup>-1</sup>, respectively. Therefore, the adsorbent will recover Pd(II), Ir(III) and Rh(III) better at lower concentrations (i.e. < 2 mg L<sup>-1</sup>). In general, the maximum tolerance for Rh(III) uptake was reached quicker than that of other elements at all concentrations.

#### 3.5. Role of flow rate on the uptake of elements

The role of flow rate on the adsorption of the elements was studied at 2 cm bed height, pH 2 and 2 mg L<sup>-1</sup> (Fig. 8). Generally, the uptake of the elements was high at lower flow rate (2 mL min<sup>-1</sup>), since there was enough time for the elements to interact with the adsorbent and access active sites (Renu et al., 2020). At lower flow rate, the intra-particle diffusion plays a major role on the uptake of elements as a result of longer residence time. Higher flow rate does not give the elements enough time to interact with active sites; therefore, most of them pass through the zeolite bed without being captured. Moreover, because there is a large amount of solution passing through the adsorbent within a short space of time, the breakthrough point becomes shorter and the maximum tolerance is reached faster, leading to lower adsorption capacity (Table 2). Thus, the external film diffusion mass transfer resistance is reduced with high flow rate, leading to fast saturation of the adsorbent. Therefore, when higher flow rate is used, insignificant amount of wastewater will be treated. Abdolali et al. (2017) also studied the adsorption of heavy metals using column studies and found similar

**Table 3**

Adams-Bohart parameters of the adsorption of elements by spent yeast-functionalised zeolite in a fixed bed system.

| Z (cm) | pH | Q <sub>v</sub> (mL min <sup>-1</sup> ) | C <sub>o</sub> (mg L <sup>-1</sup> ) | Pd(II)<br>k <sub>AB</sub> 10 <sup>-3</sup> (L mg <sup>-1</sup> min <sup>-1</sup> ) | N <sub>o</sub> (mg L <sup>-1</sup> ) | R <sup>2</sup> | Ir(III)<br>k <sub>AB</sub> 10 <sup>-3</sup> | N <sub>o</sub> | R <sup>2</sup> | Rh(III)<br>k <sub>AB</sub> 10 <sup>-3</sup> | N <sub>o</sub> | R <sup>2</sup> |
|--------|----|----------------------------------------|--------------------------------------|------------------------------------------------------------------------------------|--------------------------------------|----------------|---------------------------------------------|----------------|----------------|---------------------------------------------|----------------|----------------|
| 1      | 2  | 2                                      | 2                                    | 18.0                                                                               | 49.5                                 | 0,96           | 17.0                                        | 3.84           | 0,93           | 69.6                                        | 0.09           | 0,94           |
| 2      | 2  | 2                                      | 2                                    | 16.6                                                                               | 54.3                                 | 0,97           | 27.0                                        | 14.5           | 0,97           | 40.0                                        | 2.23           | 0,99           |
| 5      | 2  | 2                                      | 2                                    | 7.02                                                                               | 54.7                                 | 0,89           | 19.2                                        | 12.7           | 0,96           | 16.8                                        | 4.19           | 0,90           |
| 2      | 2  | 2                                      | 1                                    | 9.18                                                                               | 103                                  | 0,92           | 10.7                                        | 15.5           | 0,94           | 12.1                                        | 2.31           | 0,95           |
| 2      | 2  | 2                                      | 10                                   | 50.1                                                                               | 158                                  | 0,84           | 10.1                                        | 26.9           | 0,84           | 8.89                                        | 37.6           | 0,92           |
| 2      | 5  | 2                                      | 2                                    | 12.7                                                                               | 35.7                                 | 0,98           | 88.6                                        | 1.42           | 0,59           | 30.8                                        | 12.7           | 0,91           |
| 2      | 8  | 2                                      | 2                                    | 15.1                                                                               | 67.4                                 | 0,91           | 92.9                                        | 1.70           | 0,61           | 12.8                                        | 61.5           | 0,85           |
| 2      | 2  | 5                                      | 2                                    | 27.5                                                                               | 17.2                                 | 0,93           | 43.9                                        | 5.90           | 0,96           | 53.5                                        | 0.51           | 0,98           |

**Table 4**

Thomas model parameters of the adsorption of elements by spent yeast-functionalised zeolite in a fixed bed system.

| Z (cm) | pH | Q <sub>v</sub> (mL min <sup>-1</sup> ) | C <sub>o</sub> (mg L <sup>-1</sup> ) | Pd(II)<br>K <sub>Th</sub> (L min <sup>-1</sup> mg <sup>-1</sup> ) 10 <sup>-3</sup> | q <sub>o</sub> (mg g <sup>-1</sup> ) | R <sup>2</sup> | Ir(III)<br>K <sub>Th</sub> 10 <sup>-3</sup> | q <sub>o</sub> | R <sup>2</sup> | Rh(III)<br>K <sub>Th</sub> 10 <sup>-3</sup> | q <sub>o</sub> | R <sup>2</sup> |
|--------|----|----------------------------------------|--------------------------------------|------------------------------------------------------------------------------------|--------------------------------------|----------------|---------------------------------------------|----------------|----------------|---------------------------------------------|----------------|----------------|
| 1      | 2  | 2                                      | 2                                    | 18.1                                                                               | 214                                  | 0,96           | 17.4                                        | 14.3           | 0,93           | 69.6                                        | 10.5           | 0,94           |
| 2      | 2  | 2                                      | 2                                    | 18.1                                                                               | 206                                  | 0,98           | 24.3                                        | 54.9           | 0,98           | 45.4                                        | 10.7           | 0,97           |
| 5      | 2  | 2                                      | 2                                    | 7.15                                                                               | 256                                  | 0,90           | 19.2                                        | 60.3           | 0,96           | 22.3                                        | 60.3           | 0,81           |
| 2      | 2  | 2                                      | 1                                    | 19.2                                                                               | 195                                  | 0,95           | 22.4                                        | 29.5           | 0,94           | 228                                         | 4.88           | 0,95           |
| 2      | 2  | 2                                      | 10                                   | 3.91                                                                               | 701                                  | 0,95           | 10.1                                        | 107            | 0,84           | 8.89                                        | 150            | 0,92           |
| 2      | 5  | 2                                      | 2                                    | 11.0                                                                               | 168                                  | 0,98           | 88.6                                        | 5.65           | 0,59           | 30.8                                        | 50.4           | 0,91           |
| 2      | 8  | 2                                      | 2                                    | 15.1                                                                               | 271                                  | 0,93           | 92.9                                        | 6.75           | 0,61           | 12.8                                        | 223            | 0,94           |
| 2      | 2  | 5                                      | 2                                    | 30.4                                                                               | 68.8                                 | 0,95           | 43.9                                        | 23.4           | 0,96           | 53.5                                        | 2.09           | 0,98           |

**Table 5**

Yoon-Nelson model parameters of the adsorption of elements by spent yeast-functionalised zeolite in a fixed bed system.

| Z (cm) | pH | Q <sub>v</sub> (mL min <sup>-1</sup> ) | C <sub>o</sub> (mg L <sup>-1</sup> ) | Pd(II)<br>K <sub>YN</sub> 10 <sup>-3</sup> (min <sup>-1</sup> ) | T (min) | R <sup>2</sup> | Ir(III)<br>K <sub>YN</sub> 10 <sup>-3</sup> | T    | R <sup>2</sup> | Rh(III)<br>K <sub>YN</sub> 10 <sup>-3</sup> | τ    | R <sup>2</sup> |
|--------|----|----------------------------------------|--------------------------------------|-----------------------------------------------------------------|---------|----------------|---------------------------------------------|------|----------------|---------------------------------------------|------|----------------|
| 1      | 2  | 2                                      | 2                                    | 36.1                                                            | 55.0    | 0,96           | 35.2                                        | 3.67 | 0,94           | 173                                         | 0.10 | 0,94           |
| 2      | 2  | 2                                      | 2                                    | 33.8                                                            | 121     | 0,97           | 51.4                                        | 31.9 | 0,99           | 91.1                                        | 6.23 | 0,98           |
| 5      | 2  | 2                                      | 2                                    | 14.3                                                            | 304     | 0,89           | 384                                         | 71.7 | 0,96           | 44.7                                        | 25.5 | 0,81           |
| 2      | 2  | 2                                      | 1                                    | 19.2                                                            | 223     | 0,92           | 22.4                                        | 33.6 | 0,94           | 25.4                                        | 29.6 | 0,95           |
| 2      | 2  | 2                                      | 10                                   | 50.1                                                            | 71.3    | 0,84           | 10.1                                        | 12.2 | 0,84           | 8.89                                        | 17.0 | 0,92           |
| 2      | 5  | 2                                      | 2                                    | 28.4                                                            | 70.4    | 0,91           | 177                                         | 3.21 | 0,59           | 61.5                                        | 28.7 | 0,91           |
| 2      | 8  | 2                                      | 2                                    | 29.3                                                            | 156     | 0,93           | 186                                         | 3.8  | 0,61           | 25.5                                        | 127  | 0,80           |
| 2      | 2  | 5                                      | 2                                    | 64.9                                                            | 38.0    | 0,90           | 87.8                                        | 13.3 | 0,96           | 79.6                                        | 2.65 | 0,99           |

**Table 6**

Clark model parameters of the adsorption of elements by spent yeast-functionalised zeolite in a fixed bed system.

| Z (cm) | pH | Q <sub>v</sub> (mL min <sup>-1</sup> ) | C <sub>o</sub> (mg L <sup>-1</sup> ) | Pd(II)<br>R (min <sup>-1</sup> ) 10 <sup>-3</sup> | A    | R <sup>2</sup> | Ir(III)<br>R 10 <sup>-3</sup> | A    | R <sup>2</sup> | Rh(III)<br>R 10 <sup>-3</sup> | A    | R <sup>2</sup> |
|--------|----|----------------------------------------|--------------------------------------|---------------------------------------------------|------|----------------|-------------------------------|------|----------------|-------------------------------|------|----------------|
| 1      | 2  | 2                                      | 2                                    | 361                                               | 7.28 | 0,96           | 36.6                          | 0.89 | 0,93           | 191                           | 1.14 | 0,94           |
| 2      | 2  | 2                                      | 2                                    | 33.8                                              | 58.8 | 0,97           | 53.5                          | 5.43 | 0,99           | 97.8                          | 1.93 | 0,97           |
| 5      | 2  | 2                                      | 2                                    | 14.3                                              | 77.2 | 0,89           | 39.4                          | 16.3 | 0,95           | 47.0                          | 3.30 | 0,79           |
| 2      | 2  | 2                                      | 1                                    | 19.2                                              | 71.7 | 0,92           | 22.4                          | 2.12 | 0,94           | 25.4                          | 1.14 | 0,95           |
| 2      | 2  | 2                                      | 10                                   | 50.1                                              | 35.6 | 0,84           | 10.1                          | 3.40 | 0,84           | 8.89                          | 4.54 | 0,92           |
| 2      | 5  | 2                                      | 2                                    | 25.4                                              | 7.77 | 0,98           | 177                           | 1.77 | 0,59           | 68.6                          | 6.18 | 0,93           |
| 2      | 8  | 2                                      | 2                                    | 30.1                                              | 98.6 | 0,91           | 186                           | 2.04 | 0,61           | 25.5                          | 25.4 | 0,80           |
| 2      | 2  | 5                                      | 2                                    | 54.9                                              | 8.51 | 0,93           | 87.8                          | 3.23 | 0,93           | 107                           | 0.88 | 0,98           |

results. The maximum tolerance for Pd(II) uptake was found to be around 205 and 80 min at 2 and 5 mL min<sup>-1</sup>, respectively. The maximum tolerance for uptake of Ir(III) was found to be 105 and 55 min at 2 and 5 mL min<sup>-1</sup>. There was no significant difference ( $p > 0.05$ ) on the maximum tolerance of the adsorbent for Rh(III) uptake. Thus, lower flow rate should be considered for efficient recovery of the elements by yeast-functionalised zeolite in mining wastewaters. Moreover, the results obtained can be used as a benchmark for column processes in the mining industry.

### 3.6. Column adsorption models

The column models viz Adams-Bohart, Thomas, Yoon-Nelson, Clark,

Wolborska and modified dose response model were used to determine the breakthrough performance of the elements. There was good agreement between the experimental data and the column models as indicated by the correlation coefficient ( $R^2$ ) values. The adsorption capacity parameters from the Adams-Bohart (i.e.  $N_o$ ) (Table 3) and Thomas models (i.e.  $q_o$ ) (Table 4) were significantly high ( $p < 0.05$ ) for Pd(II) than for other elements. Moreover, the  $\tau$  value from the Yoon-Nelson model indicated that the time required to reach 50% breakthrough at different conditions was higher for Pd(II) than for Ir(III) and Rh(III) (Table 5). Thus, the yeast-functionalised zeolite had high affinity for Pd (II). This means that Pd(II) will be selectively favoured by the yeast-functionalised zeolite over other PGEs in the mining industrial wastewaters. The highest correlation coefficient values were obtained when 2

**Table 7**

Wolborska model parameters of the adsorption of elements by spent yeast-functionalised zeolite in a fixed bed system.

| Z (cm) | pH | $Q_v$ (mL min <sup>-1</sup> ) | $C_o$ (mg L <sup>-1</sup> ) | Pd(II)<br>B (h <sup>-1</sup> ) | $N_o$ (mg L <sup>-1</sup> ) | $R^2$ | Ir(III)<br>$\beta$ | $N_o$ | $R^2$ | Rh(III)<br>B | $N_o$ | $R^2$ |
|--------|----|-------------------------------|-----------------------------|--------------------------------|-----------------------------|-------|--------------------|-------|-------|--------------|-------|-------|
| 1      | 2  | 2                             | 2                           | 0.68                           | 115                         | 0.90  | 0.22               | 77.5  | 0.71  | 0.17         | 20.6  | 0.89  |
| 2      | 2  | 2                             | 2                           | 0.76                           | 79.0                        | 0.93  | 0.28               | 41.9  | 0.82  | 0.13         | 20.0  | 0.93  |
| 5      | 2  | 2                             | 2                           | 0.37                           | 63.8                        | 0.85  | 0.20               | 23.9  | 0.76  | 0.08         | 16.3  | 0.96  |
| 2      | 2  | 2                             | 1                           | 0.79                           | 70.6                        | 0.97  | 0.21               | 28.4  | 0.98  | 0.15         | 19.0  | 0.96  |
| 2      | 2  | 2                             | 10                          | 0.62                           | 251                         | 0.96  | 0.18               | 104   | 0.96  | 0.27         | 105   | 0.69  |
| 2      | 5  | 2                             | 2                           | 0.40                           | 67.4                        | 0.95  | 0.23               | 8.20  | 0.60  | 0.36         | 28.1  | 0.77  |
| 2      | 8  | 2                             | 2                           | 0.90                           | 88.4                        | 0.98  | 0.24               | 8.01  | 0.60  | 0.59         | 93.0  | 0.98  |
| 2      | 2  | 5                             | 2                           | 0.40                           | 32.6                        | 0.94  | 0.24               | 17.9  | 0.98  | 0.10         | 15.8  | 0.94  |

**Table 8**

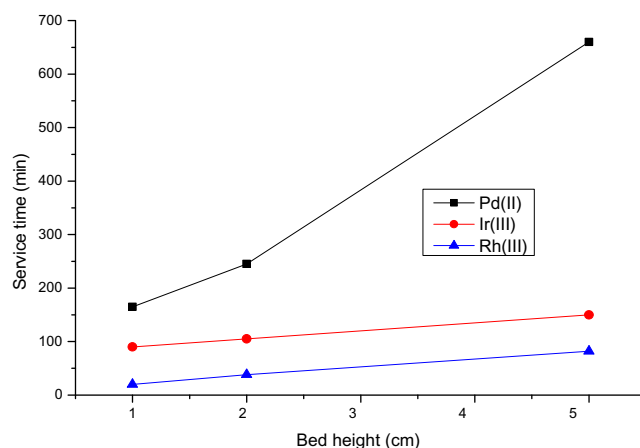
MDRM model parameters of the adsorption of elements by spent yeast-functionalised zeolite in a fixed bed system.

| Z (cm) | pH | $Q_v$ (mL min <sup>-1</sup> ) | $C_o$ (mg L <sup>-1</sup> ) | Pd(II)<br>A | $q_{mdr}$ (mg g <sup>-1</sup> ) | $R^2$ | Ir(III)<br>A | $q_{mdr}$ | $R^2$ | Rh(III)<br>A | $q_{mdr}$ | $R^2$ |
|--------|----|-------------------------------|-----------------------------|-------------|---------------------------------|-------|--------------|-----------|-------|--------------|-----------|-------|
| 1      | 2  | 2                             | 2                           | 1.68        | 14.3                            | 0.77  | 1.35         | 57.9      | 0.89  | 2.10         | 139       | 0.90  |
| 2      | 2  | 2                             | 2                           | 1.93        | 2.0                             | 0.70  | 1.95         | 9.54      | 0.87  | 1.72         | 29.3      | 0.82  |
| 5      | 2  | 2                             | 2                           | 1.64        | 17.3                            | 0.88  | 2.09         | 2.01      | 0.89  | 1.22         | 6.16      | 0.54  |
| 2      | 2  | 2                             | 1                           | 1.83        | 1.0                             | 0.67  | 0.85         | 9.43      | 0.74  | 0.60         | 26.9      | 0.83  |
| 2      | 2  | 2                             | 10                          | 1.83        | 0.71                            | 0.63  | 1.80         | 4.58      | 0.63  | 1.91         | 3.84      | 0.86  |
| 2      | 5  | 2                             | 2                           | 1.26        | 3.57                            | 0.80  | 2.18         | 42.3      | 0.77  | 1.87         | 10.9      | 0.94  |
| 2      | 8  | 2                             | 2                           | 1.71        | 1.17                            | 0.63  | 2.27         | 40.4      | 0.78  | 1.44         | 1.88      | 0.52  |
| 2      | 2  | 5                             | 2                           | 1.42        | 7.10                            | 0.77  | 1.39         | 20.8      | 0.79  | 1.42         | 59.7      | 0.87  |

**Table 9**Comparison of the equilibrium adsorption capacity ( $q_o$ ) of Pd(II) from the Thomas model, with other studies.

| Used adsorbent                                                                      | Conditions                                                                                                         | $q_o$ mg g <sup>-1</sup> | References              |
|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------|--------------------------|-------------------------|
| IL@SBA 15                                                                           | 20 mg L <sup>-1</sup> , 4 mL min <sup>-1</sup> , 2 cm, pH 4                                                        | 453                      | Sharma et al., 2016     |
| Imidazolium nitrate immobilized resin nanocomposite based silica gel/graphene oxide | 65 mg L <sup>-1</sup> , 0.5 mL min <sup>-1</sup>                                                                   | 8                        | Venkatesan et al., 2007 |
| KNiHC/SiO <sub>2</sub>                                                              | 1000 mg L <sup>-1</sup> , 0.6 mL min <sup>-1</sup> , 4 cm, pH 2                                                    | 117                      | Li et al., 2020         |
| KNiHC/SiO <sub>2</sub>                                                              | 1 mmol L <sup>-1</sup> , 0.4 mL min <sup>-1</sup> , 0.5 g adsorbent, [HNO <sub>3</sub> ] = 0.1 mol L <sup>-1</sup> | 40.9                     | Wang et al., 2020       |
| Ion-imprinted chitosan fiber (ICF)                                                  | 316 mg L <sup>-1</sup> , 0.25 mL min <sup>-1</sup> , 0.2 g ICF, pH 0.2                                             | 94.2                     | Mao et al., 2020        |
| Yeast-functionalised zeolite                                                        | 2 mg L <sup>-1</sup> , 2 mL min <sup>-1</sup> , 2 cm, pH 2                                                         | 206                      | This study              |

mg L<sup>-1</sup> initial concentration, pH 2, 2 mL min<sup>-1</sup> flow rate and 2 cm bed height were used. The  $N_o$  and  $q_o$  parameters for Rh(III) were high at pH 8 as was indicated the experimental data (Table 2). Generally, the adsorption capacities of the elements as deduced from the Adams-Bohart, Thomas and Wolborska models (Table 7); increased with increasing initial concentration due to high mass gradient driving force which enhances mass transfer to the adsorbent (Abdolali et al., 2017). Using the  $R^2$  values, the column models results indicated that the adsorption of the elements can be better described with Adams-Bohart, Thomas, Yoon-Nelson and the Clark (Table 6) column adsorption models whose correlation coefficients were very similar. However, the Thomas model described the experimental results better. The uptake of Ir(III) was poorly described by the models at pH 5 and 8 but this was improved when the modified dose response model was used, which could have resulted from the minimised error of the Thomas model at lower and higher time periods (Yan et al., 2001). The Wolborska and the modified dose response model (Table 8) poorly described the initial concentration experimental data for all elements. The Thomas equilibrium adsorption capacity ( $q_o$ ) of Pd(II) in this study was compared with other studies using different adsorbents and it is apparent that the yeast-functionalised zeolite is a competitive adsorbent for Pd(II) recovery

**Fig. 9.** Bed depth service time model for Pd(II), Ir(III) and Rh(III) uptake by spent yeast-functionalised zeolite.

(Table 9). Studies focusing on the column models for the adsorption of Ir(III) and Rh(III) were not found.

