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Recovery of platinum group elements (PGEs) from wastewater: A case for the development of predictive adsorption numerical methods

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ABSTRACT

Platinum group elements (PGEs) are very important for the modern world, and they are used in many applications due to their physical and chemical properties that cannot be found in other naturally occurring elements. This means that the availability of PGEs now and in the future is very crucial. However, research has indicated that PGEs are at the edge of becoming scarce due to gradually depleting natural resources. This review reports on the recent techniques for the recovery of PGEs from secondary sources. However, there is still a need for cheap and efficient methods and technologies that can be applied at large scale. The need for PGEs speciation information especially in adsorption and/or recovery studies is discussed. Speciation modelling codes (PHREEQC, Geochemist's workbench, MINEQL+, MINTEQA2 and WHAM) which can be used for this purpose are also discussed. These models can be used for adequate predictive adsorption of PGEs in order to determine the performance of the adsorbents beyond the available laboratory, pilot or real application data. However, most of the PGEs are not included in the available databases used in the numerical models hence, new databases should be developed, or the modification of the available databases will always be a requirement in order to simulate PGEs accurately and successfully, under various conditions. To automate the calibration of the models including calibration-constrained uncertainty analysis of the models, parameter estimation (PEST) software which can estimate important parameters and compute sensitivities of model outputs to parameters, can be coupled with the modelling codes.

1. Introduction

Platinum group elements (PGEs) *viz* platinum (Pt), palladium (Pd), rhodium (Rh), osmium (Os), iridium (Ir) and ruthenium (Ru) are very important elements in the technologically developing world, due to their unique physical and chemical properties (Merker et al., 2001). Research has shown that the concentration of PGEs in earth's crust is low hence they are also known as rare earth elements (Savignan et al., 2021). Moreover, the PGEs reserves are found in few parts of the world including South Africa (~63 000 tons), Canada (~300 tons), Russia (~5500 tons), North America (~900 tons) and Zimbabwe (~1200 tons) (Fig. 1) (Pianowska et al., 2023). The average concentration of PGEs in ores is currently known to be between 5 and 15 mg/L. Most of the PGEs are found in magma ore deposits which form during the cooling and crystallization of magma (Zientek and Loferski, 2014). The ultramafic and mafic igneous rock ore bodies contain significant concentrations of PGEs (Berger et al., 2013).

The mining and smelting of PGEs from the primary ore is very challenging, resource intensive and expensive due to the ore grade which typically has low concentration of PGEs and high content of other elements including sulphides, base metals etc. (Saurat and Bringezu, 2008). This is why the removal of PGEs from ores is a multi-step process. These steps consume large quantities of energy as well as water and produces large amount of mining waste (Mwase et al., 2012). The number of steps involved depend on the concentration of PGEs as well as the characteristics of the ore. For example, in South Africa (Merensky Reef (Bushveld complex)), PGEs are physically separated from the ores using flotation to allow for the production of a mineral concentrate. The concentrate is dried and further separated using pyrometallurgy at > 1400 °C, which results in a Cu-Ni-Fe-S matte. The Cu, Ni, Fe and other elements except PGEs are leached from the matte using concentrated sulphuric acid in autoclave under pressure (Van Schalkwyk et al., 2011).

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These steps are applied where PGEs are the primary production. In some places such as Canada (Sudbury complex, Ontario) and Russia (north-western Siberia (Noril'sk)), PGEs are by-products of nickel–cobalt and copper-nickel production, respectively (Saurat and Bringezu, 2008).

The recovery of PGEs from waste has been given much attention in the last few decades due to their high costs, almost indestructability, significantly depleting natural resources, and increased usage resulting from the improvement of current and the discovery of new technologies (Kim et al., 2000; Rao and Reddi, 2000). Thus, waste such as industrial wastewater, spent catalysts, electronic scraps and used equipment as well as recycling jewellery have been given much attention. In 2011, more than 20 % of the supply of Pt, Pd and Rh came from secondary sources (Zientek and Loferski, 2014). The existence and continuous supply of PGEs is critical since some of their important unique properties cannot be found in other elements, which means that they cannot be replaced (Merker et al., 2001). Therefore, extraction of PGEs from waste materials is becoming a very important way to close the gap between the worldwide consumption and mining production. This paper summarizes PGEs properties, uses, environmental issues, and typical waste stream recovery techniques with a special focus on reviewing adsorption modelling techniques to predict potential PGEs removal from waste streams.

2. Properties and applications of PGEs

PGEs are ductile and are also known to have high mechanical strength, chemical stability, corrosion resistance, oxidation resistance, catalytic activity, and excellent electrical properties (Kumar et al., 2021; Sahu et al., 2023). As a result, they have been used in many fields including medicine (dental implants, chemotherapy, orthopedic implants), industries (petroleum refining, nitric acid manufacturing) and electronics (mobile phones, flat screens, hard discs) (Table 1). A significant portion of PGEs is used in automotive catalytic converters since they are chemically stable and have good selectivity (Fig. 2). In 2021, about 39,4%, 84.7 % and 90.6 % of Pt, Pd and Rh, respectively, were used in catalytic converters (Morcali, 2020; Matthey, 2021; Yang et al., 2023). A minimum of two PGEs in low concentrations are used in catalytic converters. Thus, spent automotive catalysts are good secondary sources of PGEs. There are active catalysts which can convert toxic exhaust gases to products which are less toxic before they are released into the environment. These catalysts use PGEs as active catalyst for this process. For example, nitrous oxide (NOx, x = 1,2,3) and carbon monoxide (CO) are removed from the combustion residues by conversion to nitrogen and oxygen gas for NOx and carbon dioxide for CO. The production of three-way catalytic converters which involve both oxidation and reduction processes has increased so that more toxic substances can be converted to other products before they are released into the environment (Liu et al., 2021). These converters have replaced the two-way catalytic converters which cannot reduce nitrous oxide since it only deals with oxidation processes. Thus, PGEs are very important and are required for environmental protection. The concentration of PGEs in catalytic converters ranges from 50 to 1000 μg/g.

The high melting point, temperature stability and corrosion oxidation resistance of PGEs also make them good materials for catalysts and glass manufacture (Merker et al., 2001; Zientek and Loferski, 2014). Iridium is very dense and has high chemical and thermal stability. It is widely used in medicine due to its biological compatibility. Ruthenium and osmium on the other hand are used mostly in electrical and electrochemical industries due to their good conductive properties and durability. Osmium is also widely used in forensic science (stain for fingerprints and DNA) and fuel cells. Other properties of PGEs include high resistance to tarnish and chemical attack (Bossi and Gediga, 2017).

3. PGEs in the environment

When PGEs are used, they are not consumed but transferred from one manifestation to another thus, they can be recycled and reused (Kim et al., 2000). This means that their environmental impact can be reduced. However, some studies have indicated that PGEs can be released into the environment during the deterioration of products containing PGEs (Sobrova et al., 2012). A study by Bossi and Gediga (2017) indicated that as the surfaces of catalytic converters deteriorate and abrasion occurs (i.e. end-of-life products), PGEs can be deposited alongside roadways and thus, increasing the concentration of PGEs in the environment. The PGEs emissions are high in roads which normally have high traffic density and places with low dispersion conditions. The emissions can also occur in operating catalysts which are suddenly ruined by adverse operating conditions such as ignition and excess heat (Bossi and Gediga, 2017). The bioavailability of PGEs is likely to result from different factors that can affect their oxidation states. For example, PGEs in contact with organic compounds such as fulvic acid, L-methionine acid, and humic acid as well as organisms such as bacteria, fungi

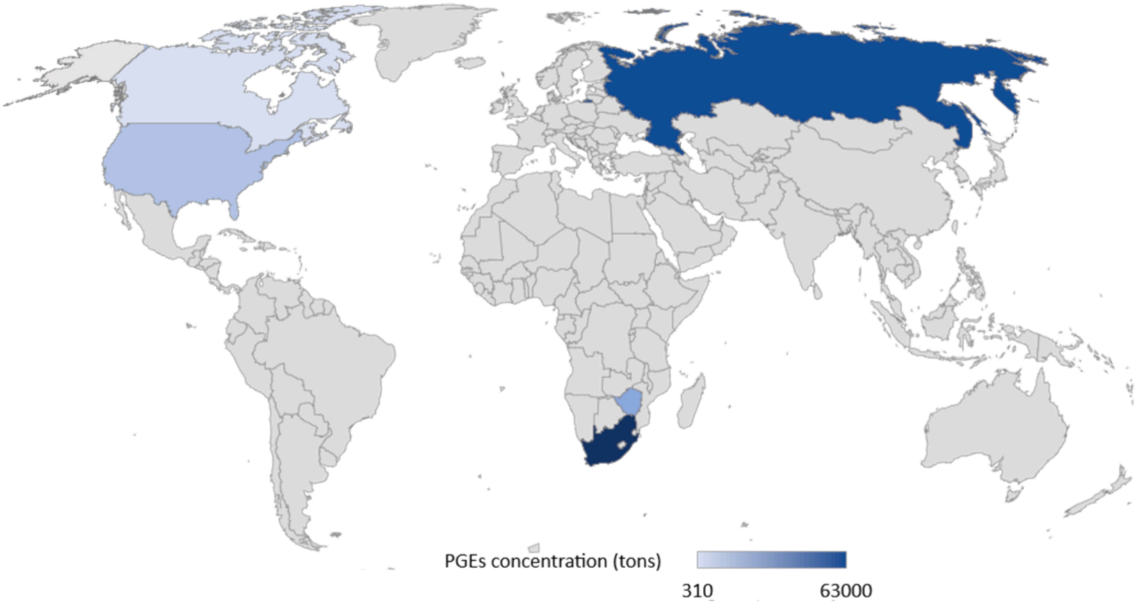


Fig. 1. Locations with rich PGEs deposits.