The BDST model can indicate the relationship between the bed height of the adsorbent and service time by taking adsorption parameters such concentration, into consideration (Golie and Upadhyayula, 2016). The plot of bed height against service time indicated that the correlation coefficients of all the elements when were  $>0.99$ , indicating that this model can be used to describe the adsorption of the elements onto yeast-functionalised zeolite. The service time increased with increasing bed height meaning that as the amount of yeast-functionalised zeolite increases, the uptake of the elements will also increase (Fig. 9). Pd(II) showed the highest service time at all bed heights indicating favourable uptake by the adsorbent more than other elements. The service time for the elements followed the trend: Pd(II)  $>$  Ir(III)  $>$  Rh(III) at 2 mL min<sup>-1</sup> flow rate at pH 2 with 2 mg L<sup>-1</sup> initial concentration.

#### 4. Conclusion

This study focused on assessing zeolite functionalised with brewer's

spent yeast as a potential adsorbent for PGEs. Column/flow through mode proved to be a suitable experimental design for the recovery of Pd(II), Ir(III) and Rh(III) from aqueous solutions. The adsorbent will work best at pH 2, 2 mL min<sup>-1</sup> flow rate, ~2 mg L<sup>-1</sup> and 2 cm bed height. However, the recovery of Rh(III) can be considered after the neutralisation of industrial wastewaters since the maximum uptake was observed at pH > 5. The adsorbent will be highly selective for Pd(II) over other platinum group elements. In order for the recovery to be an even cheaper process, the adsorbent can be used once-off and stripped as the normal ore in the process feed plants. In this way, there will be no need for more chemicals to remove PGEs from the adsorbent. This study indicated that yeast-functionalised zeolite is a suitable adsorbent for the recovery of PGEs from wastewaters.

## CRedit authorship contribution statement

**Alseno K. Mosai:** Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Writing - original draft, Visualization, Writing - review & editing.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.mineng.2020.106770>.

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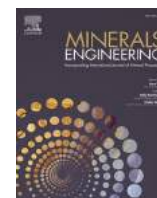
# PAPER IV

**This paper focuses on the simultaneous sorption of rare earth elements from aqueous solutions by zeolite clinoptilolite using column studies.**

**The paper published in Minerals Engineering.**

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**Contribution:** lead author, conducted experimental work and data modelling, conceptualization, methodology, software validation, formal analysis, investigation, writing - original draft and visualization.



# Simultaneous sorption of rare earth elements (including scandium and yttrium) from aqueous solutions using zeolite clinoptilolite: A column and speciation study

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## ABSTRACT

Rare earth elements including scandium and yttrium (REY) are valuable elements that are used in different economically valuable applications. Moreover, these elements are in demand especially in electronic products and energy gadgets such as solar panels and wind turbines. Thus, their recovery from industrial wastewaters will be very beneficial to the economy of the world. The current study reports on the simultaneous recovery of REY (Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb and Lu) from aqueous solutions using column studies. The role of pH (2–8), concentration (2–10 mg L<sup>-1</sup>), bed height (3–9 cm) and flow rate (2.0–5 mL min<sup>-1</sup>) on the uptake of REY was investigated. The effect of the presence of SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup> and PO<sub>4</sub><sup>3-</sup> at different conditions was also assessed. Column models were used to describe the column sorption data. The speciation of the elements was determined using PHREEQC geochemical modelling. The highest adsorption capacity was reached with 3 cm bed height and 2 mL min<sup>-1</sup> flow rate at pH 5.5, with >98% removal efficiency of all the elements. The REY removal process was ineffective in highly acidic pH. There was no significant difference on the removal of REY in the absence or presence of Cl<sup>-</sup>. >75 and 90% removal percentage of REY was observed in the presence of SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup>, respectively, but the adsorption was low in the presence of PO<sub>4</sub><sup>3-</sup>. Natural zeolite proved to be a suitable adsorbent for simultaneous removal of REY from wastewaters.

## 1. Introduction

The construction and function of magnets, ceramics, phosphor light emitting compounds and many other devices such as air pollution controls depend on different materials including rare earth elements together with scandium and yttrium (REY) (Tan et al., 2015; Ayora et al., 2016). The ever increasing development of new technologies increases the demand for REY (Moldoveanu and Papangelakis, 2013). Unfortunately, this results in more consumption of REY which naturally occur in economically viable deposits in few parts of the world such as South Africa, Russia, USA, India, Australia and China (Jun et al., 2010; Kulczycka et al., 2016). Studies have indicated that the demand for REY will increase by 5% each year (USGS, 2016; Ballinger et al., 2020). This then calls for the discovery and development of materials that can recover REY from wastewaters to ensure sustainability.

Some studies have indicated that significant concentrations of REY can be found in REY industrial wastewaters (Ayora et al., 2016; Wang et al., 2010). Cheap recovery techniques for these elements from

wastewaters can be beneficial to industries using REY. This can also reduce the mining of REY from earth's crust which is complicated and costly, thus reducing scarcity (Kulczycka et al., 2016). Removing REY from wastewaters will also be beneficial to the environment since, they can accumulate in water bodies and soils where they can change the environmental conditions and negatively affect living organisms (Wu et al., 2018a). Currently, solvent extraction, selective precipitation and electrochemical methods have been used readily for the recovery of REY, however, these methods are costly and use high amounts of energy (Josso et al., 2018; Zhao et al., 2017).

The recovery of REY using natural zeolite was introduced in this study. Zeolite is a cheap readily available clay material that is naturally occurring. It consists mainly of silicon, aluminium and oxygen hence it is commonly referred to as aluminosilicate material (Salam et al., 2020). It has outstanding chemical and physical characteristics that make it suitable for use in medicine, ecology and industrial processes (Kraljević Pavelić et al., 2018). Zeolite has been used as an ion exchanger for many elements including Cr, Cu and Fe (Motsi et al., 2009; Zanin et al., 2017).

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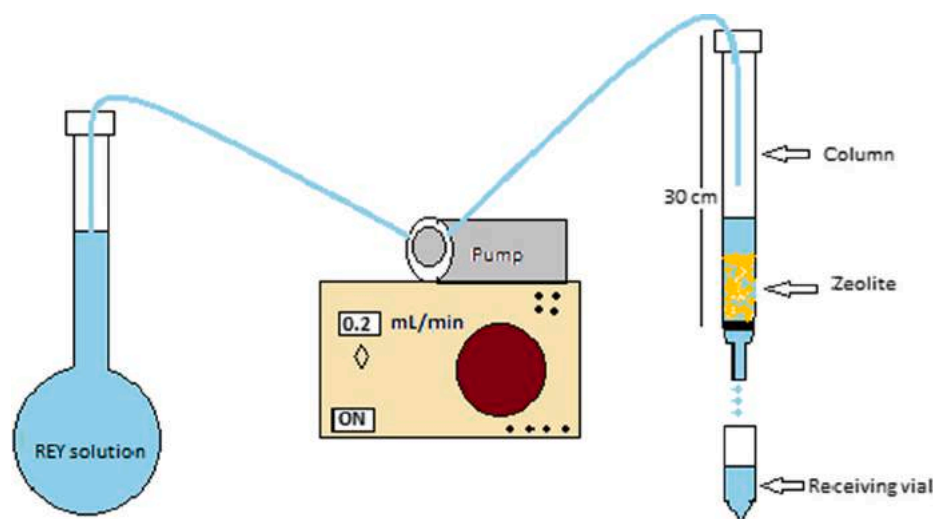


Fig. 1. Column experiments setup.

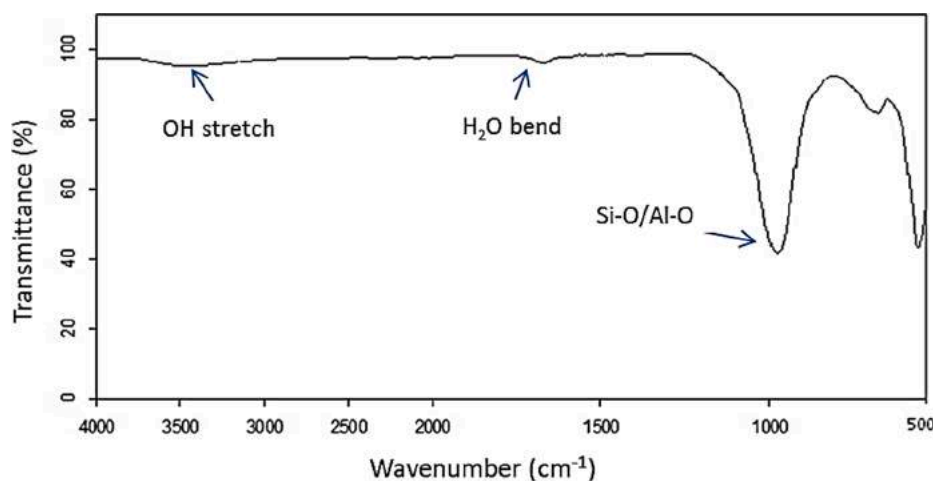


Fig. 2. Zeolite FTIR spectrum.

Some studies have used zeolite materials modified with some ligands to improve their adsorption efficiencies, but this often adds costs to recovery as some of the ligands are expensive and lead to adsorbent disposal issues (Bakatula et al., 2015; Shirzadi and Nezamzadeh-Ejhieh, 2017; Reeve and Fallowfield, 2018). The adsorption properties of natural zeolite on the recovery of REY were tested at different conditions and the results were used to determine the optimum conditions for the removal of REY from wastewaters.

PHREEQC geochemical modelling software was used to determine the speciation of the elements at different conditions (Mosai and Tutu, 2018). PHREEQC is a computer program written in the C++ programming language (Parkhurst and Appelo, 2013). Understanding the speciation of the elements can help explain the observed trends. Thus, PHREEQC is a good tool that can be used to test if the elements in wastewaters are in a state where they can be easily removed by the adsorbent or not. To get the correct speciation however, the input data (eg. pH, conductivity, temperature and concentrations) must be accurate.

## 2. Materials and methods

### 2.1. Characterisation

The zeolite used was collected from the volcanic tuffs of the

Table 1

Textural properties of the natural zeolite.

| Pore size (nm) | Pore volume ( $\text{cm}^3 \text{g}^{-1}$ ) | Surface area ( $\text{m}^2 \text{g}^{-1}$ ) |
|----------------|---------------------------------------------|---------------------------------------------|
| 13.0           | 0.052                                       | 16.3                                        |

Heidelberg-Riversdale Area in the Western Cape, South Africa. Small zeolite rocks were collected using polypropylene containers. The rocks were crushed into small particles (1.5 – 4 mm) and washed overnight by shaking with deionised water using an elliptical bench-top shaker (Labcon, USA). The solution concentration after washing was measured using inductively coupled plasma optical emission spectroscopy (ICP-OES) (Spectro Genesis, Germany). This was to determine the possible elements that may be detaching from the zeolite. In order to better understand the structure and properties, the zeolite was exposed to different characterisation techniques. X-ray fluorescence (XRF) i.e. EDXRF model (PANalytical, Netherlands) was used to analyse the chemical composition of zeolite and the X-ray spectrometers were calibrated with standards prepared from pure oxides. The main minerals of the adsorbent were determined with powder X-ray diffraction D2 Phaser (Bruker, Germany). Functional groups of the natural zeolite were determined using Fourier transform infrared spectrometer (Tensor 27, Bruker, Germany). Elemental analysis was done using VarioELcube V4.0.13 (Elementar, Germany) to determine the amount of C, H, N and

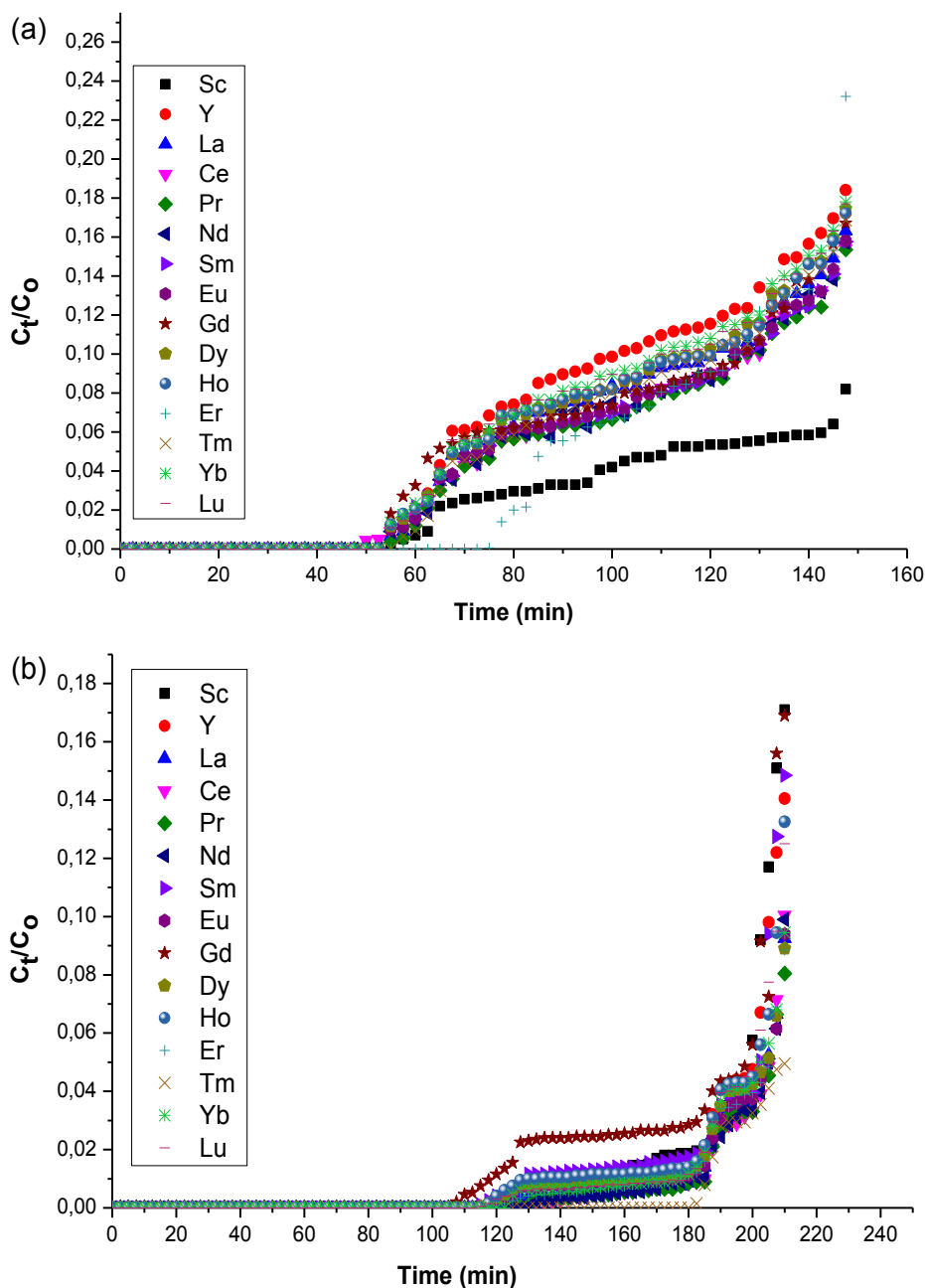


**Fig. 3.** Effect of (a) 3 cm, (b) 6 cm and (c) 9 cm zeolite bed height on the adsorption of REY ( $n = 3$ ,  $RSD < 10\%$ , temperature = 24–26 °C, pH = 5.5, concentration of each element = 2 mg L<sup>-1</sup>, flow rate = 2.0 mL min<sup>-1</sup>).

S. Micromeritics Flow Prep 060 instrument (Aachen, Germany) was used to determine surface area, pore volume and pore size of the zeolite by applying heat and inert gas. The zeolite point of zero charge (PZC) was determined using a method by [Fiol and Villaescusa \(2009\)](#).

## 2.2. Chemicals

All the chemicals used were of analytical reagent grade and required no further purification. They were obtained from Sigma Aldrich, South Africa. The working solutions were prepared daily to ensure good accuracy. A standard containing all the analytes (Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb and Lu) was used to prepare 100 mg L<sup>-1</sup> stock solutions with deionised water. The pH of the working solutions was adjusted using 0.01 mol L<sup>-1</sup> HNO<sub>3</sub> and NaOH. The pH was measured

using FE20 pH meter (Mettler Toledo, Switzerland).

## 2.3. Column studies

Column experiments were conducted using a 30 cm glass column with a diameter of 3.5 cm ([Fig. 1](#)). Natural zeolite was added to the column and supported by a porous glass wool embedded in the column so that it does not leak out. The effect of bed height, pH, initial concentration and flow rate on the simultaneous adsorption of REY was determined. The impact of these variables on the recovery of REY was assessed based on breakthrough curves which were plotted using  $C_t/C_o$  against time (where  $C_o$  is the initial concentration and  $C_t$  is the concentration of the elements at time  $t$ ). The effect of bed height (3, 6 and 9 cm) was investigated so that the amount of zeolite that can significantly

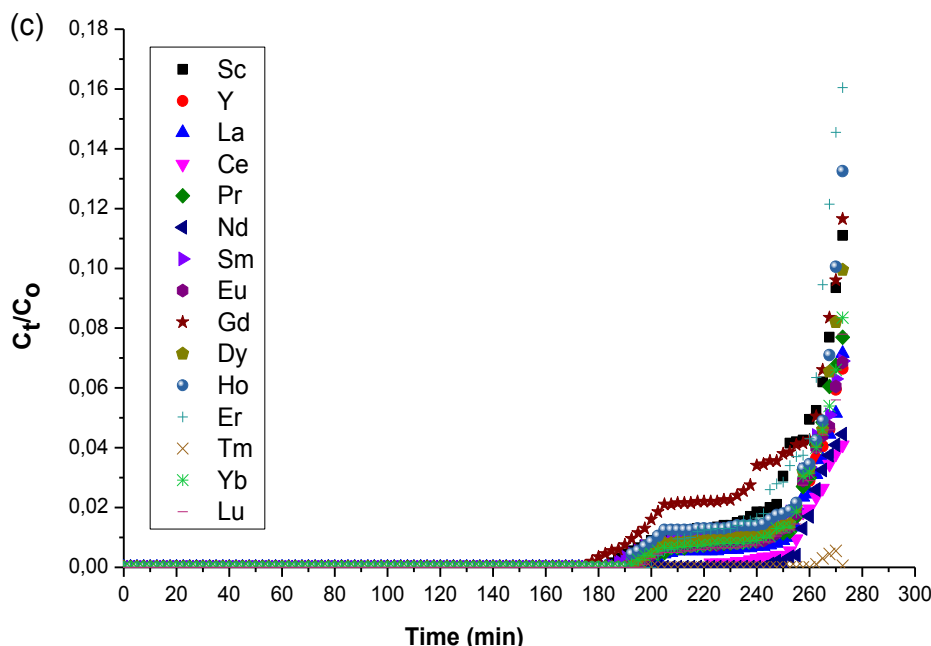


Fig. 3. (continued).

remove REY from wastewaters can be known. REY can be found in solutions of different pH values, which may affect how the adsorbent behaves. Hence, the effect of pH on the recovery of REY was investigated. REY concentration can have a significant impact on the performance of zeolite. Therefore, the effect of concentration was studied. In this study; the effect of 2, 5 and 10 mg L<sup>-1</sup> ( $\pm 0.05$ ) of each of the elements in a mixture was considered. The effect of flow rate (1 and 3 mL min<sup>-1</sup>) on recovery was also investigated. From these experiments, the optimum conditions for the recovery of REY from wastewaters were determined. The column experimental is shown in Fig. 1. The experiments were conducted by collecting the effluent at 5 mL intervals (approximately 2.5 min for every 5 mL) into receiving vials. The collected samples were analysed for the concentration of REY at time  $t$ , using ICP-OES.

The performance of the column was determined by calculating the adsorption capacity,  $q_B$  (mg g<sup>-1</sup>) of REY at 50% breakthrough using Eq. (1) (Tchobanoglous et al., 2003; Barquilha et al., 2017).

$$q_B = Q_v \left( C_o - \frac{C_B}{2} \right) \frac{t_B}{m_{Zeolite}} \quad (1)$$

where  $C_o$  and  $C_B$  are the initial concentration and breakthrough concentrations of REY (mg L<sup>-1</sup>),  $Q_v$  (mL min<sup>-1</sup>) is the flow rate of the inlet solution,  $t_B$  (min) is the breakthrough time when the effluent has a concentration of 50% of the feed REY concentration and  $m_{Zeolite}$  (g) is the mass of the zeolite used.

The removal percentage of the elements was determined with respect to flow volume using Eq. (2) (Vijayaraghavan et al., 2005).

$$\text{Removalpercentage}(\%) = \frac{m_{ad}}{m_{total}} \times 100 \quad (2)$$

$m_{ad}$  (mg) is the analyte mass adsorbed ( $m_{ad} = m_{in,t} - m_{out,t}$ ) where  $m_{in,t} = C_o Q_v t$  and denotes the amount of the element entering the column and  $m_{in,out}$  is the amount of the element which is not adsorbed by and therefore eluting into the receiving vial. where  $m_{out,t} = C_t Q_v \int_0^t \left( \frac{C_t}{C_o} \right) dt$

$m_{total}$  (mg) is the total amount of the analyte sent to the column which can be calculated using the following Eq. (3):

$$m_{total} = \frac{C_o Q_v t_e}{1000} \quad (3)$$

where  $t_e$  (min) is the total run time.

#### 2.4. REY speciation experiments

The rare earth elements and yttrium were mixed with major ligands ( $SO_4^{2-}$  and  $Cl^-$ ) and phosphates ( $PO_4^{3-}$ ) to determine their effect on adsorption using batch studies (Nisbet et al., 2018). There are different steps involved in REY processing which include beneficiation, separation, concentration, extraction and purification (Wang et al., 2020). Different chemicals are used at each step but the REY industrial wastewater is likely to contain  $SO_4^{2-}$  and  $Cl^-$  because sulphuric acid and hydrochloric acid are used in high concentrations especially for the concentrate decomposition method. Moreover, significant amounts of REY come from monazite, a phosphate mineral  $CePO_4$ . Hence,  $PO_4^{3-}$  is likely to be found in REY mining wastewaters (Wu et al., 2018b). Therefore the effect of the presence of phosphates on the removal of REY was considered. The REY raw materials can be found in chloride and fluoride forms. This is why sulphate, chloride and phosphate ions were added to the REY solutions so that their impact on adsorption can be monitored since REY may interact with these ligands and change the speciation of the elements and probably the analyte removal capacity by zeolite. The speciation of the elements in the presence of the ligands was done using PHREEQC geochemical modelling. Four sets of experiments were conducted for this study using different conditions. In the first set; 2 mg L<sup>-1</sup> REY, 3 cm, 0.5 mL min<sup>-1</sup>, pH 2 and 0.01 mol L<sup>-1</sup> of anions were used and the removal percentage was calculated. In the second set, the pH of the analytes solution was increased to pH 5.5. In the third set, the conditions of set one were kept the same and only the anions concentration was increased to 0.05 mol L<sup>-1</sup>. In the last set, the concentration of the anions was still kept at 0.05 mol L<sup>-1</sup> whilst the REY concentration was increased to 5 mg L<sup>-1</sup>.

### 3. Results and discussion

#### 3.1. Characterisation

The chemical composition of the natural zeolite was determined using XRF and the results indicated that SiO<sub>2</sub> (68.5%) dominated the zeolite. Al<sub>2</sub>O<sub>3</sub> (16.7%) was also in significant amount and K<sub>2</sub>O (3.8%),

**Table 2**

Time and adsorption capacity of the elements at different zeolite bed heights.

| REY | Z (cm) | t <sub>B</sub> (min) | Q <sub>B</sub> (mg g <sup>-1</sup> ) |
|-----|--------|----------------------|--------------------------------------|
| Sc  | 3      | 194                  | 0.24                                 |
|     | 6      | 321                  | 0.21                                 |
|     | 9      | 424                  | 0.20                                 |
| Y   | 3      | 103                  | 0.16                                 |
|     | 6      | 207                  | 0.11                                 |
|     | 9      | 233                  | 0.11                                 |
| La  | 3      | 123                  | 0.19                                 |
|     | 6      | 250                  | 0.13                                 |
|     | 9      | 285                  | 0.13                                 |
| Ce  | 3      | 130                  | 0.20                                 |
|     | 6      | 265                  | 0.14                                 |
|     | 9      | 349                  | 0.15                                 |
| Pr  | 3      | 128                  | 0.20                                 |
|     | 6      | 260                  | 0.14                                 |
|     | 9      | 344                  | 0.15                                 |
| Nd  | 3      | 126                  | 0.19                                 |
|     | 6      | 255                  | 0.14                                 |
|     | 9      | 307                  | 0.13                                 |
| Sm  | 3      | 126                  | 0.20                                 |
|     | 6      | 257                  | 0.14                                 |
|     | 9      | 314                  | 0.13                                 |
| Eu  | 3      | 118                  | 0.19                                 |
|     | 6      | 256                  | 0.13                                 |
|     | 9      | 311                  | 0.13                                 |
| Gd  | 3      | 120                  | 0.20                                 |
|     | 6      | 257                  | 0.13                                 |
|     | 9      | 302                  | 0.13                                 |
| Dy  | 3      | 125                  | 0.18                                 |
|     | 6      | 239                  | 0.14                                 |
|     | 9      | 273                  | 0.12                                 |
| Ho  | 3      | 121                  | 0.19                                 |
|     | 6      | 245                  | 0.13                                 |
|     | 9      | 284                  | 0.11                                 |
| Er  | 3      | 126                  | 0.19                                 |
|     | 6      | 254                  | 0.14                                 |
|     | 9      | 299                  | 0.13                                 |
| Tm  | 3      | 121                  | 0.19                                 |
|     | 6      | 248                  | 0.13                                 |
|     | 9      | 287                  | 0.12                                 |
| Yb  | 3      | 108                  | 0.17                                 |
|     | 6      | 223                  | 0.11                                 |
|     | 9      | 253                  | 0.10                                 |
| Lu  | 3      | 110                  | 0.17                                 |
|     | 6      | 225                  | 0.11                                 |
|     | 9      | 255                  | 0.10                                 |

**Table 3**

Comparison of adsorption capacities of REY for various adsorbents.

| Adsorbent                                    | Adsorption capacity (mg g <sup>-1</sup> ) | pH  | Reference          |
|----------------------------------------------|-------------------------------------------|-----|--------------------|
| Zeolite                                      | 0.16–0.24                                 | 5.5 | This study         |
| Diphonix resin                               | 0.65–6.65 (Nd, Ce, La)                    | 2   | Fila et al., 2019  |
| Activated carbon                             | 0.048 (La, Lu, Yb, Eu, Y, Sc)             | 3   | Kano et al., 2017  |
| Carbonized ginkgo leaves                     | 0.055–0.085 (La, Ce)                      | 3   | Ponou et al., 2016 |
| Cyanex 272 impregnated Amberlite XAD-7 resin | <1.6 (La, Pr, Nd, Sm, Eu and Gd)          | 2.5 | Inan et al., 2018  |

Na<sub>2</sub>O (1.5%), MgO (0.8%), CaO (1.2%) and Fe<sub>2</sub>O<sub>3</sub> (1.1%) in small but recognisable amounts. The mineralogy was determined with powder X-ray diffraction and indicated that clinoptilolite-Na, clinoptilolite-Ca, quartz, orthodase and boggsite were main minerals of the zeolite sample. Similar results were also obtained from FTIR (in the 4000–400 cm<sup>-1</sup> region) which indicated that strong peaks of Si-O and Al-O were apparent from the zeolite structure (Fig. 2). The IR band 992 cm<sup>-1</sup> can be attributed to the Si-O(Si) and Si-O(Al) internal vibrations (Mirzaei et al., 2019). Elemental analysis was done and indicated that the zeolite

material contained 0.20, 1.18 and 0.06% of C, H and N, respectively. The surface area, pore volume and pore size of the zeolite are reported in Table 1. Similar results were reported by Humelnicu et al. (2006) who used zeolitic volcanic tuff for the sorption of U(VI) and Th(IV). Thus, these results are typical of zeolite materials.

### 3.2. Effect of bed height

The impact of bed height (3, 6 and 9 cm) on the recovery of REY was investigated at pH 5.5, flow rate of 2.0 mL min<sup>-1</sup>, 50% breakthrough and initial concentration of 2.0 mg L<sup>-1</sup>. The height of the zeolite bed was found to have a significant effect on the adsorption of REY (Fig. 3). Abdolali et al. (2017) also found similar results. Large bed height was directly related to longer breakthrough times because of the availability of more binding sites hence mass transfer increased with bed height, and Yusuf et al. (2020) confirms the same. PHREEQC indicated that the dominant species (>96%) of the elements at the conditions used were; Sc<sup>3+</sup>, Y<sup>3+</sup>, La<sup>3+</sup>, Ce<sup>3+</sup>, Pr<sup>3+</sup>, Nd<sup>3+</sup>, Sm<sup>3+</sup>, Eu<sup>3+</sup>, Gd<sup>3+</sup>, Dy<sup>3+</sup>, Ho<sup>3+</sup>, Er<sup>3+</sup>, Tm<sup>3+</sup>, Yb<sup>3+</sup> and Lu<sup>3+</sup>. Small amount of the elements were in the form of MOH<sup>2+</sup> and MO<sup>+</sup> (where M = element). There was no significant difference (p > 0.05) in the uptake (Q<sub>B</sub>) of the elements except for Sc at 3 cm, whose adsorption capacity was significantly higher. The uptake of Gd was faster than all the elements at 6 and 9 cm bed heights, but there was no statistical difference with other elements. The adsorption capacity of the elements ranged between 0.16 and 0.24, 0.11–0.21 and 0.10–0.20 mg g<sup>-1</sup> at 3, 6 and 9 cm, respectively (Table 2). Higher adsorption capacities of the elements were reached with the lowest mass of the adsorbent. Since zeolite is a readily available adsorbent, the cost of removal will be cheap, and for the fact that a small amount can significantly take up elements simultaneously, the cost of retrieving REY will also be less. The adsorption capacities of REY in this study were compared with those from other studies as summarised in Table 3. Some adsorbents such as Diphonix resin and Cyanex 272 impregnated Amberlite XAD-7 resin showed higher adsorption capacities of REY than in this study, which was attributed to the functional groups used for modification and higher concentration of REY solutions used (Inan et al., 2018; Fila et al., 2019). However, these adsorbents are costly due to the components used for uptake. Moreover, these studies did not use a wide range of REY as in this study. Thus, zeolite would be an ideal adsorbent and it performs better than other cheap adsorbents such as activated carbon and Carbonized ginkgo leaves. Therefore, zeolite is a competitive adsorbent for the recovery of REY from industrial wastewaters.

### 3.3. Effect of pH

The role of pH (2, 5.5 and 8) on the recovery of REY by natural zeolite clinoptilolite was investigated using 3 cm zeolite bed height, 2.0 mg L<sup>-1</sup> aqueous solution concentration and 2.0 mL min<sup>-1</sup> flow rate (Fig. 4). At acidic pH, where there is high concentration of hydronium ions, the surface groups were positively charged making the overall charge of the adsorbent positive (Mosai et al., 2019). The dominating species (>95%) was in the form of M<sup>3+</sup> (i.e. Sc<sup>3+</sup>, Y<sup>3+</sup>, La<sup>3+</sup>, Ce<sup>3+</sup>, Pr<sup>3+</sup>, Nd<sup>3+</sup>, Sm<sup>3+</sup>, Eu<sup>3+</sup>, Gd<sup>3+</sup>, Dy<sup>3+</sup>, Ho<sup>3+</sup>, Er<sup>3+</sup>, Tm<sup>3+</sup>, Yb<sup>3+</sup> and Lu<sup>3+</sup>) at pH 2 (determined from PHREEQC) hence the analytes were poorly attracted to the positively charged adsorbent (Fig. 4a). The PZC of the zeolite was found to be 6.47 thus, the negative character of the surface increased with increasing pH. Hence, there was no electrostatic attraction at pH 2, and as a consequence, the adsorption of the elements reached breakthrough very early, indicating unfavourable adsorption. The breakthrough time for all the elements was directly proportional to pH because of the high concentration of OH<sup>-</sup> with increasing pH, making M<sup>3+</sup> capture possible (Oguz, 2017). PHREEQC geochemical modelling indicated that at pH 5.5, the dominant species of the elements was still M<sup>3+</sup> with M(OH)<sup>2+</sup> in very small amounts. A study by Mahmoodi and Saffar-Dastgerdi (2019) reported that the surface of the zeolite material is negatively charged and remain so at pH values > 2 hence the increase

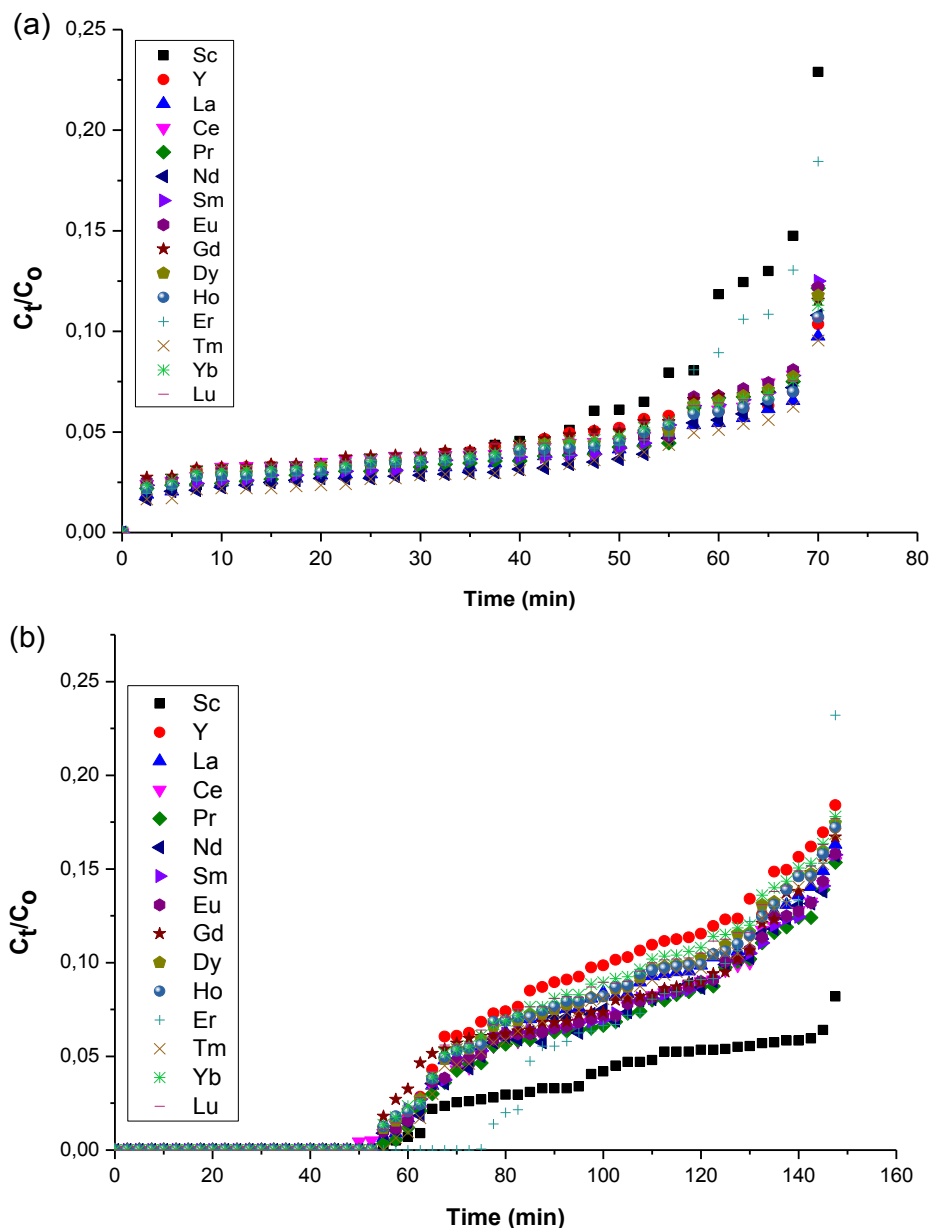


Fig. 4. Effect of pH ((a) 2, (b) 5.5, (c) 8) on the adsorption of REY by zeolite ( $n = 3$ ,  $RSD < 10\%$ , temperature =  $24\text{--}26\text{ }^{\circ}\text{C}$ , bed height =  $3\text{ cm}$ , concentration of each element =  $2\text{ mg L}^{-1}$ , flow rate =  $2.0\text{ mL min}^{-1}$ ).

on the removal of REY in aqueous solutions. Thus, REY prefer less positively charged surface for recovery because they remain positively charged even at  $\text{pH} > 5$ . For those wastewaters where the pH is highly acidic, some agents can be added to increase the pH so that the solution is suitable for efficient recovery of REY (Mosai et al., 2019). Breakthrough time was the highest at pH 8, however, adsorption and precipitation occurred concurrently. Hence,  $\text{pH} < 8$  was suitable for significant recovery.

### 3.4. Effect of concentration

The effect of initial concentration ( $2, 5$  and  $10\text{ mg L}^{-1}$ ) on the removal of REY by natural zeolite was investigated at pH 5.5,  $3\text{ cm}$  bed height and  $2.0\text{ mL min}^{-1}$  flow rate. As the initial concentration increased, the breakthrough time decreased because higher concentration led to faster saturation of the adsorbent (Fig. 5) (Mosai et al., 2019). This is because the amount of  $\text{M}^{3+}$  species increases with concentration

leading to fast occupation of binding sites. Moreover, the driving force of the positively charged species of the elements to overcome mass transfer becomes prominent at higher concentrations (Sugashini and Meera Sheriffa Begum, 2013). At lower concentrations, the breakthrough curve was reached later and resulted in higher breakthrough time which, led to the highest treated volume of the aqueous solution. The transport of the elements to the zeolite at lower concentration is slower than when the concentration is high and this improves the removal percentage of the elements. The removal percentage was found to be 98, 91 and 72% at 2, 5 and  $10\text{ mg L}^{-1}$ , respectively.

### 3.5. Effect of flow rate

The effect of flow rate on the adsorption of the elements was investigated at 2 and  $5\text{ mL min}^{-1}$ . Lower flow rate was preferred better than the higher one because the elements have enough time to disseminate through the zeolite surface groups and be captured (Fig. 6). This was

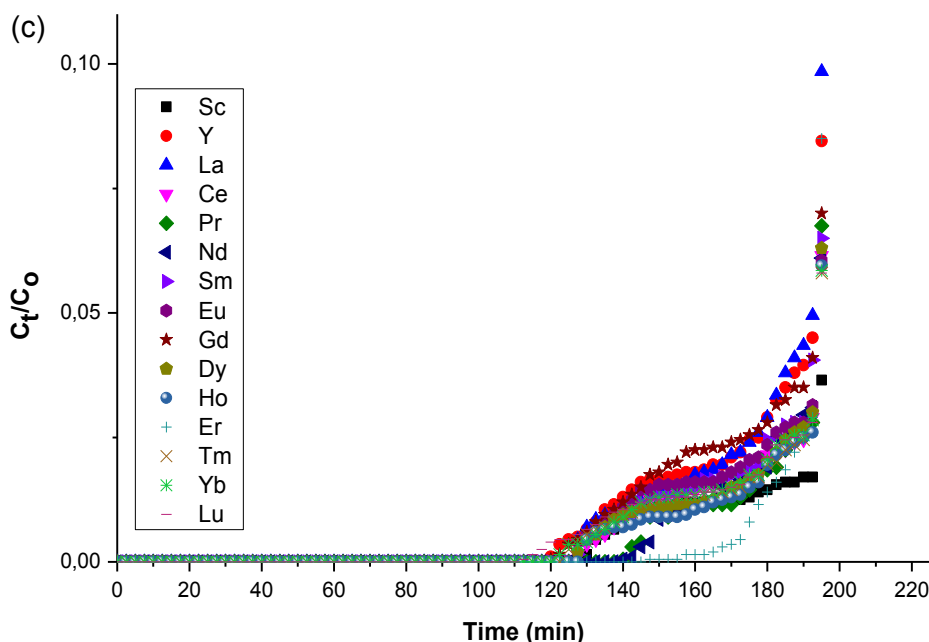


Fig. 4. (continued).

proved by the higher breakthrough time at lower flow rate and very short time at higher flow rate (Hethnawi et al., 2018). When the flow rate is high, there is large amount of aqueous solution flowing into the zeolite within a short space of time; hence, other elements pass along with the solution into the receiving vial because there is not enough time to interact with the adsorbing groups of the zeolite. The percentage removal at  $2 \text{ mL min}^{-1}$  was found to be 98% and only 28% at  $5 \text{ mL min}^{-1}$ . Therefore, when the flow rate is high, a significant concentration of REY in wastewaters will not be captured by the zeolite hence lower flow rate should be considered. The results from this study can be used to determine the flow rate that can be used in large scale with respect to the column size.