Table 1
Major applications of the PGEs.

Applications	Platinum	Palladium	Rhodium	Iridium	Ruthenium	Osmium	References
Catalytic converters for automobiles	X	X	X		X		Suoranta et al., 2015
Catalysts	X	X	X	X	X		Kettler, 2003; Liu et al., 2004; Menegazzo et al., 2007
Medicine	X		X	X		X	Suska et al., 2010; Dowling et al., 2003; Zhang et al., 2019; Gu et al., 2023
Jewellery	X	X	X				Houghton and Greer, 2021
Glass manufacture	X		X				(Coupland et al., 1995)
Fuel cells	X					X	Antolini, 2014; Thompson et al., 2018
Alloys	X	X	X	X	X	X	Suska et al., 2010; Dowling et al., 2003
Electronics and electrical components				X		X	Kumar et al.,2021

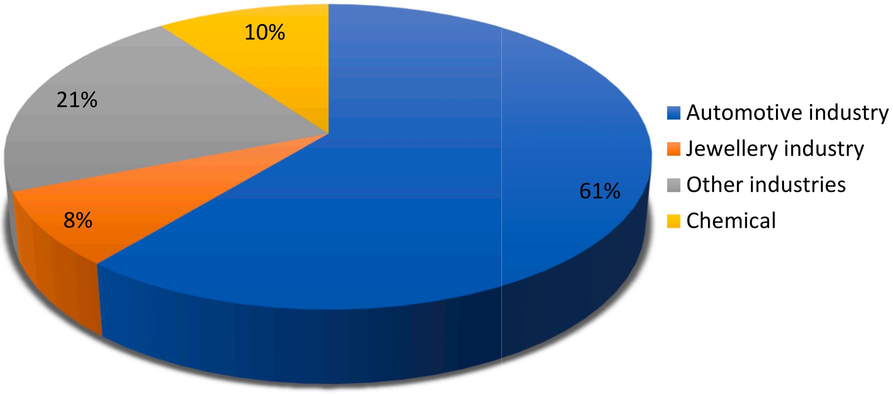


Fig. 2. Applications of PGEs in different industries (Afreximbank Research, 2024).

and plants can be bioavailable due to high oxidation states. In the absence of these compound and organisms, PGEs remain in their chemically inert state (i.e. oxidation state of zero) and will not enter the biogeochemical cycle (Sobrova et al., 2012).

The primary production of PGEs can release the elements into the environment through the production wastewater (Bossi and Gediga, 2017). Rural, urban, and industrial areas and hospitals also release PGEs into the environment through wastewater (Sobrova et al., 2012). The platinum containing cytostatics (cisplatin [*cis*-platinum diaminedichloro (II)] and carboplatin [diamine (1,1-cyclobutanedicarboxylato) platinum (II)]) as well as other antitumor metallopharmaceuticals are excreted from patients through urine and bile after successful operations (Ensslin et al., 1997; Sobrova et al., 2012). Thus, the PGEs can migrate to drainages and finally to wastewater where they could end up in the environment. Some of the waste from hospitals is used in agriculture and this increases the chance of PGEs ingestion by humans and other organisms through eating affected crops, meaning that the food chain can play a major role on the transfer of PGEs. Once in the systems of living organisms, PGEs can become toxic especially when in contact with organic acids and microorganisms. PGEs can be mobile in the environment when the conditions (soil pH, soil salinity, redox potential, and the presence of complexing agents) are suitable (Sutherland et al., 2008). In some areas, groundwater is used for drinking and domestic purposes without proper treatment, which could lead to increased contact of PGEs with humans and livestock. Some studies have reported that the concentrations of PGEs are increasing in waterbodies (sea, ocean, rivers, and groundwater). This is alarming especially because PGEs can bioaccumulate thus, aquatic animals and other living organisms may be negatively affected (Rosner et al., 1991; Essumang et al., 2008).

Hooda et al. (2008) determined the concentration of Pt, Pd and Rh in the soil near a roadside and detected the highest concentration close to the road. The further the distance from the road, the lower the concentration of PGEs, indicating that there are PGEs emissions from exhaust gases into the soil. The study further reported that the concentration of PGEs in the soil decreased with soil depth, which can be attributed to the slow migration of PGEs in the soil due to chemical inertness (Pt^0, Pd^0 and Rh^0). Thus, the properties of the soil play a very important role on the migration and bioavailability of PGEs. When the soil conditions are favourable, PGEs can migrate to groundwater, increasing their accessibility and the probability of reaching living organisms especially in areas where groundwater is used for domestic purposes and agriculture. PGEs in the soil can also accumulate in plants through the roots and migrate to biologically active substances which are rich in sulphur. The high concentration of PGEs was detected in plant roots and less, but significant concentration was detected in the stems and the leaves (Sobrova et al., 2012). The phytotoxicity of PGEs depends on the concentrations of the elements, speciation, time of exposure and characteristics of the soil wherein the plants are found (Sobrova et al., 2012). Gagnon et al. (2006) studied the effect of soluble salts of 0.1, 1 and 10 mg/L Pt^{4+}, Pd^{2+} and Rh^{3+} on *Sphagnum magellanicum* plants and found that the height of the plants decreased in the presence of PGEs especially at high concentration (10 mg/L). The bioaccumulation of the PGEs in the plants was also studied and the results showed that the concentration was high in plant tissue. The highest effect was observed at high concentrations where, brown-yellow lower parts were observed due to damaged tissue and decomposition of chlorophyll. Moreover, the plants did not increase in growth during the exposure period (Gagnon et al., 2006).

Some studies researched on the potential effects of PGEs on living organisms using rats. The results from the studies indicated that PGEs can lead to DNA damage, enhanced immune response, nephrotoxicity, the reduction of the monocytes, hypertrophy abnormalities in the three zones of the adrenal cortex, the enlargement of white pulp in the spleen, the reduction in leukocyte production and shrinkage of glomeruli in the kidney (Gagnon et al., 2006; Sobrova et al., 2012; Newkirk et al., 2014; Zhang et al., 2022). These studies indicate that PGEs can have negative effects on living organisms including possible effects on humans. Given this, the reduction of PGEs in the environment through recycling is a way to reduce exposure that can harm human health and the environment.

4. Current recovery techniques for PGEs

PGEs are mainly used in automotive catalytic converters hence they are known as the main secondary sources (Fig. 2). Thus, technologies and methods of recovery should be highly concentrated on extracting PGEs from these sources. The recovery of PGEs from catalytic converters needs smart technologies since they are present in very small quantities. Therefore, highly selective and efficient extraction techniques are required, as reviewed below. It is important to note here that the techniques described in this section are those which have been published. It is highly likely that the PGEs industry has its own developed, efficient methods which they employ to maximise recoveries, but these are not publicly available due to competitive advantage.

4.1. Recovery of PGEs from automotive catalytic converters and control catalysts

Research on the recovery of PGEs from waste has been conducted and many recovery techniques and methods have been discovered. This is also important since mining on its own does not produce enough supply due to high demand (Shaffer, 2015). The current concentration of PGEs in spent catalytic converters has been reported to be 100 times more than in natural ores hence, the importance of recycling. After 160 000 km automotive converters lose more than 25 % of their initial efficiency and once, they have reached their lifetime, they are taken to recycling facilities (Diac et al., 2020). The traditional methods used for recovery use large amounts of energy and release significant amount of pollution in the environment. Thus, the need for new methods and techniques that can recover significant amounts of PGEs with less energy and minimum waste production. This section focuses on recently developed techniques for the recovery of PGEs from spent automotive catalytic converters (Table 2).

4.1.1. Polymer inclusion membranes

Polymer inclusion membranes (PIM) have been found to be effective for the recovery of PGEs from spent automotive catalytic converters. As a result, many studies involving PIM have been conducted (Table 2). For example, Fajar et al. (2021) used PIM with an ionic liquid carrier (trioctyl(dodecyl) phosphonium chloride ($P_{88812}Cl$)) for the recovery of Pt^{4+}, Pd^{2+} and Rh^{3+} from a spent automotive catalyst leachate solution. Two membranes were developed, one was an isotropic dense membrane (ID-PIM) and the other one was anisotropic porous membrane (AP-PIM). The results showed that more than 90 % of Pt^{4+} and Pd^{2+} could be recovered from the leachate solution by both membranes. However, ID-PIM poorly (~10 %) recovered Rh^{3+} and, AP-PIM could only recover about 50 %. At a higher temperature (35 °C) more than 65 % of Rh^{3+} was recovered by AP-PIM. PIMs which contain trioctyl(dodecyl) phosphonium chloride ionic liquid have a potential to significantly recover PGEs from automotive catalysts. These membranes are greener and less expensive for PGEs recycling (Fajar et al., 2021).

4.1.1.1. Hydrometallurgy. Hydrometallurgy has been widely used for the recovery of PGEs. Méndez et al. (2021) used hydrometallurgy to treat spent automotive catalytic converters. Hydrochloric acid (HCl) and calcium chloride ($CaCl_2$) were used as leaching solutions and thiodiglycolamide derivative was used for solvent extraction (SX). The main aim was to develop a treatment that would lead to high recoveries of Pt with minimum aluminium (Al) dissolution to facilitate the application of solvent extraction. Al was considered as a significant impurity due to its high content in catalytic converters and the likelihood of having a negative impact on the solvent extraction separation process. High acid concentrations dissolve Al which is present in oxide form in the wash coat of the spent automotive catalytic converters. Soluble $CaCl_2$ salt was added to replace HCl so that there could be high solid/liquid ratio leading to less Al dissolution. This then led to high selectivity towards PGEs over other impurities. Hydrogen oxide was used in this study as an oxidant precursor and the general chemical reaction of the leaching of Pt from spent catalysts can be expressed as (Méndez et al., 2021):

$$Pt^0 + 4H^+(aq) + 6Cl^-(aq) + H_2O_2(aq) \rightleftharpoons [PtCl_6]^{2-}(aq) + 4H_2O(aq) \tag{1}$$

More than 80 % of Pt was leached with minimum leaching of Al due to the addition of chloride salt which decreased the acid concentration in the leaching phase. 8 M HCl/2 M $CaCl_2$ was found to be the best acid/

Table 2
PGEs recovery techniques from automotive catalysts.