### 3.6. Effect of anions

The results of the removal of REY in the presence of anions ( $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and  $\text{PO}_4^{3-}$ ) are reported in Table 4. The analytes were poorly adsorbed and removed from the aqueous solutions in the presence of all the anions ( $0.01 \text{ mol L}^{-1}$ ) at pH 2. This was attributed to the positively charged zeolite surface and high concentration of positively charged species of the analytes. PHREEQC indicated that at this pH > 97% of REY species were in the form of  $\text{M}^{3+}$ ,  $\text{MSO}_4^+$ ,  $\text{MCl}^{2+}$  and  $\text{MHPO}_4^+$  depending on the anions solution used. These species were not favourable for adsorption onto the positively charged species hence the removal percentage was very low. Thus, it does not matter whether the REY wastewater contains  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  or  $\text{PO}_4^{3-}$ , at highly acidic pH, the adsorption will not be favoured. The uptake of REY by the zeolite in the presence of the anions increased drastically as the pH increased to pH 5.5, due to the change in the surface charge of the zeolite. The high concentration of hydroxide ions increased the negative character of the zeolite surface. Moreover, at this pH, the dominant species of the elements were still  $\text{M}^{3+}$ ,  $\text{MSO}_4^+$ ,  $\text{MCl}^{2+}$  and  $\text{MHPO}_4^+$  as with pH 2. These positively charged species of the elements were attracted by the negatively charged surface groups of the zeolite. The removal of the analytes was > 90% for most of the elements in the presence of  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$ . In the presence of  $\text{PO}_4^{3-}$ , the removal of the elements ranged between 37.7 and 83.0%. The same conditions used for pH 5.5 were also used at pH 8 but there was no significant difference in the results ( $p > 0.05$ ).

The concentration of the anions was increased to  $0.05 \text{ mol L}^{-1}$  whilst other conditions of the aqueous solutions were kept the same (pH 5.5

and  $2 \text{ mg L}^{-1}$  REY mixture). There was no significant difference ( $p > 0.05$ ) in the observations when chloride ions were used because the dominant species were still  $\text{M}^{3+}$  and  $\text{MCl}^{2+}$ , with  $\text{MCl}_2^+$  occurring in small amounts. The ability of the zeolite to remove REY in aqueous solutions reduced with increasing concentration of  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$ . PHREEQC indicated that as the concentration of these anions increase, the  $\text{M}(\text{SO}_4)_2^-$  and  $\text{M}(\text{HPO}_4)_2^-$  species of the elements become more prevalent. These species are negatively charged and will not be favoured for adsorption by the negatively charged zeolite. The adsorption of the elements in the presence of sulphates was higher than that of the phosphate species of the elements because the positively charged species ( $\text{MSO}_4^+$ ) were still significantly high. Whereas,  $\text{M}(\text{HPO}_4)_2^-$  species were most dominant in the presence of phosphates. Thus, even though there is reduction in the removal of REY in the presence of sulphates, the adsorption is still considered to be high since the removal was > 75% for most of the elements. Moreover, this is considered effective particularly because the adsorption of the elements is simultaneous. There was no significant difference ( $p > 0.05$ ) on the adsorption of the elements in the presence of all the anions at  $0.05 \text{ mol L}^{-1}$  when the concentration of the elements was increased to  $5 \text{ mg L}^{-1}$ .

Maximum removal of REY in the presence of  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and  $\text{PO}_4^{3-}$  can be achieved at pH 5.5 or higher with a concentration of  $2 \text{ mg L}^{-1}$ . If the wastewater in which the elements are found is too acidic, a base such as NaOH can be used to increase the pH so that the adsorption using zeolite is high. To significantly remove elements in high concentration of phosphate ions, the wastewater can be passed through a series of zeolite bed materials or a longer bed height can be used.

### 3.7. Column models

The Adams-Bohart, Yoon-Nelson, Thomas and bed depth service time models were used to describe the column sorption data. The Adams-Bohart model was used to describe the initial part of the breakthrough curve since it can describe surface reactions very well (Gong et al., 2015). According to this model, the rate of analyte uptake is proportional to the concentration of the analyte in the bulk solution and the residual adsorptive capacity of the adsorbent (Xu et al., 2013). The following equation was used to fit the Adams-Bohart model:

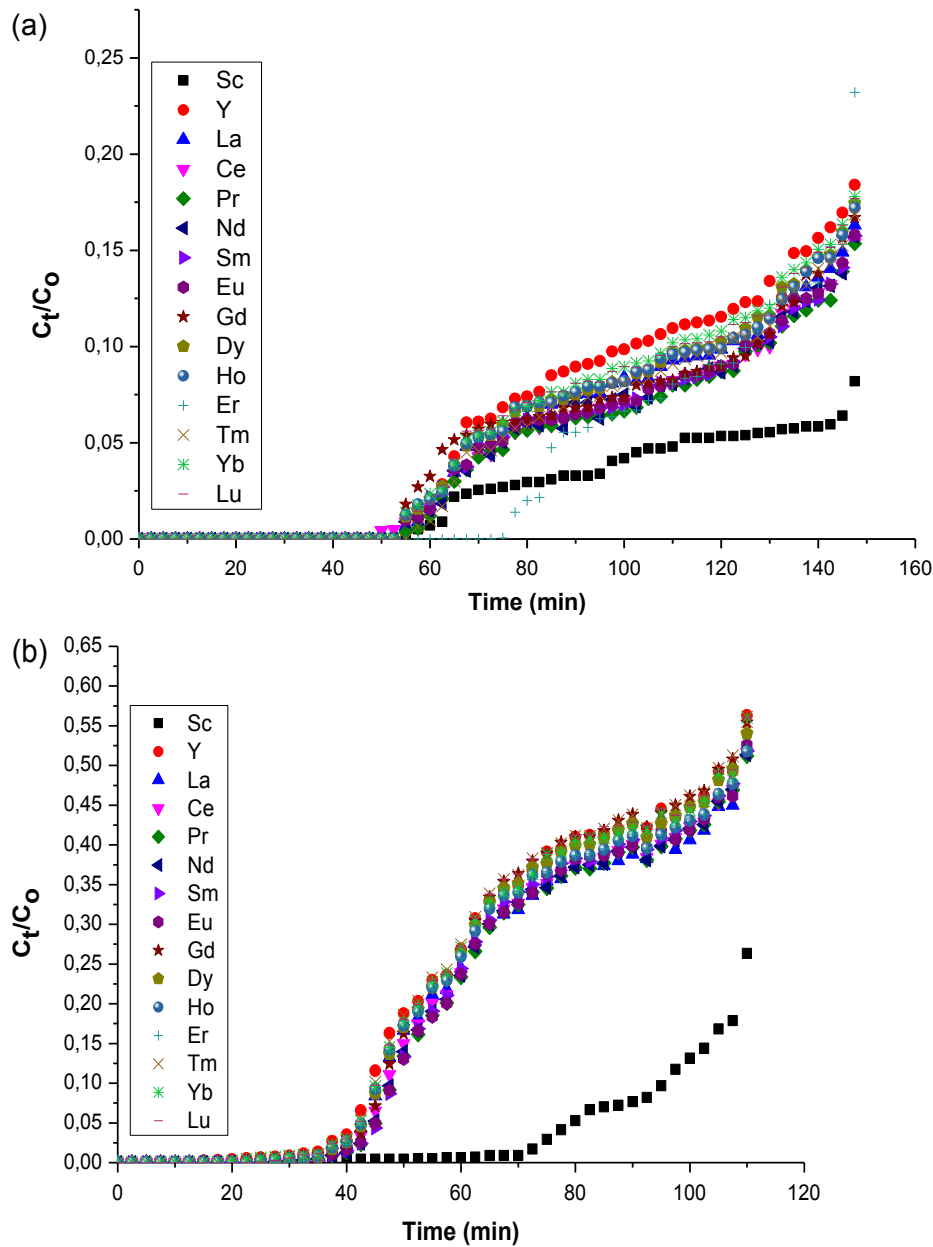


**Fig. 5.** Effect of initial concentration ((a) 2, (b) 5, (c) 10 mg L<sup>-1</sup>) on the adsorption of REY (n = 3, RSD < 10%, temperature = 24–26 °C, pH = 5.5, bed height = 3 cm, mg L<sup>-1</sup>, flow rate = 2.0 mL min<sup>-1</sup>).

$$\ln\left(\frac{C_t}{C_o}\right) = k_{AB}C_o t - \frac{k_{AB}N_o Z}{V} \quad (4)$$

where  $k_{AB}$  (L mg<sup>-1</sup> min<sup>-1</sup>) is the adsorption rate constant,  $N_o$  (mg L<sup>-1</sup>) is the saturation concentration,  $Z$  (cm) is the bed height and  $V$  (cm min<sup>-1</sup>) is the superficial velocity. The plot of  $\ln\left(\frac{C_t}{C_o}\right)$  versus  $t$  from the model equation was used to determine correlation coefficient ( $R^2$ ),  $N_o$  and  $k_{AB}$  values.

The Thomas model is based on the assumption that the flow of the inlet solution into the column bed follows the plug flow behaviour and that the adsorption is through mass transfer at the interface (Foroughi-dahr et al., 2016). The linear equation of the Thomas model can be expressed as:

$$\ln\left(\frac{C_o}{C_t} - 1\right) = \frac{k_{Th}q_o m_{adsorbent}}{Q_v} - k_{Th}C_o t \quad (5)$$

where  $C_o$  (mg L<sup>-1</sup>) is the effluent concentration,  $k_{Th}$  (L min<sup>-1</sup> mg<sup>-1</sup>) is the Thomas rate constant and  $q_o$  (mg g<sup>-1</sup>) is the equilibrium adsorption capacity which were determined from the plot of  $\ln\left(\frac{C_o}{C_t} - 1\right)$  versus  $t$ .

The Yoon-Nelson column model can be used to predict the breakthrough time of an element at a particular concentration and it is based on the assumption that the rate of decrease in the probability of adsorption of each element is proportional to the probability of adsorption of the element and the probability of breakthrough of the element on the adsorbent (Golie and Upadhyayula, 2016; Talat et al., 2018)

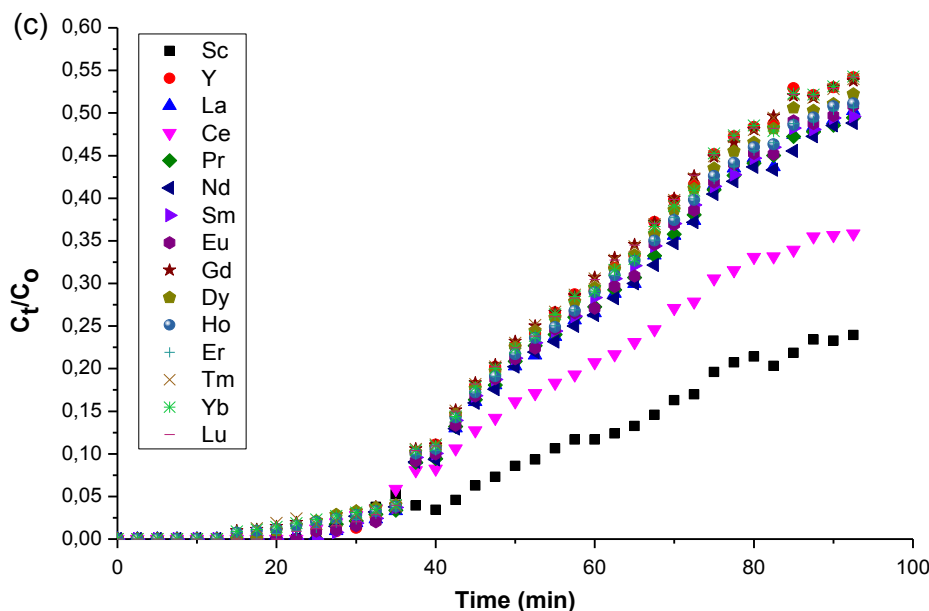


Fig. 5. (continued).

$$\ln\left(\frac{C_t}{C_o - C_t}\right) = k_{YN}t - \tau k_{YN} \quad (6)$$

where  $k_{YN}$  ( $\text{min}^{-1}$ ) is the Yoon-Nelson rate constant and  $\tau$  (min) is the time required for an element to reach 50% breakthrough. The plots of

$$\ln\left(\frac{C_t}{C_o - C_t}\right) \text{ versus } t \text{ were used to determine } k_{YN} \text{ and } \tau \text{ for each element.}$$

Bed depth service time (BDST) model which determine the capacity at different breakthrough values was also used to investigate the relationship between bed depth and service time (Afroze et al., 2016). The model assumes that forces such as the intra-particle diffusion and external mass transfer resistance are negligible. Moreover, the adsorption kinetics is controlled by a surface chemical reaction between the analyte in the solution and the unused adsorbent (Baral et al., 2009).

$$t = \left(\frac{N_o Z}{C_o U}\right) - \left(\frac{1}{K_o C_o}\right) \ln\left(\frac{C_o}{C_t} - 1\right) \quad (7)$$

where  $t$  (min) is time  $U$  ( $\text{cm min}^{-1}$ ) is the influent linear velocity and  $K_o$  ( $\text{L mg}^{-1} \text{min}^{-1}$ ) is the rate constant in BDST model.

The correlation coefficient ( $R^2$ ) was used to conclude the best fitting model for each element.

The adsorption results were modelled using the adsorption models and the results are reported in Table 5, 6 and 7. These results indicated that the Adams-Bohart, Yoon-Nelson and Thomas models described the adsorption data similarly, but the adsorption of most elements were best described by the Yoon-Nelson model at 3 cm bed height,  $10 \text{ mg L}^{-1}$ ,  $2 \text{ mL min}^{-1}$  and pH 5.5. Therefore, the Yoon-Nelson model is the best of all the models. The time required for the elements to reach 50% breakthrough ( $\tau$ ) decreased as concentration increased but  $k_{YN}$  increased with concentration. The saturation concentration ( $N_o$ ) as determined from the Adams-Bohart model which describes the initial part of the breakthrough curve was observed to decrease with increasing initial concentration of the elements and higher pH. However,  $k_{AB}$  increased with concentration. The equilibrium adsorption capacity ( $q_o$ ) increased with concentration and this indicated that the higher the concentration, the higher the uptake of REY from the liquid phase. The  $k_{Th}$  values decreased with increasing concentration.

The correlation coefficients ( $R^2$ ) of elements from the BDST model ranged between 0.89 and 0.98, which indicated that the model was applicable. The linear plots of the model are shown in Fig. 7. The  $N_o$

values for the elements were calculated from the slopes of the respective elements whilst  $K_o$  values were determined from the intercepts. The  $K_o$  were found to range between  $0.0098$  and  $0.018 \text{ L mg}^{-1} \text{min}^{-1}$ .

#### 4. Conclusion

The current study reported on the removal of rare earth elements including scandium and yttrium (REY) (Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb and Lu) from aqueous solutions using natural zeolite. REY are very important elements used in various applications including; medical, industrial and domestic. The recovery of these elements from wastewaters is very important as they have a very important use which leads to high consumption. Natural zeolite was used as it is readily available therefore making the recovery process very cheap. The highest average adsorption capacity is  $0.19 \text{ mg g}^{-1}$ , obtained with a 3 cm bed height at pH = 5.5. For zeolite to significantly remove these elements from wastewaters, the pH of the water must be  $> \text{pH } 5$  so that the zeolite is negatively charged since REY are always positively charged. The removal of REY by zeolite using columns will be highly effective at lower concentrations ( $< 5 \text{ mg L}^{-1}$ ) since high volumes of water will be treated and this was confirmed by longer breakthrough time observed at  $2.0 \text{ mg L}^{-1}$ . This is important and useful for instances of low level concentrations of the elements in waste streams. The results of this study will be very important when designing columns for REY adsorption from wastewaters. The flow rate and bed height can be determined with respect to the size of the column using the relationship determined from this study. The adsorption of REY will still be high ( $> 90\%$ ) when  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  are present in wastewaters but may be a problem in the presence  $\text{PO}_4^{3-}$  since the study indicated that the removal percentage ranged between 37 and 83%. Therefore in the presence of phosphates, the removal process should be repeated more than once so that significant amounts of REY are removed. The Yoon-Nelson adsorption model best described the adsorption of the elements in different conditions. This study indicated that natural zeolite was very effective in simultaneously removing REY from aqueous solutions with  $> 98\%$  removal efficiency in the presence of nitrate and chloride ions.

#### CRediT authorship contribution statement

Alseno K. Mosai: Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Writing - original draft,

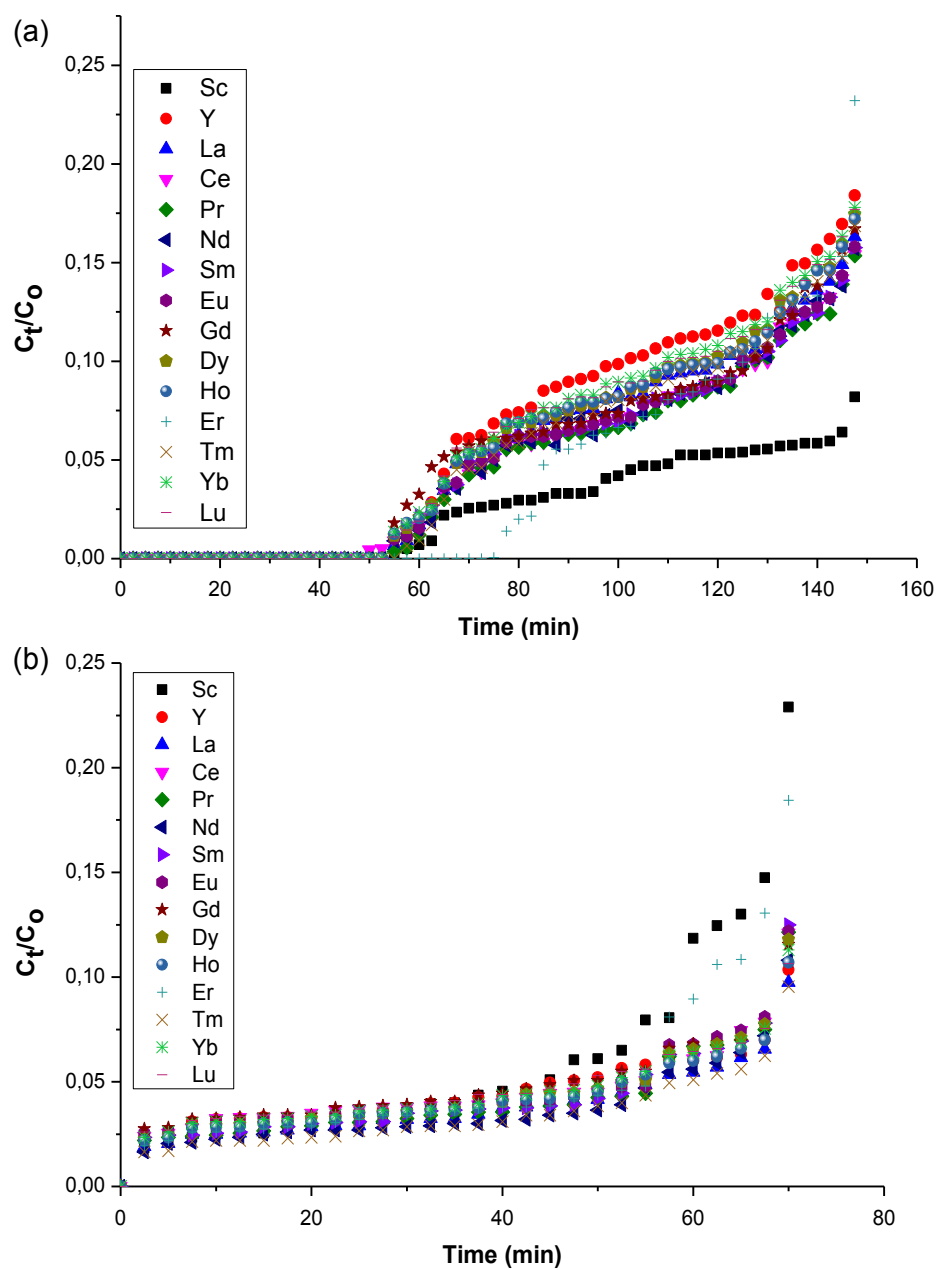


**Fig. 6.** Effect of flow rate ((a) 2 and (b) 5 mL min<sup>-1</sup>) on the removal of REY from aqueous solutions ( $n = 3$ , RSD < 10%, temperature = 24–26 °C, bed height = 3 cm, pH = 5.5, concentration of each element = 2 mg L<sup>-1</sup>).