Technique	PGEs and recovery efficiencies	References
PIM containing an ionic liquid carrier	Pt^{4+}, Pd^{2+} and Rh^{3+} (>95 % for all elements)	Fajar et al., 2020
PIM with Tris(2-ethylhexyl) Phosphate	Pd^{2+} (90 %)	Monroy-Barreto et al., 2021
PIM with a 1-alkyltriazole matrix	Pd^{2+} (98 %)	Radzyminska-Lenarcik et al., 2021
PIM doped with alkylimidazoles	Pd^{2+} (87 %) and Pt^{2+} (15 %)	Radzyminska-Lenarcik et al., 2022
PIM containing an Ionic Liquid Metal Ion Carrier	Rh^{3+} (70 %)	Hanada et al., 2020
Hydrometallurgy	Pt^{4+} (90–98 %), Pd^{2+} (99 %) and Rh^{3+} (70–96 %)	Paiva et al., 2022
Hydrometallurgical extraction	Pt^{4+}, Pd^{2+} and Rh^{3+} (>95 % for all elements)	De Aberasturi et al., 2011
Single-Step hydrometallurgical method	Pt^{4+} (>99 %), Pd^{2+} (92 %) and Rh^{3+} (>60 %)	Yakoumis et al., 2020
Hydrometallurgy	Pt^{4+} (96 %), Pd^{2+} (98 %) and Rh^{3+} (86 %)	Yousif, 2019
Hydrometallurgy	Pt^{4+} (>99 %), Pd^{2+} (>45 %)	Rzelewska-Piekut et al., 2021
Organic acids and organic extractants Phosphonium-based ionic liquid	Pt^{4+} and Pd^{2+} (>85 % for al elements) Pd^{2+} (99 %), Rh^{2+} (95 %)	Wiecka et al., 2022Firmansyah et al., 2019
XUS 43600.00	Pt^{4+} (>99 %), Pd^{2+} (>99 %) and Rh^{3+} (>75 %)	Nikoloski et al., 2015
Lewatit M+MP 600	Pt^{4+} (>97 %), Pd^{2+} (>91 %) and Rh^{3+} (8 %)	Nikoloski et al., 2015
Purolite S985	Pt^{4+} (>81 %), Pd^{2+} (>58 %) and Rh^{3+} (>87 %)	Nikoloski et al., 2015
Liquid–liquid extraction in chloride medium	Pt^{4+} (>99 %)	Marinho et al., 2010
Liquid-liquid extraction with phosphonium ionic liquids	Pt^{4+} (>99 %) Pd^{2+} (>95 %), Ru^{3+} (>80 %) and Rh^{3+} (<6%)	Rzelewska-Piekut and Regel-Rosocka, 2019
Liquid–liquid extraction using tri-octylamine	Pt^{4+} (97 %) and Rh^{3+} (<21 %)	Jaree and Khunphakdee, 2011
Liquid–liquid extraction using tri-*iso*-octylamine	Pt^{4+} (98 %) and Rh^{3+} (36 %)	Lee et al., 2009
Pyrometallurgy	Pt^{4+} (>98 %) and Pd2^{+} (>98 %)	Ivanović et al., 2011
Pyrometallurgy	Pt^{4+} (>98 %)	Liu et al., 2019

salt combination (Méndez et al., 2021). Even though this study focused on the recovery of Pt, it is believed that other PGEs could be selectively removed by the same process. Table 2 shows that hydrometallurgy can significantly recover PGEs simultaneously.

4.1.1.2. Solvometallurgy. Solvometallurgy which is a non-aqueous solution process, is a recently developed and recognised extractive metallurgy technique for the recovery of PGEs from spent catalysts (Binnemans and Jones, 2017; Lanaridi et al., 2022). Nguyen et al. (2020) used the process for the recovery of Pt, Pd and Rh from spent automotive catalysts. The solvating properties of a system change significantly due to the absence of a water phase, and this allows for selective recovery of elements. For example, oxidative leaching can be used for selective dissolution of elements in organic solvents. This study used $FeCl_3$ or $CuCl_2$ oxidizing agents for leaching and dimethyl sulfoxide (DMSO) or acetonitrile (CH_3CN) as organic solvents. These solvents were used because they can be cheaply produced in large quantities with the possibility of regeneration and low toxicity. The experiments were conducted at different conditions such as temperature, leaching time, oxidizing agent concentration, and solid-to-liquid ratio. Non-aqueous solvent extraction (NASX) was implemented using $FeCl_3$ in CH_3CN to dissolve the spent catalyst, and the resulting leachate was evaporated to dryness where CH_3CN was recovered. Other combinations i.e., $CuCl_2/CH_3CN$, $FeCl_3$/DMSO, and $CuCl_2$/DMSO were also considered. A different organic phase i.e., DMSO was used to dissolve the solid from drying. The results from the study indicated that $FeCl_3/CH_3CN$ was the best combination for the recovery of PGEs. The elements were selectively recovered by dissolution and 0.01 mol/L $FeCl_3/CH_3CN$ recovered Pd whereas 0.03 mol/L $FeCl_3/CH_3CN$ significantly recovered Pt and Rh. More than 90 % of PGEs were recovered. After recovery, CH_3CN was regenerated by distillation (Nguyen et al., 2020). Thus, solvometallurgy is a promising technique for the significant recovery of PGEs from spent catalysts.

4.1.1.3. Leaching with organic acids. de Oliveira Demarco et al. (2020) came up with a new process that can recover PGEs from spent automotive catalysts. The process involves mechanical processing followed by heat treatment and leaching. The extraction of PGEs was achieved using HCl and co-extractants *viz* malic, formic and citric acids in order to reduce the effect of acids with adverse environmental effects. The idea of using organic acids was motivated by the fact that they are less corrosive and are considered environmentally friendly. Strong acids such as HCl and HNO_3 and H_2SO_4 are very efficient when it comes to leaching elements however, the emission of harmful substances such as Cl_2, SO_3 and NO_x is highly probable. HCl has been used for the extraction of PGEs but, large quantities of the acid at high concentrations must be used in order to achieve high extraction efficiency. This process is not ideal for large scale application since the acid is expensive and the process is not environmentally friendly. The co-extractants were tested individually with HCl. The role of extraction time, concentration of acids and solid-to-liquid ratio was investigated. The leachate solution was separated from the solid material through filtration. More than 90 % of Pt and Pd was recovered using 6 M HCl with solid-to-liquid ratio of 1:30, 90 °C temperature and 20 % (v/v) citric acid. The study found that the addition of citric acid can significantly reduce the concentration of aggressive and corrosive acids which are normally used for the recovery of PGEs (Oliveira Demarco et al., 2020). Thus, the addition of organic acids on the leaching of PGEs can be a cheaper and environmentally friendly process.

4.1.1.4. Liquid-liquid extraction. Liquid-liquid extraction, a hydrometallurgical route, has been used for the recovery of PGEs from spent catalysts (Table 2). For example, Ilyas et al. (2021) used liquid–liquid extraction for the separation of Pt^{4+}, Pd^{2+} and Rh^{3+} from exhausted catalytic converters. Equal volumes (4 mL) of the PGEs and the ionic liquid were used. HCl was used as a leach solution wherein an undiluted phosphonium-based ionic liquid called Cyphos IL 101 was used. After the equilibration time, the aqueous and the organic phases were separated using centrifugation and the raffinate was analysed for the concentration of PGEs. The results showed that 30 min contact time was enough for the extraction of more than 99 % of Pt^{4+} and Pd^{2+} in the form of $[PtCl_6]^{2-}$ and $[PdCl_4]^{2-}$, respectively at 25 °C. However, the extraction of $[RhCl_6]^{3-}$ was less than 25 %. Higher temperatures led to the reduction of the extraction of PGEs. Even though the extraction of some of the elements was high, the cost of the whole process would be high since equal amounts of the ionic liquid and raffinate would be required.

4.1.1.5. Pyrometallurgy. Pyrometallurgy which involves the heating of spent catalysts at very high temperatures has been used for the significant recovery of PGEs from the catalysts (Peng et al., 2017). A study by Liang and Qu (2023) used pyrometallurgy to recover PGEs (Pt and Pd) from spent volatile organic carbons (VOCs) control catalysts. Metallurgical dust from iron and steel metallurgical factory was also considered as it forms part of environmental pollutants which pose a serious threat to living organisms including human beings. The iron-bearing metallurgical dust was used for recovery since studies have indicated that metallic iron can capture PGEs. This is known as one of the cheapest ways to recover PGEs because there is large amount of steel metallurgical dust which is freely available. Thus, pollution reduction and resource recovery were combined for efficiency enhancement. Pyrometallurgy method was used at high temperatures (1350 – 1550 °C) so that PGEs could migrate from the slag matrix to iron droplets. The resulting waste slag was separated into valuable materials to minimize waste. Strong acids or alkali were not used so that this becomes a cheap and non-toxic process. Metallurgical coke (0–20 wt%) was used for metal reduction during the pyrometallurgy process and generated high amount of CO_2 which was used during the precipitation method as an alternative for an acid. This helped achieve low emissions of carbon. The study led to iron-PGEs alloy in high yield with 1764 g/tonPt and 3297 g/ton Pd. This was achieved under pyrometallurgical conditions under 1 h of contact time. The study finally concluded that a net profit of ~$17/kg of iron-PGEs alloy can be gained by treating waste with waste (Liang and Qu, 2023). Other studies involving pyrometallurgy are shown in Table 2.

4.2. Recovery of PGEs from wastewater

During the processing of PGEs in mining sites, large amount of wastewater is released. The wastewater has been tested for the concentration of PGEs and low but significant concentration of PGEs has been detected and the amount is appreciable enough to warrant recovery. About $1.7 billion which is roughly 10 % of the total market value is lost annually by the PGEs mining industry and recycling facilities due to the elements in wastewater (Lusk et al., 2018). Therefore, salvaging PGEs from wastewater will help the mining industry and other industries using PGEs in gaining profit from the waste they produce. The wastewater released depends on the type of ore mined. In the Merensky reef, some of the PGEs are sulphides i.e. braggite (Pt,Pd)S, cooperite (PtS) and laurite (RuS_2) (Korges et al., 2021; Makvandi et al., 2021). Platinum is also found in Pt-Fe alloy, arsenide ($PtAs_2$) and telluride ($PtTe_2$). Norilsk Mining Company in Russia is one of the biggest producers of PGEs in the world. The PGEs in this region are normally found in sulphide copper-nickel ores (Bond and Levine, 2001). Thus, PGEs wastewater from different regions will contain different elements with varying concentrations. Several studies focusing on the recovery of PGEs from aqueous solutions including processing wastewater have been conducted, as discussed below. The presence of some inorganic species such as sulphates, cyanides, chlorides and other metals make it difficult for adsorbents which are either natural or synthetic to be selective for PGEs due to competition for binding sites. Moreover, PGEs in wastewater may be in different speciation which are not suitable for adsorption or in forms that make them less selective.

4.2.1. Treatment technologies

Mack et al. (2011) investigated the use of immobilised yeast *Saccharomyces cerevisiae* on the recovery of PGEs from refinery wastewater. Polyethylenimine and glutaraldehyde were used as adsorbent beds since they can be functionalised with the yeast. The results from the study indicated that only 40 % was in the form suitable for adsorption and the highest uptake was observed at pH less than 2. *Lagerstroemia speciosa* biomass modified by polyethylenimine (PEI-LS), a low-cost and eco-friendly biosorbent was developed for the recovery of Pt^{2+} from the acid-leached spent catalyst solution and refinery wastewater (Garole et al., 2018). The results of the study indicated that the uptake was spontaneous and more than 120 mg/g (>90 %) of Pt^{2+} can be removed from the solutions. The study further showed that the biomass can be reused up to four cycles. Won et al. (2010) also used polyethylenimine attached onto the surface of inactive *Escherichia coli* biomass for the recovery of Pt^{4+} from an industrial laboratory wastewater. The recovery of Pt^{4+} was found to be 21.4 mg/g and 108.8 mg/g with raw biomass and modified biomass, respectively. *Saccharomyces cerevisiae* waste biomass from the brewery fermentation industry was used for the removal of Pd^{2+}, Ir^{3+}, Pt^{2+} and Rh^{3+} aqueous solutions (Oke et al., 2014). Some of the byproduct was treated with NaOH and ethanol to improve efficiency. The biomass treated with ethanol performed better the raw and NaOH treated biomass. The removal percentage was > 95 %, ~90 %, ~60 % and > 45 % for Pd^{2+}, Pt^{2+}, Ir^{3+} and Rh^{3+}, respectively over five cycles.

Currently, large amount of cyanide is released into the environment due to different processes such as metallurgy (heap cyanidation method), electroplating and many chemical industries hence some wastewater has significant amount of cyanide which can form complexes with a number of elements such as Co, Mg and PGEs. Chen et al. (2021) developed a novel quaternary ammonium-functionalized Zr^{4+} metal–organic resin (MOR) ($H_{16}[Zr_6O_{16}(MPATP)_4]Cl_8{\cdot}xH_2O$, MPATP=2-((1-methylpyridin-1-ium-2-ylmethyl)amino)-terephthalic acid) (MOR-2-QAS) that can capture Pt^{2+} and Pd^{2+} in a solution concentrated with cyanide. The results showed that more than 90 % of PGEs could be removed by MOR-2-QAS. In the presence of cyanide, the PGEs exist as $Pt(CN)_4^{2-}$ and $Pd(CN)_4^{2-}$ hence these were the species of elements which were removed. Also, the study indicated that more than 90 % of the PGEs could be removed from the adsorbent after three desorption cycles. Dialdehyde carboxymethyl cellulose cross-linked chitosan (Ch-DCMC) was used for the recovery of Pt and Pd from aqueous solutions (Asere et al., 2019). The Ch-DCMC was developed keeping in mind that the concentration of PGEs in industrial effluents is very low. Moreover, these effluents are normally acidic with high concentration of base metals thus, a cross-linking step was added to ensure the chemical stability of the adsorbent. About 80 and 89 mg/g could be removed from the solution with an adsorbent dose of 1 g/L. A recent study addresses the use of a newly developed cheap and efficient adsorbent known as chitosan/citric acid@diatomaceous earth-sugarcane bagasse (CTS/CA@DE-SBS) for the adsorption of Pt^{4+} from wastewater (Yang et al., 2024). The study assessed the performance of the adsorbent at different conditions including pH (1–9), adsorbent dosage (10–50 mg), initial solution concentration (10–150 mg/L) and contact time (30–660 min). The study indicated that pH has an influence on the speciation of Pt^{4+} and the charge of the adsorbent. The point of zero charge was found to be 4.3, where a positive surface charge was observed below this pH. The Pt ions are surrounded by negatively charged ions, resulting in overall negatively charged platinum species were better adsorbed at acidic pH. The amount of adsorbent used also had an influence of the adsorption rate of Pt. the adsorption efficiency increased as the adsorbent amount increased from 10 mg (23 % efficiency) to 50 mg (86 % efficiency). This is because, the amount of adsorption sites increases with increasing adsorbent amount. The uptake of Pt was inversely proportional to initial concentration due to the limitation of adsorption sites. Moreover, the highest uptake was achieved beyond 500 min. The optimum conditions of the study were concluded to be 30 mg adsorbent, 50 mg/L initial concentration, pH 3 and contact time of > 500 min.

The adsorption of Pt^{4+}, Pd^{2+} and Rh^{3+} from diluted HCl solutions by magnetic Fe_3O_4 nanoparticles was studied by Uheida et al. (2006). Fe_3O_4 nanoparticles were used due to large surface area and high surface reactivity. More than 90 % of PGEs were adsorbed within 60 min of contact. To elute the PGEs from the nanoparticles, 0.5 mol/L HNO_3 was used. Mosai and Tutu (2022) investigated the recovery of Pd^{2+}, Rh^{3+} and Ir^{3+} from aqueous solutions using 3-aminopropyl(diethoxy)methylsilane (APDEMS) modified bentonite and found that the maximum recovery was achieved at pH 2 due to speciation. At pH 2, $[PdCl_4]^{2-}$, $[RhCl_6]^{3-}$ and $[IrCl_6]^{3-}$ were the dominant species of Pd^{2+}, Rh^{3+} and Ir^{3+}, respectively. More than 95 % of PGEs were recovered in the presence of competing ions (Fe^{3+}, Co^{3+}, Ni^{2+}, Ca^{2+}, Mg^{2+}, K^{+}, Au^{+}, Hf^{4+} and Zn^{2+}). As pH increased, the speciation of the elements also changed and was less favourable for adsorption. For example, the precipitate $Pd(OH)_2$ was the dominant species of Pd beyond pH 4.5. Mosai et al. (2020) functionalised bentonite with brewer's yeast waste to recover Pt^{4+}, Pd^{2+}, Rh^{3+} and Ir^{3+}. The results indicated that brewer's yeast has active sites that can selectively capture PGEs from aqueous solutions. In the presence of competing ions, the recovery of Rh^{3+} and Ir^{3+} decreased by 17 and 57 %, respectively, as a result of the limitation of active sites. Thus, in order to significantly recover PGEs, a process that can remove competing ions should be applied first before recovery. This will also ensure that the desorption process becomes more efficient, fast and cheap. The presence of other ions such as Fe^{3+} can be beneficial for the recovery of Pt and Pd due to the possibility of the adsorbent-Fe-(Pd or Pt) synergistic effect.

A recently new and environmentally friendly method known as iron electrocoagulation (Fe-EC) was used for the extraction and recovery of PGEs from aqueous wastewater (Dai et al., 2023). During the Fe-EC process, flocculants are produced through in situ adsorption, and this leads to continuous and spontaneous recovery of elements from aqueous solutions. Iron anode is used during the process and when the electric current is applied, Fe^{2+} ions are produced which are hydrolysed and polymerised to form iron hydroxide flocs. The generated flocs have the ability adsorb PGEs and reduced them to elemental forms by $Fe(OH)_2$. The selectivity of the process for PGEs over other elements such as Mg, Ni, Mn and Zn which may be present in aqueous solutions is due to the fact that PGEs have high electronegativity and standard reduction potentials hence high extraction ability. The obtained solid flocs with PGEs were dried dissolved in 4 mol/L nitric acid with solid-to-liquid ratio of 1:50. The resulting product was heated for 2 h in order to come up with an acid wash solution which contain precipitates of PGEs. The PGEs were recovered using an organic membrane which was dried to obtain the PGEs. The results indicated that Fe-EC was able to extract > 81.2, 81.3 and 99 % of Pt, Pd and Rh, respectively. High purities (>97 %) of PGEs were obtained after washing and filtration (Dai et al., 2023). Other technologies/methods used for the adsorption of PGEs are provided in Table 3.