**Table 4**

Removal percentage of REY in the presence of anions at different conditions (total run time = 360 min, n = 3, RSD &lt; 10%).

| REY | A                             |                 |                               | B                             |                 |                               | C                             |                 |                               | D                             |                 |                               |
|-----|-------------------------------|-----------------|-------------------------------|-------------------------------|-----------------|-------------------------------|-------------------------------|-----------------|-------------------------------|-------------------------------|-----------------|-------------------------------|
|     | SO <sub>4</sub> <sup>2-</sup> | Cl <sup>-</sup> | PO <sub>4</sub> <sup>3-</sup> | SO <sub>4</sub> <sup>2-</sup> | Cl <sup>-</sup> | PO <sub>4</sub> <sup>3-</sup> | SO <sub>4</sub> <sup>2-</sup> | Cl <sup>-</sup> | PO <sub>4</sub> <sup>3-</sup> | SO <sub>4</sub> <sup>2-</sup> | Cl <sup>-</sup> | PO <sub>4</sub> <sup>3-</sup> |
| Sc  | 20.2                          | 8.6             | 4.5                           | 93.4                          | 99.2            | 74.7                          | 80.1                          | 97.2            | 45.6                          | 78.9                          | 98.5            | 33.5                          |
| Y   | 10.5                          | 5.2             | 4.9                           | 91.9                          | 99.3            | 61.7                          | 76.4                          | 95.9            | 30.6                          | 76.5                          | 98.0            | 30.0                          |
| La  | 10.0                          | 7.2             | 6.3                           | 92.3                          | 99.3            | 51.4                          | 80.0                          | 95.3            | 51.6                          | 82.4                          | 96.9            | 46.4                          |
| Ce  | 3.5                           | 3.3             | 2.1                           | 99.6                          | 99.8            | 83.0                          | 95.3                          | 94.8            | 43.6                          | 99.7                          | 99.7            | 46.8                          |
| Pr  | 29.8                          | 6.8             | 5.5                           | 66.8                          | 99.8            | 82.1                          | 42.9                          | 95.8            | 45.5                          | 36.6                          | 98.8            | 44.2                          |
| Nd  | 2.2                           | 6.7             | 1.4                           | 99.8                          | 99.8            | 73.8                          | 96.5                          | 95.1            | 37.2                          | 99.7                          | 99.8            | 33.0                          |
| Sm  | 11.6                          | 8.4             | 6.3                           | 90.0                          | 99.0            | 70.2                          | 75.6                          | 95.1            | 33.4                          | 75.4                          | 99.8            | 33.7                          |
| Eu  | 21.0                          | 10.5            | 4.0                           | 85.5                          | 99.5            | 63.4                          | 55.3                          | 93.2            | 30.0                          | 58.5                          | 92.5            | 30.0                          |
| Gd  | 36.2                          | 3.5             | 7.7                           | 75.6                          | 99.6            | 37.5                          | 54.6                          | 96.5            | 17.1                          | 48.5                          | 97.6            | 17.8                          |
| Dy  | 8.6                           | 6.6             | 7.1                           | 94.2                          | 99.3            | 61.2                          | 79.8                          | 96.2            | 30.0                          | 85.5                          | 99.2            | 30.1                          |
| Ho  | 8.1                           | 6.3             | 2.1                           | 94.7                          | 99.7            | 59.4                          | 81.6                          | 96.8            | 27.2                          | 86.6                          | 98.2            | 27.5                          |
| Er  | 9.6                           | 6.8             | 3.3                           | 92.4                          | 99.4            | 59.3                          | 77.3                          | 95.5            | 21.7                          | 81.4                          | 97.6            | 27.5                          |
| Tm  | 11                            | 4.7             | 5.3                           | 91.3                          | 99.3            | 55.5                          | 76.2                          | 96.2            | 26.2                          | 76.9                          | 99.2            | 26.3                          |
| Yb  | 10.8                          | 5.8             | 6.2                           | 91.8                          | 99.8            | 55.7                          | 78.3                          | 96.1            | 27.0                          | 77.4                          | 99.6            | 27.3                          |
| Lu  | 14.9                          | 7.4             | 5.7                           | 85.7                          | 99.7            | 53.0                          | 76.4                          | 98.0            | 25.5                          | 66.5                          | 99.8            | 26.3                          |

where A - D indicate the conditions used (i.e. (A) 2 mg L<sup>-1</sup> REY, pH 2, 0.01 mol L<sup>-1</sup> anion, (B) 2 mg L<sup>-1</sup> REY, pH 5.5, 0.01 mol L<sup>-1</sup> anion, (C) 2 mg L<sup>-1</sup> REY, pH 5.5, 0.05 mol L<sup>-1</sup> anion and (D) 5 mg L<sup>-1</sup> REY, pH 5.5, 0.05 mol L<sup>-1</sup> anion)

**Table 5**Modelling properties of the adsorption of REY by natural zeolite at 3 cm bed height, 2 mg L<sup>-1</sup>, 2 mL min<sup>-1</sup> and pH 5.5 (n = 3, RSD < 10%).

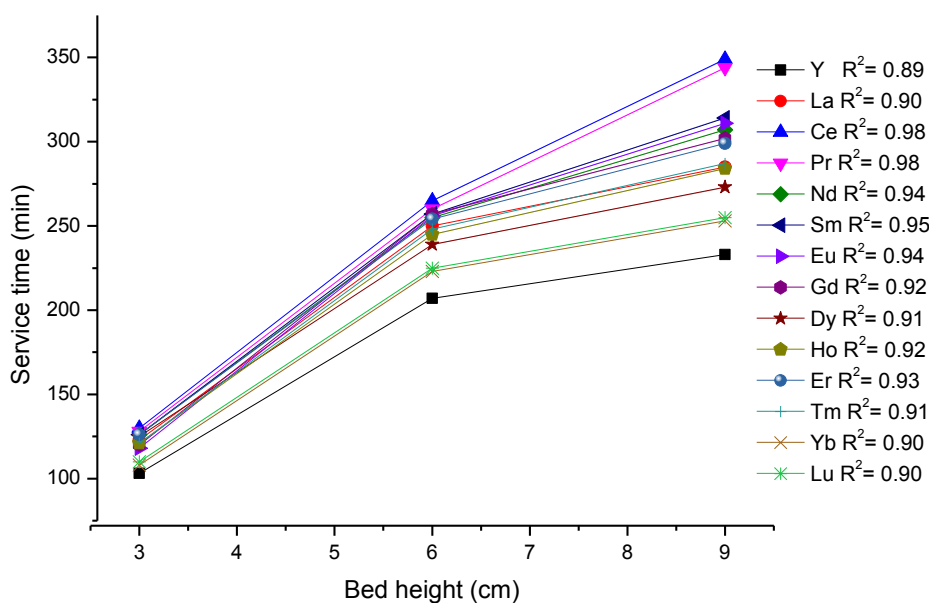
| C <sub>0</sub> mg L <sup>-1</sup> | Adams-Bohart                                         |                                   |                | Thomas                                               |                                   |                | Yoon-Nelson                       |       |                |
|-----------------------------------|------------------------------------------------------|-----------------------------------|----------------|------------------------------------------------------|-----------------------------------|----------------|-----------------------------------|-------|----------------|
|                                   | k <sub>AB</sub> L mg <sup>-1</sup> min <sup>-1</sup> | N <sub>0</sub> mg L <sup>-1</sup> | R <sup>2</sup> | k <sub>Th</sub> L min <sup>-1</sup> mg <sup>-1</sup> | q <sub>0</sub> mg g <sup>-1</sup> | R <sup>2</sup> | K <sub>YN</sub> min <sup>-1</sup> | τ min | R <sup>2</sup> |
| Sc                                | 0.0046                                               | 39,379                            | 0.67           | 0.0046                                               | 127                               | 0.67           | 0.012                             | 1795  | 0.67           |
| Y                                 | 0.0069                                               | 30,579                            | 0.84           | 0.0070                                               | 98.4                              | 0.83           | 0.017                             | 1395  | 0.82           |
| La                                | 0.0061                                               | 31,985                            | 0.93           | 0.0063                                               | 102                               | 0.92           | 0.016                             | 1313  | 0.92           |
| Ce                                | 0.0075                                               | 30,591                            | 0.74           | 0.0076                                               | 98.6                              | 0.74           | 0.019                             | 1394  | 0.74           |
| Pr                                | 0.0095                                               | 28,783                            | 0.73           | 0.0096                                               | 92.9                              | 0.73           | 0.024                             | 1312  | 0.73           |
| Nd                                | 0.011                                                | 27,098                            | 0.77           | 0.012                                                | 87.6                              | 0.77           | 0.011                             | 1241  | 0.77           |
| Sm                                | 0.0063                                               | 32,447                            | 0.82           | 0.0064                                               | 104                               | 0.83           | 0.016                             | 1471  | 0.83           |
| Eu                                | 0.0051                                               | 35,545                            | 0.87           | 0.0052                                               | 115                               | 0.87           | 0.013                             | 1822  | 0.87           |
| Gd                                | 0.0077                                               | 29,281                            | 0.75           | 0.0078                                               | 94.6                              | 0.75           | 0.020                             | 1333  | 0.75           |
| Dy                                | 0.0059                                               | 34,037                            | 0.85           | 0.0059                                               | 110                               | 0.85           | 0.015                             | 1545  | 0.84           |
| Ho                                | 0.0055                                               | 35,440                            | 0.91           | 0.0056                                               | 114                               | 0.91           | 0.014                             | 1606  | 0.91           |
| Er                                | 0.021                                                | 24,452                            | 0.98           | 0.021                                                | 79.2                              | 0.97           | 0.053                             | 1123  | 0.97           |
| Tm                                | 0.0053                                               | 35,685                            | 0.86           | 0.0054                                               | 115                               | 0.86           | 0.013                             | 1620  | 0.86           |
| Yb                                | 0.0062                                               | 33,041                            | 0.85           | 0.0063                                               | 107                               | 0.85           | 0.018                             | 1419  | 0.78           |
| Lu                                | 0.0064                                               | 32,507                            | 0.79           | 0.0065                                               | 105                               | 0.79           | 0.016                             | 1475  | 0.79           |

**Table 6**Modelling properties of the adsorption of REY by natural zeolite at 3 cm bed height, 5 mg L<sup>-1</sup>, 2 mL min<sup>-1</sup> and pH 5.5 (n = 3, RSD < 10%).

| C <sub>0</sub> mg L <sup>-1</sup> | Adams-Bohart                                         |                                   |                | Thomas                                               |                                   |                | Yoon-Nelson                       |       |                |
|-----------------------------------|------------------------------------------------------|-----------------------------------|----------------|------------------------------------------------------|-----------------------------------|----------------|-----------------------------------|-------|----------------|
|                                   | k <sub>AB</sub> L mg <sup>-1</sup> min <sup>-1</sup> | N <sub>0</sub> mg L <sup>-1</sup> | R <sup>2</sup> | k <sub>Th</sub> L min <sup>-1</sup> mg <sup>-1</sup> | q <sub>0</sub> mg g <sup>-1</sup> | R <sup>2</sup> | K <sub>YN</sub> min <sup>-1</sup> | τ min | R <sup>2</sup> |
| Sc                                | 0.0056                                               | 36,610                            | 0.94           | 0.0061                                               | 116                               | 0.94           | 0.031                             | 827   | 0.94           |
| Y                                 | 0.0059                                               | 28,670                            | 0.80           | 0.0068                                               | 86.2                              | 0.84           | 0.034                             | 616   | 0.84           |
| La                                | 0.0059                                               | 29,161                            | 0.72           | 0.0067                                               | 88.5                              | 0.76           | 0.032                             | 632   | 0.76           |
| Ce                                | 0.0055                                               | 29,566                            | 0.63           | 0.0064                                               | 88.9                              | 0.69           | 0.032                             | 635   | 0.69           |
| Pr                                | 0.0065                                               | 28,996                            | 0.71           | 0.0073                                               | 88.3                              | 0.76           | 0.034                             | 630   | 0.76           |
| Nd                                | 0.0059                                               | 29,413                            | 0.70           | 0.0073                                               | 81.5                              | 0.75           | 0.034                             | 667   | 0.75           |
| Sm                                | 0.0052                                               | 29,809                            | 0.64           | 0.0061                                               | 89.3                              | 0.70           | 0.031                             | 637   | 0.70           |
| Eu                                | 0.0063                                               | 28,986                            | 0.75           | 0.0072                                               | 88.1                              | 0.79           | 0.036                             | 629   | 0.79           |
| Gd                                | 0.0060                                               | 28,788                            | 0.74           | 0.0069                                               | 86.6                              | 0.79           | 0.035                             | 593   | 0.79           |
| Dy                                | 0.0053                                               | 29,435                            | 0.60           | 0.0062                                               | 87.9                              | 0.66           | 0.031                             | 628   | 0.66           |
| Ho                                | 0.0053                                               | 29,448                            | 0.70           | 0.0062                                               | 88.2                              | 0.76           | 0.031                             | 630   | 0.76           |
| Er                                | 0.0051                                               | 29,650                            | 0.62           | 0.0060                                               | 88.5                              | 0.68           | 0.030                             | 632   | 0.68           |
| Tm                                | 0.0056                                               | 28,989                            | 0.72           | 0.0065                                               | 86.7                              | 0.77           | 0.033                             | 619   | 0.77           |
| Yb                                | 0.0059                                               | 28,769                            | 0.75           | 0.0068                                               | 86.6                              | 0.80           | 0.034                             | 619   | 0.80           |
| Lu                                | 0.0057                                               | 38,921                            | 0.64           | 0.0067                                               | 86.6                              | 0.70           | 0.033                             | 619   | 0.70           |

**Table 7**Modelling properties of the adsorption of REY by natural zeolite at 3 cm bed height, 10 mg L<sup>-1</sup>, 2 mL min<sup>-1</sup> and pH 5.5 (n = 3, RSD < 10%).

| C <sub>0</sub> mg L <sup>-1</sup> | Adams-Bohart                                         |                                   |                | Thomas                                               |                                   |                | Yoon-Nelson                       |       |                |
|-----------------------------------|------------------------------------------------------|-----------------------------------|----------------|------------------------------------------------------|-----------------------------------|----------------|-----------------------------------|-------|----------------|
|                                   | k <sub>AB</sub> L mg <sup>-1</sup> min <sup>-1</sup> | N <sub>0</sub> mg L <sup>-1</sup> | R <sup>2</sup> | k <sub>Th</sub> L min <sup>-1</sup> mg <sup>-1</sup> | q <sub>0</sub> mg g <sup>-1</sup> | R <sup>2</sup> | K <sub>YN</sub> min <sup>-1</sup> | τ min | R <sup>2</sup> |
| Sc                                | 0.0080                                               | 19,379                            | 0.89           | 0.0013                                               | 523                               | 0.90           | 0.050                             | 677   | 0.89           |
| Y                                 | 0.010                                                | 15,189                            | 0.75           | 0.0020                                               | 243                               | 0.76           | 0.056                             | 507   | 0.77           |
| La                                | 0.010                                                | 15,614                            | 0.78           | 0.0020                                               | 250                               | 0.79           | 0.053                             | 254   | 0.81           |
| Ce                                | 0.0083                                               | 17,563                            | 0.83           | 0.0017                                               | 282                               | 0.83           | 0.045                             | 286   | 0.85           |
| Pr                                | 0.0091                                               | 16,070                            | 0.81           | 0.0019                                               | 257                               | 0.81           | 0.050                             | 258   | 0.83           |
| Nd                                | 0.0089                                               | 16,315                            | 0.81           | 0.0018                                               | 261                               | 0.82           | 0.049                             | 262   | 0.84           |
| Sm                                | 0.0097                                               | 15,546                            | 0.75           | 0.0020                                               | 249                               | 0.76           | 0.053                             | 253   | 0.79           |
| Eu                                | 0.011                                                | 14,909                            | 0.78           | 0.0021                                               | 239                               | 0.79           | 0.058                             | 247   | 0.81           |
| Gd                                | 0.011                                                | 14,691                            | 0.88           | 0.0021                                               | 236                               | 0.88           | 0.057                             | 242   | 0.90           |
| Dy                                | 0.010                                                | 15,172                            | 0.85           | 0.0020                                               | 243                               | 0.85           | 0.054                             | 247   | 0.87           |
| Ho                                | 0.011                                                | 14,619                            | 0.87           | 0.0022                                               | 235                               | 0.87           | 0.059                             | 243   | 0.89           |
| Er                                | 0.011                                                | 14,573                            | 0.82           | 0.0022                                               | 234                               | 0.83           | 0.060                             | 243   | 0.85           |
| Tm                                | 0.010                                                | 14,966                            | 0.86           | 0.0021                                               | 240                               | 0.87           | 0.056                             | 244   | 0.89           |
| Yb                                | 0.011                                                | 14,680                            | 0.88           | 0.0022                                               | 236                               | 0.88           | 0.058                             | 242   | 0.90           |
| Lu                                | 0.011                                                | 14,648                            | 0.81           | 0.0022                                               | 235                               | 0.81           | 0.059                             | 242   | 0.84           |

**Fig. 7.** Bed depth service time (BDST) model for the removal of REY by natural zeolite (n = 3, RSD < 10%, temperature = 24–26 °C, bed height = 3 cm, pH = 5.5, concentration = 2 mg L<sup>-1</sup>).

**Visualization. Hlanganani Tutu:** Conceptualization, Writing - review & editing, Resources, Supervision, Project administration, Funding acquisition.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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**SECTION 4.5:**

**MODELLING OF**

**SORPTION OF**

**PALLADIUM USING**

**PHREEQC**

**GEOCHEMICAL**

**MODELLING AND**

**PARAMETER**

**ESTIMATION**

# PAPER I

**This paper addresses the modelling of the recovery of palladium using PHREEQC geochemical model coupled to parameter estimation (PEST).**

**The paper is published in the Journal of Environmental Management.**

**Impact Factor: 5.647.**

**Contribution:** lead author, conducted experimental work and data modelling, conceptualization, methodology, software validation, formal analysis, investigation, writing - original draft and visualization.



## Research article

## Modelling of palladium(II) adsorption onto amine-functionalised zeolite using a generalised surface complexation approach

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## ABSTRACT

The many uses of palladium in medicine, catalysts and other industries make it a very important precious element. Many industries using palladium discharge process wastewaters that may release elevated concentrations of palladium into the environment. This study focused on the recovery of palladium from aqueous solutions by zeolite functionalised with spent brewer's yeast. Batch experimental results were used to calibrate a generalised surface complexation model based on coupling parameter estimation (PEST) to the PHREEQC geochemical modelling code. PHREEQC is an acronym which stands for pH, redox, equilibrium and C programming language. Calibration was based on the determination of sorption constants for the reactions of palladium with the adsorbent. The generalised amine surface groups (derived from yeast), the moles of adsorption sites and surface area were specified. The recovery of palladium was assessed as a function of solution pH, adsorbent dosage and initial concentration of palladium in the presence of other cations and anions at different concentrations. The highest recovery of palladium (>97%) was observed at pH 2 and 10 g L<sup>-1</sup> adsorbent dosage which, decreased with increasing solution pH. The amount of palladium removed increased in the presence of competing ions and anions. There was no significant difference ( $p > 0.05$ ) between the modelled and measured data, which indicated that PHREEQC modelling code coupled with PEST can accurately determine the recovery of palladium using amine-based adsorbents when all the required information is specified. This is very useful in instances where limited experimental data is available for non-conventional and novel surfaces to make accurate predictions of sorption processes involving them.