Research focusing on the recovery of PGEs from the automotive industry is also required. Most studies as indicated previously, focus on the recovery of PGEs from spent catalyst however, research on the recovery of the elements from wastewater released during the manufacturing of automobiles will also be of high importance since the concentration of PGEs especially Pt, Pd and Rh might be significant. China, Europe, Japan and North America are the main consumers of PGEs as they have the dominant automotive markets. Thus, new research on the development of techniques and methods that can target PGEs in wastewater from the automotive industries can focus on these regions.

4.2.2. Significance of including competing ions when testing the efficiency of adsorbents

It is important to include competing ions when investigating the

Table 3
Some adsorbents used for the recovery of PGEs from wastewater at different conditions.

Adsorbent	pH	Initial concentration (mg/L)	Other conditions	Adsorption capacity (mg/g) and/or adsorption efficiency	Reference
Marine macroalga, *Ulva lactuca*	7.9–8.4	0.01	Contact time (up to 100 h)	Pt^{4+} (95 %) Pd^{2+} (80 %) Rh^{3+} (40 %)	Turner et al., 2007
Saccharomyces cerevisiae waste biomass from brewery fermentation industry	3 (opt.)	0.1–10 10 mg/L (opt.)		Pt^{4+} (90.4 %) Pd^{2+} (96.7 %) Rh^{3+} (79.9 %) Ir^{3+} (81.7 %)	Oke et al., 2014
Fungi *Aspergillus* sp.	0.5–11 2 (opt. for Pt) 3.5 (opt. for Pd)	0.01 – 20	Contact time (5 – 1440 min) (opt. 120 min) Adsorbent dosage (0.025 to 0.5 g) (opt. 0.1 g)	Pt^{4+} (90.7 %) Pd^{2+} (93.7 %)	Godlewska-Żyłkiewicz et al., 2019
chitosan/citric acid@diatomaceous earth-sugarcane bagasse	1–9 3 (opt.)	10–150	Contact time (30–660 min), adsorbent mass (10–50 mg) and competing ions	Pt^{4+} (83 %) Pd^{2+} (80 %)	Yang et al., 2024
l-lysine modified crosslinked chitosan resin	1–10	10–400	Contact time (6–420 min) and temperature (30–50 °C)	Pt^{4+} (129.26) Pd^{2+} (109.47)	Fujiwara et al., 2007
Glycine modified crosslinked chitosan resin	1–11 2 (opt.)	50–500	Contact time, ionic strength (0–0.1 mol/L NaCl)	Pt^{4+} (122.47) Pd^{2+} (120.39)	Ramesh et al., 2008
Thiourea-modified chitosan microspheres	1–9 2 (opt.)	10–400	Contact time (0–350), temperature (298–328 K)	Pt^{4+} (129.9, >97 %) Pd^{2+} (112.4 > 97 %)	Zhou et al., 2009
Amberlite IRA 400 J CL resin	0.5–4 4 (opt.)	1000	Contact time (30–240 min) and competing ions	Pt^{2+} (188) Pd^{2+} (184) Rh^{3+} (13)	Gandhi et al., 2015
Amberlite IRA 400 J CL resin	1.5	From automotive catalytic solution		Pt^{2+} (57.41 %) Pd^{2+} (67.53 %) Rh^{3+} (19.51 %)	Gandhi et al., 2015
Amberlite IRA 411 resin	1.5	From automotive catalytic solution		Pt^{2+} (55.42 %) Pd^{2+} (66.51 %) Rh^{3+} (16.98 %)	Gandhi et al., 2015
Weak-base anion exchanger diethylaminoethyl cellulose		5 (for Pt and Pd) 0–20000 (other ions)	Contact time (0–1440 min), competing ions	Pt^{4+} (32.57, 96 %) Pd^{2+} (36.86, 98 %)	Mpinga et al., 2018
3-aminopropyl(diethoxy)methylsilane (APDEMS) functionalised bentonite	2–9 2 (opt.)	0.5–10 2 (opt.)	Adsorbent mass (50–500 mg), contact time (0 – 360 min) and competing ions	Pd^{2+} (>99 %) Rh^{3+} (>95 %) Ir^{3+} (>85 %)	Mosai and Tutu, 2022
Fe_3O_4@PEG@Cyphos® IL 101	Acidic	$2.5x10^{-8}$ –$1.5x10^{-7}$ mol/L	Contact time (5–60 min), adsorbent mass (5–50 mg), ionic liquid content, ionic liquid structure	Pt^{4+} (>98 %) Pd^{2+} (>99 %)	Mokhodoeva et al., 2020
Localized Triethylamine-Based Poly (Ionic Liquid)	0–6 1 (for both Pt) 0 (for Ir)	20–1400	Contact time (2–120 min)	Pt^{2+} (315, 94.94 %) Pt^{4+} (264, 97.52 %) Ir^{3+} (194, 59.17 %)	Zhang et al., 2023
Iron-electrocoagulation	6	2		Pt^{4+} (81.26 %) Pd^{2+} (81.32 %) Rh^{3+} (99.66 %)	Dai et al., 2023

potential of adsorbents to recover PGEs since they are never found in isolation. Therefore, studies using synthetic solutions should also include other elements and species that are normally found with PGEs in wastewater. Some studies have reported that their adsorbents can recover significant amounts (>70 %) of PGEs without considering the effect of other ions on adsorption (Uheida et al., 2006; Zhou et al., 2010; Vidal Treber et al., 2024). On the other hand, some studies have indicated that the presence of competing species can reduce the adsorption of elements even if the adsorbents contain functional groups that are selective for PGEs over other elements (Mosai et al., 2020). Moreover, the developed adsorbents should be tested in real wastewater since certain adsorbents have been observed to perform very well in synthetic solutions but not as efficient in real solutions. This is because real wastewater is very different from synthetic solutions since, they normally have high ionic strengths and may also contain other species such as organic and inorganic species which are not considered in synthetic solutions. Other conditions such as pH, temperature, concentration of competing ions also play a major role on adsorption. As mentioned before, the concentration of PGEs in wastewater is usually very low whilst other elements may be in very high concentration, thus, designed materials for adsorption should consider this fact. The loading capacity or adsorption capacity of adsorbents should also be taken into consideration. Loading capacity is known as the quantity of an adsorbate or the number of ions that are captured by the adsorbent per unit mass of the adsorbent (Chen et al., 2001). This is based on the number of active sites on the adsorbent.

4.2.3. *Active groups for the adsorption of PGEs*

The recovery of PGEs using different adsorbents has been investigated and the studies show that specific functional groups are responsible for the uptake of the elements. Different instruments such as Fourier transform infrared spectroscopy (FTIR), X-ray fluorescence (XRF) and scanning electron microscopy (SEM) are used to determine the groups present in adsorbents however, FTIR is normally used to identify the functional groups in adsorbents. Most adsorbents used for the uptake of Pt and Pd consist of amine functional groups which can interact with PGEs. Asere et al. (2019) used dialdehyde carboxymethyl cellulose cross-linked chitosan for the adsorption of Pd and Pt and found that the amine group was responsible for the uptake of the elements.

5. Speciation modelling of PGEs

There are many recent studies dealing with the adsorption of PGEs from aqueous solutions however, there is often lack of speciation information (Asere et al., 2019; Chen et al., 2021; Dai et al., 2023). Speciation information is crucial since, the performance of some recovery techniques including adsorption, depends on the speciation of the elements. Some studies only specify the oxidation state of the elements that are considered e.g. Pd^{2+}, Rh^{3+} or Ir^{3+}, but not the actual speciation. Moreover, some elements can have more than one oxidation state due to certain solution conditions or quality (Florence et al., 1992). The lack of speciation information at the different conditions considered in the adsorption process can have serious consequences. For example, in certain conditions, such as less acidic or alkaline pH, elements can precipitate out of solution which, can sometimes be mistaken for adsorption, meaning that the obtained results may not be a representation of the performance of adsorbents (Verma et al., 2018). Other factors such as concentration of elements, competing ions and seasonal variations (i.e., temperature) can affect the speciation of analytes such as PGEs and consequently, their adsorption (Davis et al., 2020; Serbin et al., 2017).

Without the speciation information, the actual amounts of PGEs which are supposedly recovered using adsorbents and the adsorption capacity may not be accurately known. Knowing the speciation of analytes and of competing ions at different conditions will also help with identifying elements that can be removed before the recovery process e.g., precipitation, so that the adsorption efficiency can be maximized. To get the speciation information of analytes, the elements in the solution under consideration must be identified thus, instruments such as inductively coupled plasma optical emission spectroscopy (ICP-OES), inductively coupled plasma mass spectroscopy (ICP-MS) and ion chromatography should be used to measure the presence and concentrations of metals and ions, respectively. Other factors such as pH, redox, temperature and alkalinity should also be measured.