## 1. Introduction

Palladium has been found to be a very important element in medicine since, Pd(II) complexes have anticancer, antitumor, antibacterial, anti-inflammatory and antimalarial activities (Lazarević et al., 2017). Palladium is also widely used in fuel cell catalysis, bimetallic catalysts, jewellery, automotive catalytic converters and multilayer ceramic capacitors (Jadhav et al., 2017; Liu et al., 2020). All these uses deem palladium as a very important element for many industries and life in general. However, the demand for palladium has been increasing over the years due to improving technologies and products of the above mentioned industries. This demand for palladium has also led to increasing palladium prices from mining which automatically means a rise in prices of palladium based-products (Cowley, 2019; Bourgeois et al., 2020). Already, mining and production of platinum group

elements which includes palladium has been struggling in recent years due to strikes in South Africa which holds 80% of the reserves (Mnwana, 2015; McKay, 2018). In addition to this, Fontàs et al. (2003) indicated that palladium is facing scarcity. All these allude to the fact that ways of recovering palladium from industrial (jewellery, automobile, medical etc.) wastewaters are of utmost importance.

Despite the importance of palladium, there are negative impacts it can bestow to living organisms hence the recovery from wastewaters will not only be of economical but also medical importance. In humans, high concentrations of palladium can cause kidney failure, cancer, asthma and many others (Awual, 2016). There are a number of ways in which humans can be exposed to high concentrations of palladium but, the main ones are through direct ingestion by drinking contaminated water or through the food chain and inhalation (Kielhorn et al., 2002). To reduce the concentrations of palladium in wastewaters and recovery,

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recycling methods such as ion exchange chromatography, pyrometallurgy and solvent extraction have been employed but, they are often ineffective since the concentrations of palladium are very low ( $<10\text{--}40\text{ mg L}^{-1}$ ) (Umeda et al., 2011). Therefore, palladium can be transported from industrial wastewaters to water sources such as rivers, lakes and dams where it is easily accessible to humans and other living organisms. Industrial wastewaters always contain high concentrations of base elements such as (Ca, Mg, Na, K etc.) but low concentrations of precious elements hence the recovery of palladium is often very difficult due to selectivity problems (Ju et al., 2016).

The selectivity of palladium over other elements which may or may not be in high concentration is very important when undertaking the recovery processes. For selectivity to occur ligands that have high affinity for palladium should be used. Palladium has been found to chemically interact with nitrogen therefore, nitrogen ligands can be used for significant recovery (Kumbhar, 2017; Li et al. (2017). Mosai et al. (2020) have reported on the recovery of palladium using yeast functionalised zeolite and indicated that the recovery was effective. Reddy et al. (2010) have indicated that palladium can be recovered from spent automobile catalyst leach liquor using Alamine 336, which is a tertiary amine. Palladium was successfully recovered using chitosan derivatives (Chassary et al., 2005). These studies indicate that the strong interaction between palladium and nitrogen ligands can be used for selective recovery of palladium. Despite this evidence, there is a need for studies that show potential of palladium recovery from industrial wastewaters which contain high concentrations of base elements (e.g. typical mining and fuel cells wastewaters). In this study, geochemical modelling using PHREEQC (which stands for pH, redox, equilibrium and C programming language) was used to simulate the recovery of palladium in wastewater solutions of different conditions that best represent industrial wastewaters (Parkhurst and Appelo, 2013; Abdelaziz et al., 2019). PHREEQC was also used to explain results obtained from laboratory experiments and to simulate conditions that were not done with laboratory experiments. Amine-generalised zeolite surface was used as an adsorbent. This amine-generalised surface is a surface in which surface groups are not specified individually but rather the different amine groups as a result of different amino acids in the yeast are generalised into ( $-\text{NH}_2$ ) in PHREEQC input script. Automated parameter estimation (PEST) software was used to determine sorption constants of reactions.

## 2. Methodology

### 2.1. Functionalisation of zeolite with amine ligands

Zeolite was used in this study because it is naturally occurring, readily available and relatively cheap. More importantly, zeolite is an aluminosilicate with a high cationic exchange capacity (CEC) and ion adsorption capacity (Yu et al., 2001; Sheta et al., 2003). The zeolite in this study was used as a support or anchor for amine groups as these would form amine-metal complexes in solution on their own and ultrafiltration will have to be conducted to remove those complexes from solutions (Jin and Ranford, 2000; Mosai et al., 2020). The zeolite was contacted with spent brewer's yeast (*Saccharomyces cerevisiae*) solution which contains a number of amino acids such as lysine, leucine, alanine, threonine, glutamine and arginine (Yang et al., 2018; Ring, 2019). Amino acids have amine ( $-\text{NH}_2$ ) groups which have an affinity for palladium (Mosai et al., 2020). The spent brewer's yeast is usually a waste product from craft breweries and other brewing industries, making it a cheap source of amine groups (Kerby and Vriesekoop, 2017; Rachwai et al., 2020). To get the functionalised zeolite, 40 mL brewer's spent yeast waste was mixed with 10 g zeolite and shaken for 24 h in an elliptical bench-top shaker (Labcon, USA). The mixture was filtered and the solid residue dried at room temperature. The natural and functionalised zeolite (dried residue) were characterised with a Bruker Tensor 27 Fourier transform infrared spectroscopy (FTIR) (Bruker, Germany) to determine the success of the functionalisation; a D2 Phaser powder

X-ray diffraction (PXRD) (Bruker, Germany) to determine the dominant mineralogy; an X-ray fluorescence (XRF) (PAAnalytical, Netherlands) to determine elemental composition. A Micromeritics Flow Prep 060 instrument (Aachen, Germany) was used to determine the pore size, pore volume and surface area. A VarioELcube V4.0.13 (Elementar, Germany) was used to determine the amount of carbon, hydrogen and nitrogen (C, H and N). The results from characterisation were used to build the PHREEQC model. The surface area of the adsorbent after functionalisation was specified in the PHREEQC script so that the adsorbent is best represented and the mineralogy has to be known in order to simulate the interaction of Pd(II) with the adsorbent. Zeolite alone poorly adsorbed palladium ( $<10\%$  removal) hence the functionalised adsorbent was used.

### 2.2. Adsorption experiments

In order to get accurate results for testing a PHREEQC sorption model for palladium under various conditions, the model had to be calibrated. The calibration was done by conducting batch laboratory experiments. Variables such as solution pH (2–10), concentration of Pd(II) in chloride solutions, adsorbent dosage, temperature ( $20\text{--}50\text{ }^\circ\text{C}$ ) and the presence of other elements: cations (Al, Co, Cr, Fe, K, Mg, Mn and Ni) and anions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$  and  $\text{SO}_4^{2-}$ ) were investigated by preparing solutions in these conditions. One variable was investigated whilst keeping the others constant. The pH was investigated since studies have indicated that the uptake of elements by adsorbents can be highly dependent on the pH of the solution (Wei et al., 2016; Mosai et al., 2020). This is because the speciation of elements and the surface charge can change with pH (Aljerf, 2018). The concentration of elements can affect adsorption efficiency of adsorbents hence the role of concentration on recovery was determined (Fakhre et al., 2018). Palladium and other platinum group elements (PGEs) usually occur in chloride forms in wastewater and thus, the solutions were prepared in a chloride matrix (Rao and Reddi, 2000; Godlewska-Żyłkiewicz et al., 2019). The effect of high and low adsorbent mass was also considered in this study in order to find the efficient adsorbent mass. The effect of different elements on the recovery of palladium was also investigated since other elements may enhance or reduce the adsorption of elements of interest (Babu et al., 2009; Mosai et al., 2020). Elements such as Ca and Mg may occur in very high concentrations in wastewater therefore; this was considered to best represent the various effects. Moreover, the effect of individual high levels of nitrate, sulphate and phosphate ions on the adsorption of Pd(II) was also studied as a function of pH. The variations in geochemical conditions were varied to capture a reasonable range of expected conditions in real industrial wastewater (Aljerf, 2018). Thermodynamic parameters such as  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$  were also determined since they lead to highly accurate simulations (Sahmoune, 2019).

The chemicals used for the experiments were of analytical reagent grade and purchased from Sigma Aldrich, South Africa. Deionised water was used to prepare solutions. For pH adjustment, HCl and NaOH were used and the pH was determined using a pH meter (Mettler Toledo, Switzerland). The experiments were conducted in triplicates ( $n = 3$ ) and the reliability and uncertainty in the data was assessed using the relative standard deviation (%RSD). The results obtained were used to calibrate the PHREEQC model together with sorption constants (explained later). Analysis of variance (ANOVA) was used to compare the measured and modelled data for each variable.

### 2.3. PHREEQC model construction

The PHREEQC interactive geochemical modelling code version 3.3.5–10806 (US Geological Survey, USA) was used to simulate the recovery of Pd(II) from aqueous solutions at different conditions. PHREEQC is written in the C programming language and is used to perform aqueous geochemical calculations, batch-reaction and one-dimensional transport calculations (Parkhurst and Appelo, 1999;

Garneau et al., 2017; Vaneckhaute et al., 2018). Thus, PHREEQC can be used to determine the efficiency of sorption in experimental columns. The relationship between surface adsorption sites and elements can be determined by interconnecting equilibrium and kinetic reactions. The saturation index (SI) and the distribution of aqueous species can be calculated. Elements in different valence states and speciation can be determined using PHREEQC. Thus, the way in which elements interact with adsorbents can be accurately determined when all the important data is added in the input script. The details on the keywords in Fig. 1 can be found in the PHREEQC manual (Parkhurst and Appelo, 1999).

An example of the input script of the PHREEQC model used in this study is shown in Fig. 1. Surf\_si represents silica sites on the surface zeolite whilst Surf\_aa represents amino acids attached on the zeolite. Generalised amine surface groups (-aaNH<sub>2</sub>) were used since the amines responsible for recovery could be from many amino acids which cannot be identified individually. To determine the speciation of the elements, PHREEQC first runs SOLUTION 1 by itself and indicates all possible species with the specified conditions. All possible major species of palladium were considered in this study. PHREEQC allows the user to specify the number of moles of surface sites, surface area, mass of adsorbent used, temperature etc. hence all the conditions used in the laboratory experiments were included in the input script. Thermodynamic parameters were provided by the SIT database as it contains palladium and other elements of interest.

#### 2.4. Parameter estimation (PEST)

Model-Independent parameter estimation (PEST) was used in this study to accurately determine the thermodynamic log *k* values of the reactions occurring between the adsorbent surface and the elements similar to the procedures discussed in Johnson et al. (2016). PEST is a freely available software that is used to calibrate model input parameters by matching model outputs to measurements of system state

(Doherty, 2019). PEST uses model input and output files to run a model many times where, measured and modelled output values are compared to achieve the best model calibration based on changing the input parameter values.

### 3. Results and discussion

#### 3.1. Characterisation of zeolite

The natural and functionalised zeolite were characterised to confirm if the amino acids were indeed attached onto the zeolite. This functionalisation was also very important for determining surface sorption equations in the PHREEQC model. Fourier transform infrared spectroscopy (FTIR) determined the functional groups of the raw and functionalised zeolite and indicated that there was peak at 1483 cm<sup>-1</sup> which indicated N-H stretching, most likely from the amine groups of the amino acids (Fig. 2) (Chiang et al., 1980). The amount of nitrogen increased notably after functionalisation (Table 1). The peak at 1025 cm<sup>-1</sup> was due to the overlapping Al-O and Si-O signals (Fig. 2) (Schroeder, 2002). XRF indicated that the zeolite is composed of SiO<sub>2</sub> (69%) and Al<sub>2</sub>O<sub>3</sub> (17%) which have played a major role on the attachment of yeast functional groups. D2 Phaser powder X-ray diffraction (PXRD) indicated that clinoptilolite-Ca, clinoptilolite-Ca, boggsite, quartz, sanidine and silica were main minerals of zeolite and were observed at 11°, 20°, 26°, 30.5°, 31.5° and 26.9°, respectively (Fig. 3) (Jorfi et al., 2017). The pore size, pore volume and surface area of the zeolite were found to be 12.97 nm, 0.052 cm<sup>3</sup> g<sup>-1</sup> and 16.28 m<sup>2</sup> g<sup>-1</sup>, respectively and changed to 5.45 nm, 0.053 cm<sup>3</sup> g<sup>-1</sup> and 2.13 m<sup>2</sup> g<sup>-1</sup>, respectively when functionalised with yeast. A schematic representation of the preparation of yeast functionalised zeolite was shown in Fig. 4.

```

SURFACE_MASTER_SPECIES
  Surf_aa      Surf_aaNH2
  Surf_si      Surf_siOH

SURFACE_SPECIES
  Surf_surface species = Surf_surface species
  log_k      value

PHASES
  fix_pH
    H+ = H+
    log_k      0
  fix_pe
    e- = e-
    log_k      0

SOLUTION 1
  temp      value
  pH        value
  pe        value
  redox     pe
  units     mg/l
  density   1
  Cl        concentration value in mol L-1
  Pd        concentration value
  -water    value # kg

SURFACE 1
  Surf_aaNH2 #no. of moles# #Surface area (m2 g-1)# #mass of adsorbent (g)#
  Surf_siOH  #no. of moles#

```

Fig. 1. PHREEQC input script.

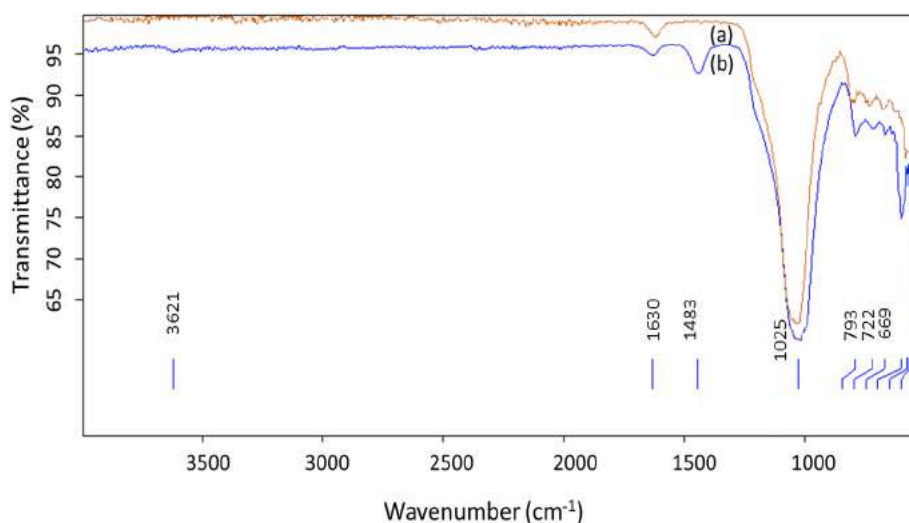


Fig. 2. FTIR spectra of the (a) raw and (b) functionalised zeolite.

Table 1

Elemental analysis of the raw and functionalised zeolite.

| Sample                       | C (%) | H (%) | N (%) |
|------------------------------|-------|-------|-------|
| Natural zeolite              | 0.20  | 1.18  | 0.06  |
| Yeast-functionalised zeolite | 2.68  | 1.51  | 0.78  |

### 3.2. Role of pH on Pd(II) sorption and calibration of the PHREEQC model

The results from the characterisation techniques were used to build the PHREEQC model as indicated in Fig. 5. To get a good representation of the yeast functionalised zeolite surface in the model, the functional groups with their respective number of moles were specified. Moreover, the surface area and the mass of the adsorbent were specified as discussed previously (Fig. 1).

Batch experiments were conducted to calibrate the PHREEQC model using the effect of pH (2–10) with  $2 \text{ mg L}^{-1}$   $\text{PdCl}_4^{2-}$  solution and  $10 \text{ g L}^{-1}$  dosage of the functionalised zeolite at  $25^\circ \text{C}$  (Johnson et al., 2016). The

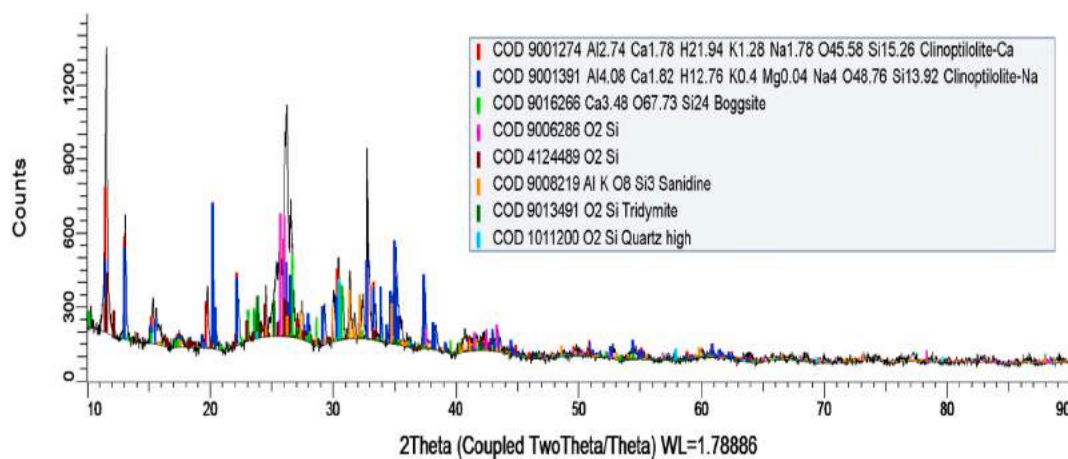


Fig. 3. PXRD pattern of the raw zeolite.

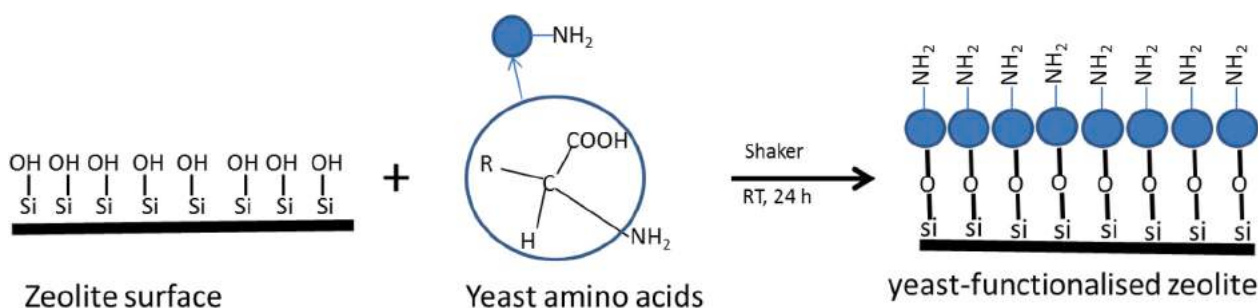


Fig. 4. Schematic representation of the preparation of yeast functionalised zeolite.

```

SURFACE_MASTER_SPECIES
  Surf_aa      Surf_aaNH2
  Surf_si      Surf_siOH

SURFACE_SPECIES
Surf_aaNH2 = Surf_aaNH2          log_k      0
PdCl42- + Surf_aaNH2 = Surf_aaNH2PdCl42-    log_k      5.55820
PdCl3- + Surf_aaNH2 = Surf_aaNH2PdCl3-      log_k      0.124114
PdCl+ + Surf_aaNH2 = Surf_aaNH2PdCl+      log_k      1.63879
PdCl2 + Surf_aaNH2 = Surf_aaNH2PdCl2      log_k      -0.04
Surf_siOH = Surf_siOH          log_k      0
Surf_siOH = Surf_siOH- + H+          log_k      -6.65
Surf_siOH + PdCl2 = Surf_siOHPdCl2      log_k      -1.29213
Surf_siOH + Pd(OH)2 = Surf_siOHPd(OH)2  log_k      0.585182
Surf_siOH + Pd(OH)3- = Surf_siOHPd(OH)3-  log_k      2.45182
Surf_siOH + Pd(OH)42- = Surf_siOHPd(OH)42- log_k      3.685182

PHASES
fix_pH
  H+ = H+          log_k      0
fix_pe
  e- = e-          log_k      0
SOLUTION 1
  temp      25
  pH        2
  pe        4
  redox     pe
  units     mg/l
  density   1
  Cl        0.01 Mol/l
  Pd        2
  -water    0.001 # kg
SURFACE 1
  Surf_aaNH2 8.789e-05  2.13  0.1
  Surf_siOH  0.000545
END
USER_PUNCH 1
  -headings
  -start
10 q_sorb = mol("Surf_aaNH2PdCl42-") + mol("Surf_aaNH2PdCl3-") + mol
("Surf_aaNH2PdCl+") + mol("Surf_siOHPdCl2") + mol("Surf_siOHPd(OH)2")
+ mol("Surf_aaNH2PdCl2") + mol("Surf_siOHPd(OH)3-") + mol("Surf_siOHPd(OH)42-")
20 punch q_sorb/1.88e-5*100
  -end
USE solution 1
USE surface 1
EQUILIBRIUM_PHASES 1
  CO2(g)      -3.5 10
  fix_pH      -2 HCl      10
END

```

Fig. 5. PHREEQC input script incorporating results from characterisation techniques and equations of the palladium (II) species.

removal percentage of palladium at different conditions was determined using Eq. (1). The recovery of palladium species from aqueous solutions at different pH values using functionalised zeolite was observed to decrease with increasing pH (Fig. 6) (Chassary et al., 2005; Mosai et al., 2020). At lower pH, the functionalised zeolite surface was positively charged due to high concentration of H<sup>+</sup> (i.e. -aNH<sub>3</sub><sup>+</sup>) and has high

affinity for negatively charged palladium species hence the highest removal (97.2%) was seen at pH 2 (Nagireddi et al., 2018). The charge of the functionalised zeolite becomes less positive as pH increases because of the increasing concentration of OH<sup>-</sup> (Mosai et al., 2020). Experimental results were used to calibrate the sorption equilibrium constants.