Speciation in different solutions can be determined in situ using analytical techniques but, they often take time and are costly (Sigg et al., 2006). There are different speciation modelling techniques such as PHREEQC, Geochemist's workbench, MINEQL+and MINTEQA2 which can be used to determine the speciation of elements in solutions, discussed below (Parkhurst and Appelo, 1999; Kocaoba and Akcin, 2002; Cloutier-Hurteau et al., 2007; Magu et al., 2016). Table 4 provides some of the advantages and limitations of the models. These programs do the same basic calculation and follow the same procedure: 1) the input data is specified, 2) a thermodynamic database is selected and 3) the speciation is calculated. Given the same data set, any differences in output are mainly dependent upon the database being used (Haase et al., 2016; Lu et al., 2022). The subsequent sections discuss variations between computer programs. The best database to use is the one with all the important elements and is used to define static data for the thermodynamic model. The different valance states of the elements must be included in the databases so that that the best results can be obtained (Parkhurst and Appelo, 1999; Parkhurst and Appelo, 2013). Also, all the possible major species that can be formed when the elements of interest interact with other elements in the wastewater e.g. the interaction of PGEs with chlorides, sulphates or hydroxides. The different computer modelling programs can estimate the major and minor species of elements depending on the quality of the solution. When the major species of elements are known, it will be easy to develop recovery techniques since speciation plays a major role on the behaviour and performance of techniques such as adsorbents. Also, by changing conditions such as pH and temperature, the computer programs can provide the speciation of the elements based on the specified conditions. Thus, the user will be able to see how changing different conditions affect the speciation. This is important because wastewater keep on changing in pH, concentrations of elements, temperature and so forth. As indicated some conditions can affect the speciation and consequently, the performance of recovery techniques hence, knowing speciation is critical. In certain conditions, some elements precipitate out of the solution and when the speciation is not considered, one can think that the recovery technique is performing well in removing PGEs from solutions when it is not the case. Also, some of the species of PGEs may be in speciation form that is not suitable for adsorption onto the adsorbent, but this cannot be known unless a simulation using geochemical models is done or experiments which could be very expensive. Knowing speciation of elements can also help with developing suitable adsorbents for recovery in specific wastewater. As mentioned previously, different regions or mines produce different qualities of wastewater, which may require unique treatment strategies. Thus, developed adsorbents for the recovery of PGEs from wastewater are not universal as some studies may claim (Yabe and de Oliveira, 2003; Chaudhuri et al., 2023).

Table 4
Some advantages and limitations of the models under consideration.

Model	Version	Advantages/ capabilities	Limitations	Reference
PHREEQC	3.7.3	Equilibrium reached through the adjustment of the concentration of the element at a specified phase, various concentration units of different elements can be used in the same solution, combinations of solutions and gas phases are possible, can perform 1D and batch reaction calculations.	High ionic strength solutions cannot be modelled accurately, there is not internal consistency in the data of the different databases,	Parkhurst and Appelo, 2013
Geochemist's workbench	17.0.1	Good graphical user interface, can calculate stability diagrams, can produce speciation diagrams at various pH, can change units on the data sheet, equilibrium temperature can be calculated when the activities of the elements and the fugacity of the gas are known, determine the minerals formed	Unconstrained extrapolation of the osmotic coefficient data, some elements are not included in databases	Bethke et al., 2024
MINEQL+	5.0	Can be used for solutions with low (0 mol/L) to moderate (<0.5 mol/L) ionic strength, better problem visualisation and output management	Can perform calculations at low temperature	Schecher and McAvoy, 1992
MINTEQA2	4.03	Extensive thermodynamic database that allows for solving a variety of problems, database can be modified to suit the user's needs, There are options to stop the precipitation of solids and to allow the oversaturated solids to precipitate,	the thermodynamic database contains equilibrium constant values which are referenced to 25 ℃ with ionic strength of zero. Thus, other constants should be calculated if the temperature is not 25 ℃, uncorrected log K values at 25 ℃ are used.	Allison et al., 1991; United States Environmental Protection Agency, 2006
WHAM	7	Accurately performs chemical speciation calculations for field situations when important input data is included.	Suitable for use when the organic matter dominates the chemical speciation.	Tipping, 1994; Tipping, 1998; Tipping et al., 2011

5.1. PHREEQC geochemical modelling and parameter estimation

PHREEQC is a freely available application that can be downloaded from the United States Geological Survey (USGS). PHREEQC which stands for **pH**, **re**dox, **eq**uilibrium and **C** programming language is a geochemical modelling software which is developed by Parkhurst and Appelo, 2013. It is written in the C and C++ programming languages and can simulate kinetic and equilibrium reactions when required data is available (Steefel et al., 2015). PHREEQC can perform aqueous geochemical calculations, when data such as the concentration of elements present, solution pH, redox, temperature, total dissolved solids, pe, density and alkalinity is available. The calculations include the distribution of aqueous species, surface complexation, saturation indices and ion exchange equilibria. Moreover, the activities of solutes can be calculated using ion-association, Pitzer, or specific ion interaction theory equations to account for the nonideality of aqueous solutions. In order to get the right calculations, the user must choose a suitable database which has all the elements under consideration. In this case, a database that has PGEs and other major and minor elements must be selected. The speciation calculation will ensure that all the PGEs species are determined with their molalities. The speciation of the elements will depend on the quality of the solution or wastewater under consideration. Thus, the pH, pe, density and temperature must be included in the input file.

PHREEQC uses databases (phreeqc.dat, wateq4f.dat, llnl.dat, minteq.dat, minteq.v4.dat, and iso.dat) where, aqueous models including ion-association models that use Debye–Huckel formulations are implemented (Parkhurst and Appelo, 2013). Pitzer.dat database uses the Pitzer specific-ion interaction

model whilst the sit.dat database uses the specific-ion interaction theory (SIT) model. The activity coefficient constants included in the models are dependent on temperature which should always be specified in the input file. The input file is used to specify the solution of interest i.e. wastewater and to define the types of calculations to be done by the software. It is also used to modify the data in the database. The Lawrence Livermore National Laboratory (llnl.dat) and the sit.dat databases are the only ones that have PGEs and some of the PGEs are not included but, they can be added through programming when all the important data such as activity coefficients, log k values at different temperatures, stoichiometry and speciation is available. Thus, the user can add important data to the available databases to suit their needs. This will, however, require a lot of data and some experiments will have to be conducted. There are keyword data blocks in the input file used by PHREEQC so that the user can specify important parameters. The log K values of the different reactions of PGEs with other elements will have to be included in the database. Also, the temperature dependence of log K values must be taken into consideration. The Van't Hoff expression or an analytical expression can be used for this purpose. When the Van't Hoff equation is used, PHREEQC uses the delta_h to give the standard enthalpy of reaction at 25 °C. The analytical expression for a reaction can be defined with an identifier as follows (Eq. (2):

$$log_{10}k = A_1 + A_2T + \frac{A_3}{T} + A_4log_{10}T + \frac{A_5}{T^2} + A_6T^2 \quad (2)$$

Where A_x are values defining log k as a function of temperature dependence in the given expression and T is temperature in Kelvin (K). The dependence of log k on pressure must also be taken into consideration when using the geochemical model since the reaction constants of the species and the solubilities of minerals depend on pressure. They are calculated from the volume change of the reaction.

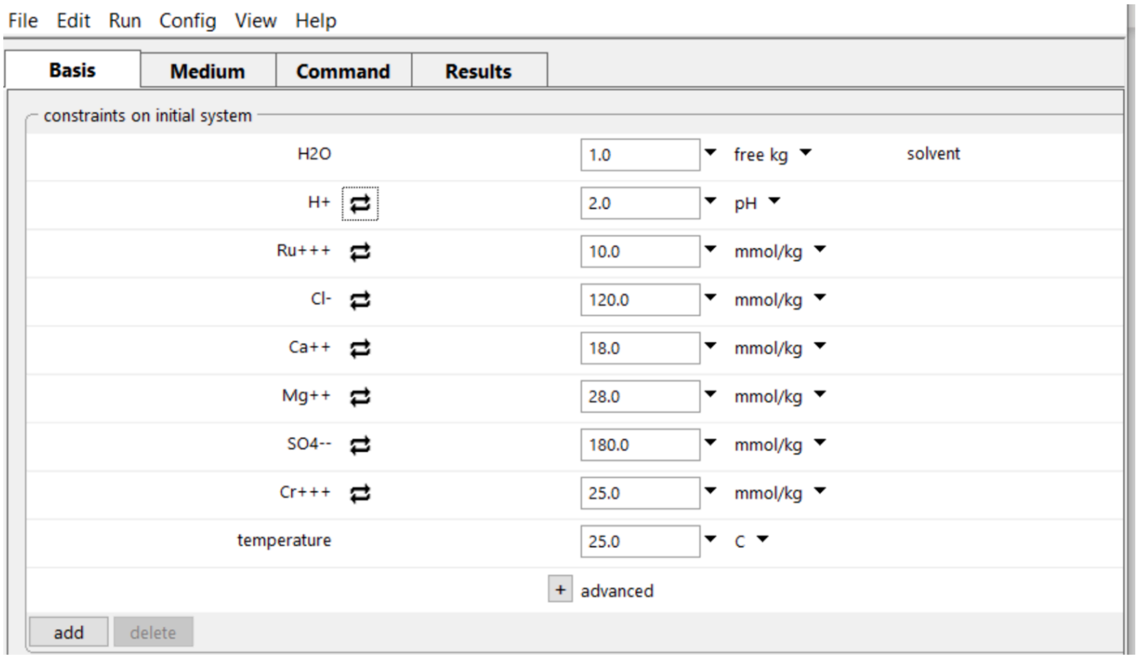
5.2. Geochemist's workbench

The Geochemist's workbench (GWB) is geochemical modelling software package that can construct numerical simulations of reactions to produce equilibrium fluid speciation and for natural fluid and theoretical systems as well as reaction path modelling (Bethke and Yeakel, 2014; Bethke, 2022). The accurate simulations will result when the thermodynamic data files with temperatures and pressures of the solution are available. The log K approach to perform the numerical simulations. Thus, the thermodynamic data files contain information of the dependence of log K values of reactions on temperature and pressure. When performing calculations, the software will use log K values based on experimental log K data or at the conditions of interest from the thermodynamic parameters such as entropy, enthalpy and Gibb's energy (Bethke and Yeakel, 2014). Speciation modelling using GWB is possible since the incorporated data files have information on the basis species, minerals, oxides, aqueous species and redox couples. These are accessed through the data blocks in GWB. For example, to determine the speciation of PGEs in a particular solution, the aqueous species data block should be used.

The SpecE8 and React programs in GWB can be used to determine the equilibrium distribution of aqueous species in a fluid using the LLNL thermodynamic database as is or in modified form since not all the PGEs are included. These programs can also calculate the equilibrium state of the system as well as the saturation state of the fluid. When the performing the adsorption simulation, the amount of species attached onto the specified sorption sites will be calculated by the programs. Fig. 3 shows the input script of the SpecE8 program where ruthenium is considered. As shown, the elements involved in the solution under consideration must be specified with their concentrations. Table 5 shows the output script of the solution with ruthenium. The output script shows the aqueous speciation of the elements involved. The resulting minerals based on the presence of the elements are also shown. Other parameters such as solution mass, mineral mass, fluid density, electrical conductivity and the activity of water are also depicted. Thus, important information about the solution of interest can be obtained using the Geochemist's workbench.

5.3. MINEQL+

MINEQL+is a chemical equilibrium modelling system that can perform water chemistry calculations, pH calculations, chemical speciation, ion adsorption, redox and solubility diagrams among others (Kocaoba, 2020). The calculations can only be performed at low to moderate ionic strength (<0.5 M) and low temperatures (0–50 °C) using one of the thermodynamic databases incorporated in the model. In order to successfully run the MINEQL+model, components (e.g. ions), which are the basic building blocks from which all species are formed must be specified (VanBriesen et al., 2010). MINEQL+is a user-friendly program which does not require programming expertise. There are databases incorporated into the program however, the user should set preferences which MINEQL+will use to scan and find the most suitable database. There are four subsequent software modules in MINEQL+viz chemical components selection module, species tableau module, runtime manager and output manager. All the chemical components available in the program are shown under the chemical components selection module which has both pre-defined and NULL components (Fig. 4a) (Hartog, 2000). The tableau module indicates the chemical reaction data based on the species present in the system. Moreover, the thermodynamic data based on the chemical species in the system and the overall concentration associated with chemical components will be shown under the tableau module before running any calculation (Fig. 4b). Other parameters such as pH (fixed or calculated), redox options and dissolved inorganic carbon are also specified under the tableau module. The runtime manager shows some conditions based on the information in the model input script before running model calculations. This allows the user to check if all the information added including the chemical conditions is correct. The output manager allows the user to access output files from the model. The database with enough data on some important elements can be modified by adding PGEs so that speciation modelling is



H2O	1.0	free kg	solvent
H+	2.0	pH	
Ru+++	10.0	mmol/kg	
Cl-	120.0	mmol/kg	
Ca++	18.0	mmol/kg	
Mg++	28.0	mmol/kg	
SO4--	180.0	mmol/kg	
Cr+++	25.0	mmol/kg	
temperature	25.0	C	

Fig. 3. GWB input script using the SpecE8 program.

possible (Cobelo-Garcia et al., 2007; Sako et al., 2009).

5.4. MINTEQA2

MINTEQA2 is a geochemical equilibrium speciation model for aqueous systems, developed by the U.S. Environmental Protection Agency (EPA) and can be accessed through the Visual MINTEQ package (Gustafsson, 2011). The model can only deal with dilute natural or synthetic (i.e. laboratory) aqueous systems where, the equilibrium compositions of the dilute solutions are calculated based on the chemical analysis which involve the total concentrations of the elements of the system, pH, pe (conventional negative log of the activity of the electron) and other parameters (Truesdell, 1968; Parkhurst and Appelo, 1999). As with the other speciation models, the thermodynamic database can be modified if it does not suit the current situation or some of the important information such as the data on PGEs is not primarily included. The application of MINTEQA2 involves four steps (Gustafsson, 2011). The first step is to formulate chemical questions that must be answered by the model also, considering the limitations of the site under consideration e.g. sampling that was not completed or missing data on the collected samples. The second step is to pose the chemical questions to the model using symbols and formats that the model understands. Step three involves leading the model to read the input file so that the mathematical problems can be solved. This step is automatic and does not require any intervention from the user once executed. The last step is to interpret the output file of the model based on the solved problem. MINTEQA2 has an interactive program (PRODEFA2) which is used to create input files which is designed to perform the second step (Gustafsson, 2011). When executed, the program guesses the activity of each component in order to calculate the concentration of each species based on mass action expressions. All the species containing a particular component must be accounted for in order to determine the total mass of that component. A new estimate of the activity of the component will be made if the known mass and the calculated mass do not agree. Thus, the process will be repeated again until the mass imbalance is less than the tolerable level of every component. All the species concentrations leading to this will be selected by the model and the system will be considered to have reached aqueous phase equilibrium composition. At this stage, the saturation index (SI) of each of the solids which formed will be determined. If SI>0, then the solids can precipitate out of solution hence depleting the dissolved concentrations of the components making up the solid. In this case, the model will re-equilibrate with one less degree of freedom. If SI<0, it means dissolution has occurred and re-equilibration will still occur but with one more degree of freedom. This will be the case until equilibrium is reached with the absence of over- or undersaturated solids.

The equilibrium constants used in MINTEQA2 thermodynamic database are based on the temperature of 25 °C and ionic strength of zero but, since this might be the case with the solution under consideration, a new set of equilibrium constants will have to be determined before performing model calculations. MINTEQA2 also uses the form of Eq. (3) to adjust equilibrium constants at a particular temperature, if the necessary data are available (Serkiz et al., 1996). The ionic strength can affect the activity coefficients of the components which in turn affect the adjusted equilibrium constants, which is why, MINTEQA2 has the option calculate the new ionic strength based on the concentration of the species at each iteration or to specify a fixed ionic strength. The ionic strength of the solution can be calculated using Eq. (3) (Peng and Wan, 1998; Gustafsson, 2011):

$$ {}_{i=1}^{m}Ionicstrength = \frac{1}{2}\sum\left(C_iZ_i^2\right) \tag{3} $$

where C_i is the concentration of the ionic species i, m is the number of charged species in the solution and Z is the charge on species i. MINTEQA2 can also construct titration curves and solubility diagrams (Kocaoba and Akcin, 2002). It can also calculate mineral equilibria, ion balance, corrosion, pH, redox and many others.

5.5. Windermere humic aqueous model (WHAM)

Windermere Humic Aqueous Model (WHAM) is a chemical equilibrium model and computer code which is designed to calculate the chemical speciation of elements in waterbodies, soils and sediments (Tipping, 1994; Masakorala et al., 2008). It is particularly useful when the chemical speciation is dominated by humic substances in dissolved or particulate forms. The interaction of humic substances with different elements has been found to be difficult without the use of a suitable speciation code hence the importance of WHAM. The computer code

Table 5
GWB output script.

Provided and calculated parameters				
Temperature = 25.0 °C	Fluid density = 1.013 g/cm^3			
Pressure = 1.013 bar	Expansivity = 0.0002350 /C			
Charge imbalance = -0.327000 eq/kg	Viscosity = 0.009 P			
Activity of water = 0.997195	Chlorinity = 0.123120 molal			
Solvent mass = 1.0000 kg	Dissolved solids = 25339 mg/kg sol'n			
Solution mass = 1.0260 kg	Elect. Conductivity = 17209.89 uS/cm (or umho/cm)			
Mineral mass = 0.0000 kg	Hardness = 1801.60 mg/kg sol'n as $CaCO_3$			
Aqueous species	**molality solution**	**mg/kg**	**activity coefficient**	**log activity**
SO4–	0.1727	1.617e + 04	0.1814	−1.5041
Cl-	0.08338	2881.	0.6378	−1.2743
Cr+++	0.02553	1294.	0.0909	−2.6342
CaSO4	0.01116	1481.	1.0000	−1.9524
CuCl2-	0.009330	1223.	0.6784	−2.1986
Ca++	0.006640	259.4	0.2568	−2.7683
RuCl++	0.004539	604.0	0.2200	−3.0006
CuCl3–	0.002940	486.8	0.1814	−3.2729
Ru(Cl)2+	0.002803	469.8	0.6784	−2.7209
Ru+++	0.001830	180.2	0.0743	−3.8666
RuSO4+	0.0004638	89.11	0.6784	−3.5022
Ru(Cl)3	0.0004036	81.59	1.0000	−3.3941
Ru(SO4)2-	0.0001985	56.71	0.6784	−3.8709
RuCl4-	1.972e-05	4.669	0.6784	−4.8736
RuCl5–	2.064e-06	0.5600	0.1814	−6.4264
RuCl6—	3.715e-07	0.1136	0.0201	−8.1258
Mineral saturation states				
	log Q/K		*log Q/K*	
Ru(OH)3^H2O (am)	0.3278 s/sat	CaCl2^H2O	−13.2440	
Gypsum	0.1120 s/sat	MgCr2O4	−13.3258	
Anhydrite	−0.0630	Brucite	−14.8379	
Bassanite	−0.6926	Hydrophilite	−16.8301	
Cr2O3	−0.7011	MgOHCl	−17.6014	
CaSO4^1/2H2O(beta)	−0.8612	MgCl2^2H2O	−17.6067	
	In fluid	*Sorbed*		
Elemental composition	total moles	moles	mg/kg	
Calcium	0.01847	0.01847	721.4	
Chlorine	0.1231	0.1231	4254.	
Chromium	0.02565	0.02565	1300.	
Copper	0.01231	0.01231	762.6	
Ruthenium	0.01026	0.01026	1011.	
Sulphur	0.1847	0.1847	5771.	