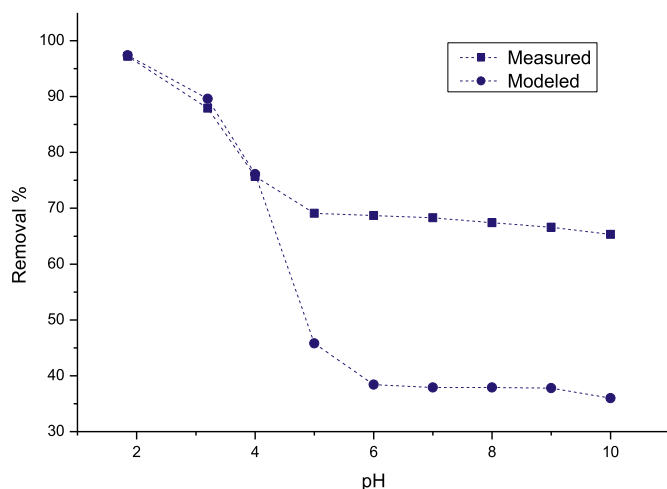
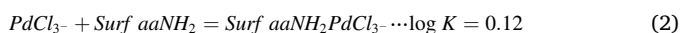


**Fig. 6.** Measured and PHREEQC modelled data of the recovery of palladium as a function of pH (Concentration = 2 mg L<sup>-1</sup>, adsorbent dosage = 10 g L<sup>-1</sup>, time = 300 min, temp = 25 °C, n = 3, RSD <5%, ANOVA comparison between measured and modelled data =  $p < 0.05$ ).

$$\text{Removal \%} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

where  $C_0$  is the initial concentration of Pd(II) and  $C_e$  (mg L<sup>-1</sup>) is the equilibrium concentration of Pd(II).

To get the correct simulations, all the possible reactions involved in the recovery of palladium should be specified in the input script. To determine the reactions between the functionalised zeolite and the species of palladium, the conditions of the initial solution were first determined by running the solution in PHREEQC to perform aqueous geochemical calculations. The PHREEQC model output file of the initial solution is shown in Table 2. The solution results indicated that  $\text{PdCl}_4^{2-}$ ,  $\text{PdCl}_3^-$ ,  $\text{PdCl}_2$ ,  $\text{Pd(OH)}_2$ ,  $\text{PdCl}_2$ ,  $\text{PdOH}^+$ ,  $\text{Pd(OH)}_3$ ,  $\text{Pd(OH)}_4^{2-}$  and  $\text{PdCl}_3(\text{OH})^{2-}$  were species of palladium in different amounts (Nagireddi et al., 2018). The amounts would change depending on the conditions of the solutions. The amounts of the different species are given in molality in the PHREEQC model output. The molality of the species is determined from the initial concentration specified. These species were then used to determine surface reactions with respective log  $k$  values as indicated in Eq. (2). The surface reactions were then added in the input script as indicated in Fig. 5.



To get the correct sorption constants, PEST coupled with PHREEQC was used (Johnson et al., 2016). Sorption constants were estimated from PEST. In order to do this however, these constants must be determined from either historical data or laboratory experiments and run in PHREEQC with the initial solution used to calibrate the model. There is

**Table 2**

Palladium speciation from PHREEQC model output file.

| Species                         | Molality (mol Kg <sup>-1</sup> ) | Activity                |
|---------------------------------|----------------------------------|-------------------------|
| Pd                              | $1.880 \times 10^{-05}$          |                         |
| $\text{PdCl}_3^-$               | $1.392 \times 10^{-05}$          | $1.242 \times 10^{-05}$ |
| $\text{PdCl}_2$                 | $3.507 \times 10^{-06}$          | $3.507 \times 10^{-06}$ |
| $\text{PdCl}_4^{2-}$            | $1.099 \times 10^{-06}$          | $6.972 \times 10^{-07}$ |
| $\text{PdCl}^+$                 | $2.776 \times 10^{-07}$          | $2.487 \times 10^{-07}$ |
| $\text{Pd}^{+2}$                | $3.488 \times 10^{-10}$          | $2.220 \times 10^{-10}$ |
| $\text{Pd(OH)}^+$               | $2.430 \times 10^{-10}$          | $2.169 \times 10^{-10}$ |
| $\text{Pd(OH)}_2$               | $1.803 \times 10^{-10}$          | $1.803 \times 10^{-10}$ |
| $\text{PdCl}_3(\text{OH})^{2-}$ | $3.562 \times 10^{-12}$          | $2.259 \times 10^{-12}$ |
| $\text{Pd(OH)}_3$               | $1.036 \times 10^{-20}$          | $9.244 \times 10^{-21}$ |
| $\text{Pd(OH)}_4^{2-}$          | $3.832 \times 10^{-32}$          | $2.430 \times 10^{-32}$ |

another output file from PHREEQC which the user can create to get the removal percentage. The results from this file were used to match those from batch experiments. Measured and PHREEQC modelled data using manually determined sorption constants are shown in Fig. 6. There is no match between the two graphs because sorption constants do not best represent the data obtained. One-way ANOVA was used to compare the results obtained and indicated that there was a significant difference ( $p < 0.05$ ) between the modelled and the measured data hence unsuccessful calibration of the model. The constants could not account for the sorption of palladium species at  $\text{pH} > 4$  and this is because of the changing speciation. Beyond pH 4, the main species of palladium are  $\text{Pd(OH)}_2$ ,  $\text{PdCl}_2$ ,  $\text{PdOH}^+$ ,  $\text{Pd(OH)}_3$ ,  $\text{Pd(OH)}_4^{2-}$  and  $\text{PdCl}_3^-$ . More than 90% of the species are in the form of  $\text{Pd(OH)}_2$  and the measured results indicated that these species could be adsorbed since the % removal was  $>60\%$  at  $\text{pH} \geq 5$ . Thus, at  $\text{pH} > 4$ , chloride species of palladium stop playing a major role on adsorption. PEST was then incorporated in the study so as to estimate sorption constants since there was no correlation between the results when just the PHREEQC was used. PEST proved to be a useful tool in estimating sorption constants to best represent the results obtained in the laboratory as shown in Fig. 7. Statistical analysis from ANOVA indicated that there was no significant difference ( $p > 0.05$ ) between the measured and modelled data. The results indicate that acidic wastewater is ideal for the amine functionalised zeolite to work to maximum capacity and probably other amine-based adsorbents. The obtained sorption constants were used to determine the response of other variables thus, PEST was no longer needed for simulations.

### 3.3. Role of concentration

When the concentration of palladium was increased to 5 mg L<sup>-1</sup>, the adsorption capacity decreased however, the maximum recovery was still achieved at highly acidic pH (Fig. 8). A study by Negm et al. (2018) also reported a decrease in the uptake of Cu and Pb at similar conditions. At 5 mg L<sup>-1</sup>, palladium uptake by the adsorbent decreased from pH 2 to pH 5. The reduction in adsorption was caused by palladium the type of dominant species at this range. PHREEQC indicated that  $\text{PdCl}_3^-$  and  $\text{PdCl}_4^{2-}$  were dominant and the reduction was due to the decreasing positive character of the adsorbent. An interesting observation was evidenced beyond pH 5 since the recovery increased instead of decreasing as with 2 mg L<sup>-1</sup>. The increase was attributed to  $\text{Pd(OH)}_2$  species which were dominant beyond pH 5. From pH 6 onwards, the recovery was fairly the same. The recovery of palladium decreased even

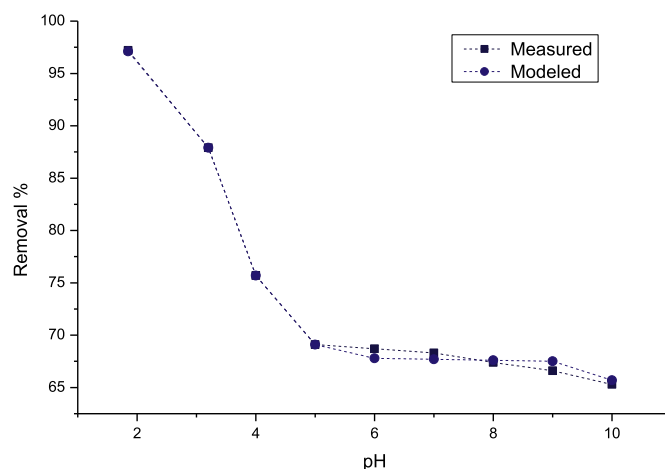


**Fig. 7.** Measured and PHREEQC modelled data of the recovery of palladium as a function of pH using PEST estimated sorption constants (Concentration = 2 mg L<sup>-1</sup>, adsorbent dosage = 10 g L<sup>-1</sup>, time = 300 min, temp = 25 °C, n = 3, RSD <5%, ANOVA comparison between measured and modelled data =  $p > 0.05$ ).

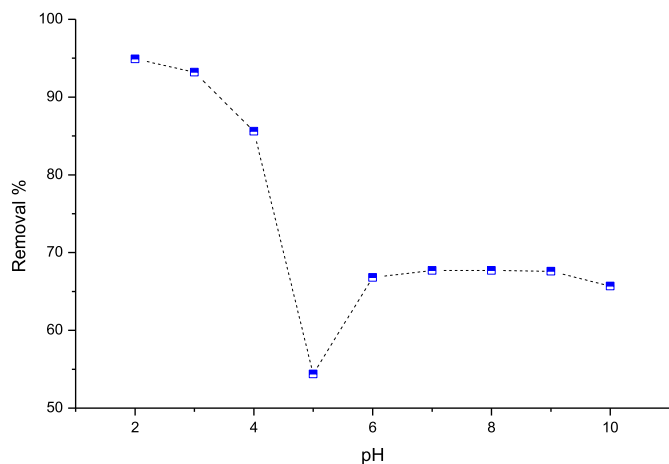


**Fig. 8.** PHREEQC modelled results of the recovery of palladium at 5 mg L<sup>-1</sup> as a function of pH (Concentration = 5 mg L<sup>-1</sup>, adsorbent dosage = 10 g L<sup>-1</sup>, temp = 25 °C, ANOVA comparison between measured and modelled data =  $p > 0.05$ ).

further at 10 mg L<sup>-1</sup> but a similar trend to that 5 mg L<sup>-1</sup> was observed (Fig. 9). The results also indicated that there was no significant difference on the adsorption of palladium beyond pH 6 at all concentrations. Saturation indices of the dominant Pd(OH)<sub>2</sub> species beyond pH 5 were determined by PHREEQC and were found to be on the supersaturated side (i.e. SI > 0). Thus beyond pH 6, most of the palladium species were removed through precipitation on the surface of the adsorbent instead of adsorption because of the insolubility of the species (Kim et al., 2008; Wei et al., 2020). Hence, the adsorption was similar. The amine functionalised adsorbents will therefore be efficient at pH < 5 since the removal of palladium is highly dependent on pH.

### 3.4. Role of adsorbent dosage

The effect of adsorbent dosage (1, 5, 10, 20, 30 and 50 g L<sup>-1</sup>) on the recovery of palladium was studied at pH 2 with 2 mg L<sup>-1</sup> initial concentration (Fig. 10). The removal of palladium increased with increasing adsorbent dosage due to relatively high amount of amine binding sites (Omidinasab et al., 2018). Adsorption capacity calculation (Eq. (3)) was used to decide on the best adsorbent dosage and indicated that the adsorption capacity of palladium decreases with increasing dosage. According to these results, 10 g L<sup>-1</sup>, was selected as the best adsorbent

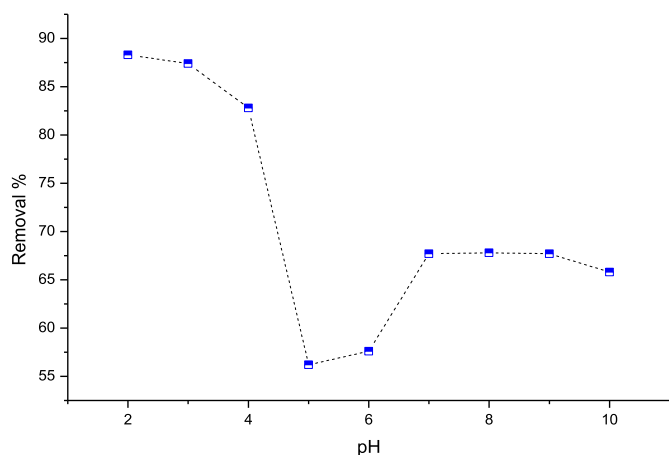


**Fig. 9.** PHREEQC modelled results of the recovery of palladium at 10 mg L<sup>-1</sup> as a function of pH (Concentration = 10 mg L<sup>-1</sup>, adsorbent dosage = 10 g L<sup>-1</sup>, temp = 25 °C, ANOVA comparison between measured and modelled data =  $p > 0.05$ ).

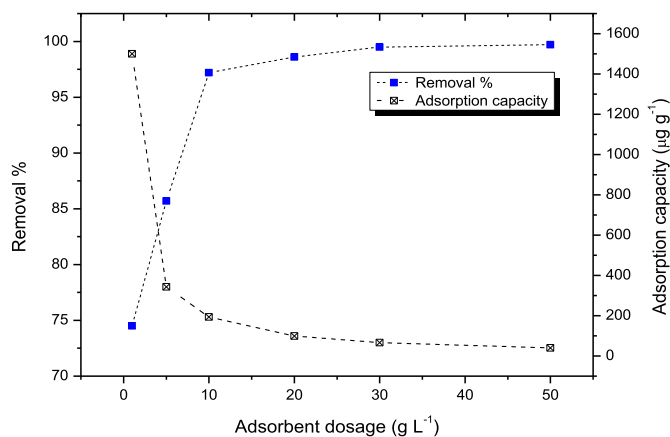


**Fig. 10.** Effect of adsorbent dosage on the recovery of palladium by function-alised zeolite (Concentration = 2 mg L<sup>-1</sup>, pH 2, temp = 25 °C, ANOVA comparison between measured and modelled data =  $p > 0.05$ ).

dosage since a significantly high palladium removal percentage (97.2%) was achieved. The palladium removal percentage at 20, 30 and 50 g L<sup>-1</sup> was 98.6, 99.5 and 99.7%, respectively. Though these percentages were significant, the adsorption capacity was very low because there were still active sites that were free and could take up more of the palladium hence 10 g L<sup>-1</sup> can be considered in wastewaters containing palladium.

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (3)$$

where  $V$  (L) is the volume of the solutions in and  $M$  (g) is the mass of the adsorbent.

The recovery of palladium at different dosages was also studied at pH 2–10 with 5 mg L<sup>-1</sup> (Fig. 11). A clear reduction on the removal % was observed at dosages of 5–50 g L<sup>-1</sup> from pH 2 to pH 5 as alluded before. The removal percentage of palladium at 5 mg L<sup>-1</sup> was found to be 95% when 10 g L<sup>-1</sup> was used and this further confirms that this is the best adsorbent dosage because the adsorption capacity beyond 10 g L<sup>-1</sup> was significantly low ( $p < 0.05$ ). The recovery of palladium was still high even at this concentration due to increasing chloride species of palladium (PdCl<sub>3</sub><sup>-</sup> and PdCl<sub>4</sub><sup>2-</sup>) that are susceptible for adsorption (Mosai et al., 2020). This study is particularly important because it helps one to use sufficient adsorbent for recovery and ensures that most of the active sites are being used. This also prevents using too much of the adsorbent that may later on require disposal if not reused. It is therefore important to know the concentration of palladium in wastewater before applying the amine based adsorbents. There was no significant difference on

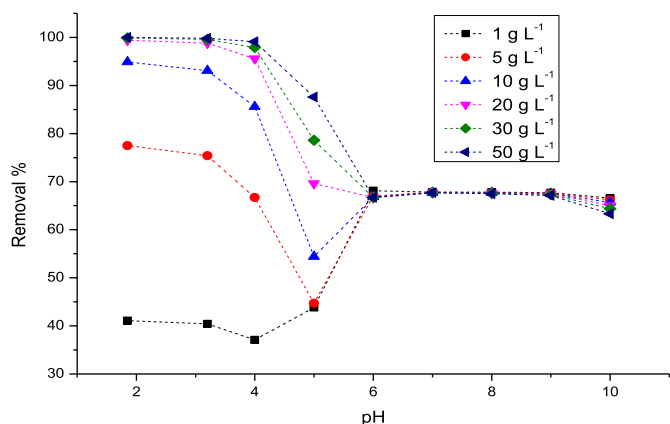


**Fig. 11.** Modelled recovery of palladium as a function of pH at different adsorbent dosages (Concentration = 5 mg L<sup>-1</sup>, pH 2, temp = 25 °C, ANOVA comparison between measured and modelled data =  $p > 0.05$ ).

adsorption at pH 6 and beyond between the dosages (1–50 g L<sup>-1</sup>) because of precipitation.

### 3.5. Role of competing ions

The recovery of palladium at pH 2 in the presence of cations (Al, Co, Cr, Fe, K, Mg, Mn and Ni) and anions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup> and SO<sub>4</sub><sup>2-</sup>) at different concentrations was investigated. The concentration of palladium was kept constant at 2 mg L<sup>-1</sup> at all conditions. The concentrations of cations were increased simultaneously. The recovery of palladium increased with increasing concentration of cations and this was not only observed in PHREEQC but also when batch studies were conducted (Fig. 12). A study by Mosai et al. (2020) indicated that the adsorption of Pd(II) increased in the presence of Pt, Ru, Os, Au, Hf, Co, Ni, Ca, Mg, Fe, K and Zn. The cations and anions were all together with palladium so that the solution best represents wastewater solutions (Awul et al., 2015). The recovery of palladium also increased with increasing concentration of anions. This might be because as the anions increase, more of the negatively charged species of palladium that are highly prone for adsorption at pH 2 results. PHREEQC indicated that more than 95% of palladium species are in the form of chlorides even in the presence of other anions (NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup> and SO<sub>4</sub><sup>2-</sup>) hence increasing adsorption was observed and thus allowing palladium to get most of the chloride ions. Most of the other cations were either free or in their sulphate or phosphate species (i.e. M<sup>2+</sup>, M<sup>3+</sup>, MSO<sub>4</sub> or M(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub><sup>+</sup>). The affinity of the cations for sulphate ions was in the order: Al > Mg > Ni > Co > Mn > Cr > Fe > Pd and the concentrations of these cations associated with sulphate ions decreased with increasing pH. The affinity for phosphate ions was in the order: Cr > Fe > Al > Mg > K > Mn > Co > Ni > Pd at lower pH regions (2–4) but as the pH increases further, the phosphates species of Mn, Mg and Ni start increasing which changed the order of affinity to Mn > Mg > Cr > Co > Ni > Fe > K > Al > Pd. Only Ni, Fe and Mg had affinity for nitrate ions indicating that the elements will strongly interact with sulphate and phosphate ions (Yang et al., 2005). The affinity of the cations for sulphate and phosphate ions simply means that most of the palladium ions were available to react with chloride ions. Industries involved with palladium use high concentration of HCl hence wastewaters would contain high amount of chloride ions. The ability of amine functionalised zeolite to recover palladium in the presence of competing ions and anions makes it a good adsorbent to use in real wastewaters since there is good selectivity for palladium. The concentrations of anions and cations are always higher than those of palladium species in wastewaters; this means that the recovery of palladium using amine functionalised zeolite materials will always be high as evidenced in this study (Awul et al., 2015).

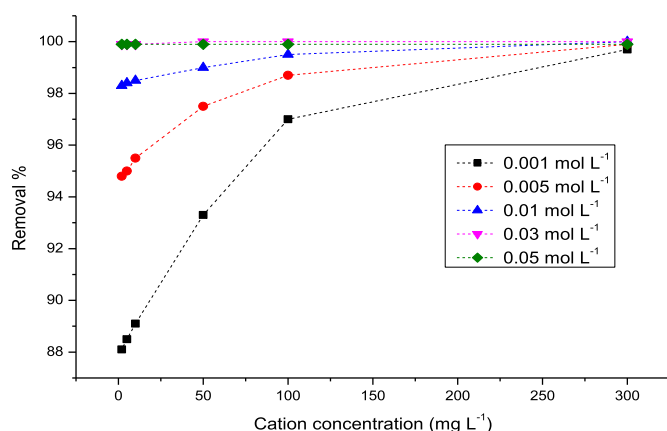


Fig. 12. Effect of competing ions at different concentrations on the recovery of palladium (Pd(II) concentration = 2 mg L<sup>-1</sup>, pH 2, temp = 25 °C, ANOVA comparison between measured and modelled data =  $p > 0.05$ ).

### 3.6. Role of temperature on the adsorption Pd(II) and thermodynamic study

The effect of temperature on the adsorption of Pd(II) was determined by plotting changing temperature (1/T) against the distribution constant ( $K_d$ ) which can be expressed as (Sahmoune, 2019):

$$K_d = \frac{C_{ad}}{C_s} \quad (4)$$

where  $C_{ad}$  represents the concentration of the element adsorbed and  $C_s$  represents the concentration of the element in solution. The results indicated that  $\ln K_d$  decreased with increasing temperature, meaning that the ability of the adsorbent to take up Pd(II) decrease at higher temperatures (Fig. 13). The spontaneity of the adsorption of Pd(II) at different temperatures was studied using the Gibbs energy change ( $\Delta G^\circ$ ) (Eq. (5)).

$$\Delta G^\circ = -RT \ln K_d \quad (5)$$

where R is the gas constant which has a value of 8.314 J (mol K)<sup>-1</sup>. The negative  $\Delta G^\circ$  values at all temperatures indicate that the adsorption process of Pd(II) onto the spent yeast functionalised zeolite is spontaneous and feasible (Table 3) (Ahmad and Mirza, 2018). In order to understand the adsorption process better, the entropy ( $\Delta S^\circ$ ) and the enthalpy ( $\Delta H^\circ$ ) of the reaction should be determined. Eq. (6) indicates that the values of  $\Delta S^\circ$  and  $\Delta H^\circ$  can be computed from the intercept and slope of the plot of 1/T vs  $\ln K_d$ , respectively (Mahmoud et al., 2020).

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (6)$$

The negative  $\Delta S^\circ$  obtained signifies that there is a decreased randomness at the adsorbent-Pd(II) solution interface and reversibility during the adsorption process (Table 3) (Sahmoune, 2019). The negative enthalpy obtained means that the adsorption process is exothermic in nature.

## 4. Conclusion

The recovery of palladium from wastewaters is important, but current methods used are often expensive and inefficient since the concentration of palladium is very low compared to that of base elements such as Mg, Ca, K and Mn. This study demonstrated the possibility of using amine functionalised zeolite as an adsorbent to remove palladium from typical PGE mine wastewaters. The impact of pH, adsorbent dosage, initial concentration of palladium and competing ions in different concentrations was considered. Batch experiments were

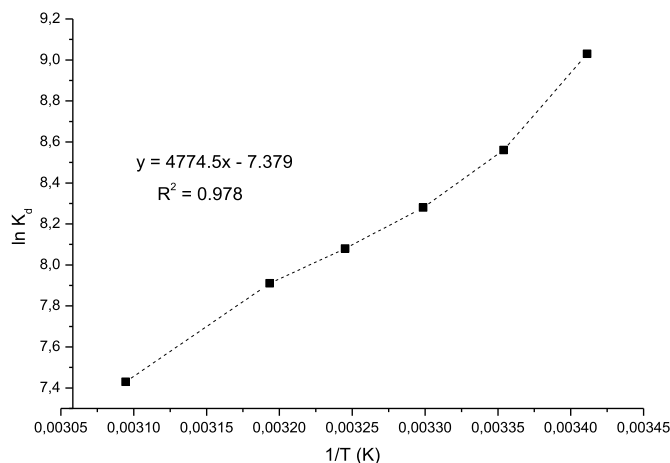


Fig. 13. The plot of  $\ln K_d$  against 1/T for the adsorption of Pd(II) onto yeast functionalised zeolite.

**Table 3**

Thermodynamic parameters for the adsorption of Pd(II) onto yeast functionalised zeolite.

|                                          |        |        |        |        |        |        | $\Delta H^\circ$ (kJ mol <sup>-1</sup> ) | $\Delta S^\circ$ J (mol K) <sup>-1</sup> | R <sup>2</sup> |
|------------------------------------------|--------|--------|--------|--------|--------|--------|------------------------------------------|------------------------------------------|----------------|
| T (K)                                    | 293,15 | 298,15 | 303,15 | 308,15 | 313,15 | 323,15 | -39,7                                    | -61,4                                    | 0,98           |
| $\Delta G^\circ$ (kJ mol <sup>-1</sup> ) | -22,01 | -21,23 | -20,87 | -20,69 | -20,55 | -19,94 |                                          |                                          |                |

conducted to calibrate PHREEQC geochemical model so that the results of the mentioned variables could be simulated. Parameter estimation (PEST) software was used to determine sorption constants of the reactions of palladium with the adsorbent so that the simulations best represent the laboratory experimental results. PHREEQC was also used to determine the speciation of palladium in different conditions. Amine-generalised zeolite surface was used in PHREEQC since the amines responsible for adsorption could be from any of the amino acids present in the spent yeast. The recovery of palladium was observed to be elevated at highly acidic conditions (<pH 3) as indicated by agreeing measured and modelled data. Adsorbent dosage of 10 g L<sup>-1</sup> was found to be suitable for increased recovery of palladium. The ability of the spent brewer's yeast functionalised zeolite to recover low concentrations of palladium (<10 mg L<sup>-1</sup>) in the presence high or low concentrations of other cations and anions makes it a suitable choice of adsorbent for potential recovery in real wastewaters. The study indicated that when PHREEQC is coupled to PEST, the reactions of palladium with the adsorbent at different conditions can be accurately determined. Thus, the recovery of palladium in wastewaters can be determined with PHREEQC modelling when all the conditions of the water are determined and specified in the input script. Therefore, before administering the recovery process, one can use PHREEQC modelling and the results obtained from this study to determine the amount of the adsorbent to be used depending on pH, concentrations of the elements and the volume of the water to be treated. The successful coupling of PHREEQC and PEST suggests that limited experimental data can potentially be used to do predictions of sorption processes in generalised surfaces.

### CRedit authorship contribution statement

**Alseno K. Mosai:** Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Writing - original draft, Visualization. **Raymond H. Johnson:** Conceptualization, Software, Data curation, Writing - review & editing. **Hlanganani Tutu:** Conceptualization, Writing - review & editing, Resources, Supervision, Project administration, Funding acquisition.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Appendix A. Supplementary data

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# **CHAPTER 5:**

## **GENERAL**

### **CONCLUSIONS**

**The outputs of the study are summarised in this chapter and recommendations are outlined herein as well. Optimum conditions for the recovery of precious elements are also summarised.**

# GENERAL CONCLUSIONS

The main aim of this research was to use cost-effective engineered materials to recover valuable elements that are lost from mining processing plants through waste streams and the objectives were to functionalise cost-effective adsorbents such as zeolite and bentonite with various ligands (including amine based ligands such as polyethyleneimine, lysine, arginine, histidine and yeast) to test their ability in selectively removing the elements of interest from aqueous solutions and to characterise the functionalised adsorbents with Fourier transform infrared (FT-IR) spectroscopy, powder X-ray diffraction (PXRD), X-ray fluorescence (XRF) and elemental analyser to confirm functionalisation. The aim was achieved by assessing the capability of the functionalised adsorbents to remove elements of interest (in batch and column/flow through mode) from aqueous solutions under a variety of conditions such as adsorbent dosage, solution pH, initial concentration, contact time and competing ions. Geochemical modelling simulations (using PHREEQC and PEST) were also conducted to augment experimental work and gain insight into the processes involved.

All the objectives were achieved and this study found that out of all the ligands used, only hydrazine, 3-aminopropyl(diethoxy)methylsilane (APDEMS) and spent brewer's yeast were successfully attached onto zeolite and bentonite. Functionalisation using these ligands was also ideal because production of the final adsorbents was cost-effective i.e. minimal energy was used and no extra chemicals were required. Characterisation using FT-IR and element analyser indicated that the amine groups from the ligands were present. The structure of zeolite and bentonite did not change after functionalisation.

Natural forms of the adsorbents recovered REEs better than functionalised forms but, the adsorption of PGEs with natural zeolite and bentonite was very poor to non-existent, making functionalisation very important. Batch and column/flow-through modes proved to be

suitable experimental designs for the recovery of REEs and PGEs using natural and functionalised adsorbents, respectively. The batch process can be administered by sprinkling suitable adsorbents in wastewaters containing elements of interest. The adsorbents could be left for a particular period of time (e.g. two days) to allow for the uptake of the elements before they can be removed and transported to the process feed plants, to be processed with the new ore. Two days or less will be sufficient for contact with waste streams since the results from this study indicated that 6 h is enough for the maximum adsorption of the elements. The column system used in this study can also be applied in real wastewater solutions where, water can be pumped from waste streams into large columns packed with adsorbents that can take up elements of interest from the passing stream. The adsorbents could then be taken into process feed plants when the active sites are exhausted (as determined by breakthroughs).

The best working conditions for the recovery of Pt(IV), Pd(II) and Ir(III) from aqueous solutions using functionalised adsorbents (hydrazine, APDEMS and yeast-functionalised zeolite or bentonite) were found to be at  $\text{pH} \leq 2$ ,  $10 \text{ g L}^{-1}$  adsorbent dosage, with concentrations less than  $5 \text{ mg L}^{-1}$ . Thus, the adsorbents will be efficient in highly acidic wastewaters and should be applied before neutralisation of the industrial wastewaters. This makes the adsorbents suitable for PGEs industrial wastewaters which are acidic. This study indicated that sufficient recovery of Rh(III) will occur when the pH of solutions is less acidic, owing to the prevalence of positively charged Rh(III) species and negative charges on the adsorbent surface. Thus, the recovery of Rh(III) can be implemented after neutralisation using the same adsorbents. The study showed that the functionalised zeolite and bentonite with the ligands will be highly efficient for Pd(II) and Pt(IV) than for Ir(III) and Rh(III).

A flow rate of  $2 \text{ mL min}^{-1}$  was suitable for maximum adsorption of both PGEs and REEs using functionalised and natural adsorbents, respectively, in flow- through column mode.

This flow rate and a 30 cm column, with a diameter of 2 cm as used in this study, can be used as a benchmark to determine large column parameters which will be suitable for treating large volumes of wastewaters. The recovery process will be cheaper because there is no need for desorption to be conducted to release adsorbed elements. Instead, the loaded adsorbents will be processed together with fresh ore.

The batch process was found to be very effective at recovering REEs using natural bentonite, with adsorption efficiency >98% under all the conditions. This makes this an even cheaper option for potential application.

The study also indicated that natural and functionalised adsorbents can effectively recover PGEs and REEs, respectively, in the presence of competing ions at different concentrations, likely as a result of enhancement effects. This is ideal for waste streams that usually contain a mixture of elements.

Preliminary cost-benefit analyses showed that the adsorbents have the capability to recover value (in orders of several ounces) from waste streams that would otherwise have been lost. This has been comparable to or better than the acceptable amounts for economical extraction.

Geochemical modelling simulations using PHREEQC coupled to parameter estimation (PEST) software were found to be useful in augmenting the experimental data and give insight into the intricate processes involved in the recovery of elements.

## RECOMMENDATIONS FOR FUTURE WORK

These recommendations could not be done because of time constraints. Moreover, they were not part of the initial study. Thus, the study is sufficient without them being conducted however; they would be beneficial to the mining industry and other institutions interested.

- A two-step experimental method could be done whereby the first step is the recovery of Pt(IV), Pd(II), Ir(III) and Rh(III) from aqueous solutions at highly acidic conditions. In step two, the treated solution could then be neutralised and allowed to undergo the recovery process to test for the success of the recovery of Rh(III) which was poor in the first step. A column setup as in this study could be used for this purpose.
- Different organic compounds such as humic and fulvic acids could be added to the solutions to determine their effect on the recovery of the elements in different conditions using batch and column/flow-through modes. This is because of the perceived presence of these components in some of the waste streams outside of mining wastewaters.
- Geochemical modelling simulations for the simultaneous recovery of other PGEs and REEs using generalised amine surfaces could be conducted since they were not studied here due to the complex nature of the input scripts that should be constructed and the absence of some physical chemistry data of the elements. To do this, the stability constants of the reactions at different conditions should be determined. A database should then be created in PHREEQC so that the calculations and the estimations are possible.

- A column packed with both natural and functionalised adsorbents could be used for selective recovery of PGEs in the presence of other elements. The column should be set up in such a way that the solution first encounters the natural adsorbents so that elements such as Mn, Co and Ni could be captured, allowing PGEs to pass through and be recovered by the functionalised adsorbent beds below the column.

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# APPENDICES

## APPENDIX A – PEST control file

pcf

\* control data

restart estimation

6 9 1 0 1

# no of parameters, observations, group parameters, prior infos , groups

1 1 single point 1 0 0

# no of template files, no of instruction files, ....

10.0 2.0 0.3 0.03 10

3.0 3.0 0.001

0.1

30 0.001 3 3 0.01 3

1 1 1

\* parameter groups

k1 relative 1e-2 0.000001 switch 2 parabolic

\* parameter data

k1 none relative 5.554 -2.0 12.0 k1 1.0 0.0 1

#param\_name,type, initial, min, max, .....

k2 none relative 0.17 -4e-3 4.0 k1 1.0 0.0 1

k3 none relative 1.63 -5 2.0 k1 1.0 0.0 1

k4 none relative -4e-4 -4e-2 5.0 k1 1.0 0.0 1

k5 none relative -1.156 -10 2.0 k1 1.0 0.0 1

k6 none relative 0.585 -4e-3 5.0 k1 1.0 0.0 1

\* observation groups

group\_1

\* observation data

c1 97.2 1 group\_1

# obs\_name, value, weight, group no

c2 87.9 1 group\_1

c3 75.7 1 group\_1

c4 69.1 1 group\_1

c5 68.7 1 group\_1

c6 68.3 1 group\_1

c7 67.4 1 group\_1

c8 66.6 1 group\_1

c9 65.3 1 group\_1

\* model command line

phreeqc.exe PESTstudies\Palladium\_1.pqi PESTstudies\Palladium\_1.pqo C:\Users\user\phreeqc-3.3.7-11094-x64\database\sit.dat

\* model input/output

PESTstudies\Palladium\_1.tpl PESTstudies\Palladium\_1.pqi

PESTstudies\Palladium\_1.ins C:\Users\user\PESTstudies\Palladium\_1.txt

\* prior information

## **APPENDIX B – PEST instruction file**

pif @

l2 [c1]1:25

l1 [c2]1:25

l1 [c3]1:25

l1 [c4]1:25

l1 [c5]1:25

l1 [c6]1:25

l1 [c7]1:25

l1 [c8]1:25

l1 [c9]1:25

## APPENDIX C – PEST template file

```
ptf @
SURFACE_MASTER_SPECIES
  Surf_aa    Surf_aaNH2
  Surf_si    Surf_siOH
  Surf_al    Surf_alOH

SURFACE_SPECIES
Surf_aaNH2 = Surf_aaNH2
  log_k    0
Surf_aaNH2 + PdCl4-2 = Surf_aaNH2PdCl4-2
  log_k    @k1      @
Surf_aaNH2 + PdCl3- = Surf_aaNH2PdCl3-
  log_k    @k2      @
Surf_aaNH2 + PdCl+ = Surf_aaNH2PdCl+
  log_k    @k3      @
Surf_aaNH2 + PdCl2 = Surf_aaNH2PdCl2
  log_k    @k4      @
Surf_siOH = Surf_siOH
  log_k    0
Surf_siOH = Surf_siO- + H+
  log_k    -6.65
Surf_siOH + PdCl2 = Surf_siOHPdCl2
  log_k    @k5      @
Surf_siOH + Pd(OH)2 = Surf_siOHPd(OH)2
  log_k    @k6      @
Surf_alOH = Surf_alOH
  log_k    0
Surf_alOH = Surf_alO- + H+
  log_k    -13.16

PHASES
fix_pH
  H+ = H+
  log_k    0
fix_pe
  e- = e-
  log_k    0
SOLUTION 1
  temp    25
  pH      2
  pe      4
  redox    pe
  units    mg/l
  density  1
  Cl      0.01 Mol/l
  Pd      2
  -water  0.001 # kg

SURFACE 1
  Surf_aaNH2 8.789e-05 2.13 0.1
  Surf_siOH 0.000545
END
SELECTED_OUTPUT 1
```

```

-file          C:\Users\user\PESTstudies\Palladium_1.txt
-high_precision true
-reset         false

USER_PUNCH 1
-headings
-start
10 q_sorb = mol("Surf_aaNH2PdCl4-2")+mol("Surf_aaNH2PdCl3-")
+mol("Surf_aaNH2PdCl+") +mol("Surf_siOHPdCl2")+mol("Surf_siOHPd(OH)2")+mol("Surf_aaNH2PdCl2")
20 punch q_sorb/1.88e-5*100
-end

USER_GRAPH 1
-axis_titles      "pH" "Recovery %" ""
-chart_title      "Recovery of Pd"
-initial_solutions false
-connect_simulations true
-plot_concentration_vs x
-start
10 q_sorb = mol("Surf_aaNH2PdCl4-2")+mol("Surf_aaNH2PdCl3-")+mol("Surf_aaNH2PdCl+")
+mol("Surf_siOHPdCl2")+mol("Surf_siOHPd(OH)2")+mol("Surf_aaNH2PdCl2")
20 PLOT_XY -LA("H+"),q_sorb/1.88e-5*100, symbol = square, color = blue, symbol_size = 7
-end
-active           true

USE solution 1
USE surface 1

EQUILIBRIUM_PHASES 1
CO2(g) -3.5 10
fix_pH -1.85 HCl 10
END

USE solution 1
USE surface 1

EQUILIBRIUM_PHASES 1
CO2(g) -3.5 10
fix_pH -3.27 NaOH 10
END

USE solution 1
USE surface 1

EQUILIBRIUM_PHASES 1
CO2(g) -3.5 10
fix_pH -4 NaOH 10
END

USE solution 1
USE surface 1

EQUILIBRIUM_PHASES 1
CO2(g) -3.5 10
fix_pH -5 NaOH 10
END

```

USE solution 1

USE surface 1

EQUILIBRIUM\_PHASES 1

CO2(g) -3.5 10

fix\_pH -6 NaOH 10

END

USE solution 1

USE surface 1

EQUILIBRIUM\_PHASES 1

CO2(g) -3.5 10

fix\_pH -7 NaOH 10

END

USE solution 1

USE surface 1

EQUILIBRIUM\_PHASES 1

CO2(g) -3.5 10

fix\_pH -8 NaOH 10

END

USE solution 1

USE surface 1

EQUILIBRIUM\_PHASES 1

CO2(g) -3.5 10

fix\_pH -9 NaOH 10

END

USE solution 1

USE surface 1

EQUILIBRIUM\_PHASES 1

CO2(g) -3.5 10

fix\_pH -10 NaOH 10

END