Select Components for Calculation

No Surface Complexation Selected

☐ e(-)	☐ H2O	☐ H(+)	☐ Ag(+)	☐ Al(3+)
☐ AsO3(3-)	☐ AsO4(3-)	☐ Au(+)	☐ Ba(2+)	☐ Be(2+)
☐ Br(-)	☐ B(OH)3	☐ Ca(2+)	☐ Cd(2+)	☐ Ce(3+)
☐ Cl(-)	☐ CN(-)	☐ OCN(-)	☐ SCN(-)	☐ CO3(2-)
☐ Co(2+)	☐ Co(3+)	☐ CrO4(2-)	☐ Cr(2+)	☐ Cr(OH)2(+)
☐ Cs(+)	☐ Cu(2+)	☐ Cu(+)	☐ Fe(2+)	☐ Fe(3+)
☐ F(-)	☐ Hg2(2+)	☐ Hg(OH)2	☐ I(-)	☐ K(+)
☐ La(3+)	☐ Li(+)	☐ Mg(2+)	☐ Mn(2+)	☐ Mn(3+)
☐ MoO4(2-)	☐ Na(+)	☐ NH2OH	☐ NH4(+)	☐ Ni(2+)
☐ NO2(-)	☐ NO3(-)	☐ P2O7(4-)	☐ P3O10(5-)	☐ Pb(2+)

Name		Cd(2+)	Cl(-)	Co(2+)		Log K	Delta H
OH	(−1)	0	0	0		−13.997	13.339
CaOH	(+1)	0	0	0		−12.697	15.323
CdOH	(+1)	1	0	0		−10.097	13.100
Cd(OH)2 (aq)		1	0	0		−20.294	0.000
Cd2OH	(+3)	2	0	0		−9.397	10.949
Cd(OH)4	(−2)	1	0	0		−47.288	0.000
Cd(OH)3	(−1)	1	0	0		−32.505	0.000
CdOHCl (aq)		1	1	0		−7.404	4.355
CoOOH−	(−1)	0	0	1		−32.092	62.250
CoOH+	(+1)	0	0	1		−9.697	0.000
Co(OH)2 (aq)		0	0	1		−18.794	0.000
Co(OH)4−2	(−2)	0	0	1		−46.288	0.000
Co4(OH)4+4	(+4)	0	0	4		−30.488	0.000
Co(OH)3−	(−1)	0	0	1		−31.491	0.000

Fig. 4. (a) Chemical components selection module and (b) Tableau showing the speciation of the elements (MINEQL+software, version 5.0).

uses Humic Ion-Binding Model V with inorganic speciation code for aqueous solutions and assumes discrete-site electrostatic binding. Thus, the model shows discrete-site binding of the elements which is modified by the electrostatic interactions. Other factors such as the precipitation of aluminium and iron oxyhydroxides, cation exchange on idealised clay minerals and the adsorption–desorption reactions on fulvic acid are also taken into consideration (Guthrie et al., 2005). WHAM is a commercially available software with different versions. The recent version is WHAM VII which can perform better than the previous versions. For example, a study by Wang et al. (2019) developed mechanistic kinetics model using WHAM 7 in order to describe the kinetics of element dissociation from dissolved organic matter (DOM). The study indicated that the WHAM based kinetics model was able to account for the different qualities of solutions considered and the heterogeneity of DOM binding sites (Wang et al., 2019). Since PGEs can end up in waterbodies of different qualities, WHAM should be used to determine the speciation of PGEs in solutions with high concentrations of humic substances. Other computer models may not be suitable as they do not take organics into consideration. Not all PGEs are included in the WHAM code hence, more information will be required so that they can be included.

5.6. *The need for new PGEs databases*

The databases available as indicated above, do not include other PGEs such as rhodium, ruthenium, osmium and iridium. There is therefore a need to come up with databases which contain all the PGEs at different conditions so that their speciation can be easily and accurately determined. This means that compendia of logarithms of equilibrium constants (log Ks) and enthalpies of reaction from various literature sources will be required (Parkhurst and Appelo, 2013). However, more experimental data may still be required so that all the major and important species of PGEs at different conditions can be accounted for (Alsemgeest et al., 2021). Moreover, most of the databases are suitable for low ionic strength solutions (Alsemgeest et al., 2021; Mercer and Tobiason, 2008). Thus, there is a need to conduct experiments using solutions with ionic strengths or to collect data from high ionic strength solutions so that databases can be developed using the results.

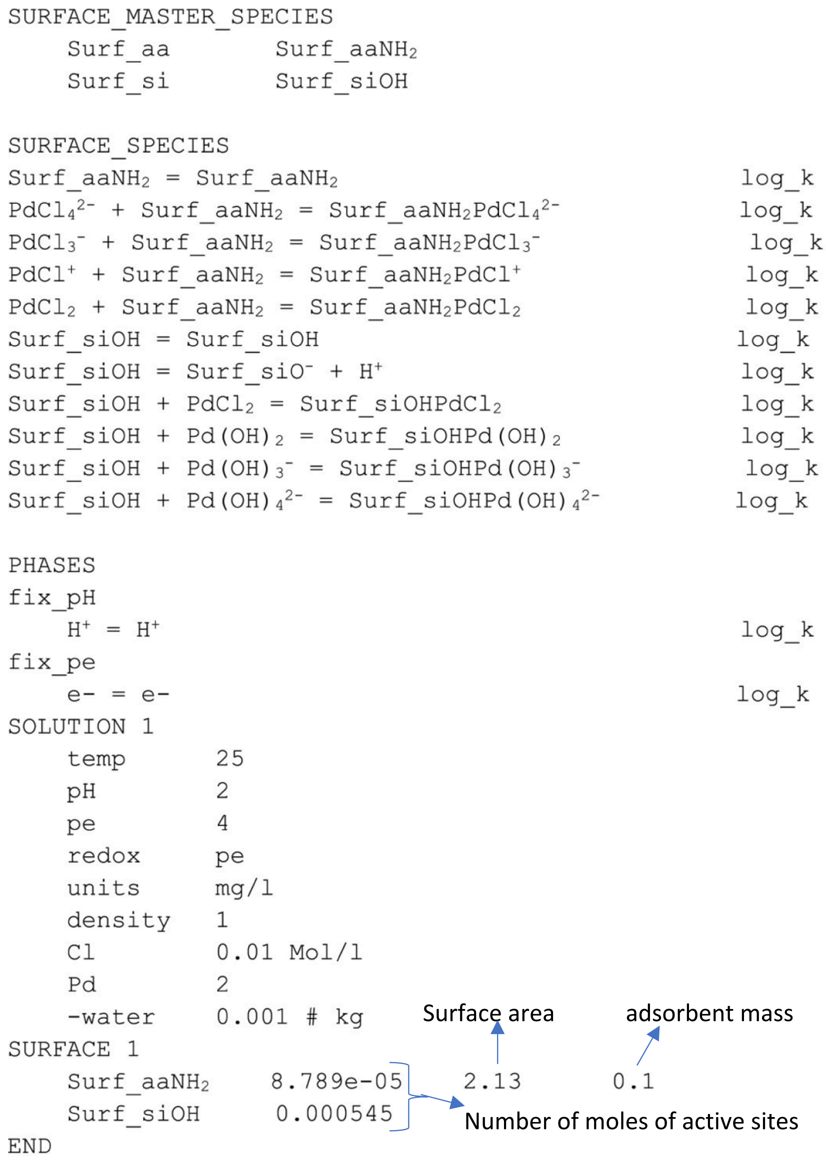
6. Predictive adsorption

There is lack of adequate predictive adsorption of PGEs which can be important in determining the performance of adsorbents beyond what has been analysed. A study by Apul et al. (2013) used Quantitative

Structure–Activity Relationship (QSAR) and Linear Solvation Energy Relationship (LSER) techniques to develop predictive models with multiple linear regression analysis for the adsorption of organic contaminants by multi-walled carbon nanotubes (MWCNTs) with less than 5 % oxygen content. Adsorption data from different sources was used. As a result, a database was created for the adsorption of organic compounds from different studies. The study found that the created models were useful for the assessment of the adsorption of aromatic compounds by MWCNTs. The study also indicated that the modelling can be extending beyond the available data using the validated models. Such models for the adsorption of PGEs can also be developed however, the speciation information in the presence of anions and cations must be known. The effect of pH, ionic strength and other factors that can influence adsorption must be available. The surface coverage and the possible chemical reactions between the elements and the adsorbents should be taken into consideration as they play a major role (Sverjensky and Fukushi, 2006). There are many studies with relevant information dealing with different adsorbents that can remove PGEs from solutions by adsorption (Uheida et al., 2006; Asere et al., 2019; Mosai et al., 2020; Chen et al., 2021). These studies can be used to create a modifiable database that can be used for predictive adsorption modelling. This will help in coming up with new suitable adsorbents and testing their capabilities before the application process. For example, a researcher can look at the available adsorbents and active sites involved in removing PGEs from aqueous solutions, hence decide to develop a new adsorbent that has a combination of active sites that were selective for PGEs and showed good efficiencies. This way, time will not be wasted on developing adsorbents which may be expensive and showing low adsorption efficiencies.

6.1. *Simulating the adsorption of PGEs*

Applications such as PHREEQC, Geochemist's workbench and MINTEQA2 have capabilities of modelling surface reactions when important data such as the concentrations of elements involved, chemical reactions between elements and the adsorbent, number of moles of active sites and surface area as well as the mass of adsorbents are available. The activity, K_d (distribution coefficient), Langmuir, Freundlich, ion exchange, constant capacitance, triple-layer and diffuse layer models are incorporated in the applications to allow for the modelling of surface reactions (Parkhurst and Appelo, 2013). However, these models do not usually have the thermodynamic database files with the required reactions



```
SURFACE_MASTER_SPECIES
    Surf_aa          Surf_aaNH2
    Surf_si          Surf_siOH

SURFACE_SPECIES
Surf_aaNH2 = Surf_aaNH2                                   log_k     0
PdCl4^2- + Surf_aaNH2 = Surf_aaNH2PdCl4^2-                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_siO^- + 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)4^2- = Surf_siOHPd(OH)4^2-              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
```

Fig. 5. PHREEQC input script for the adsorption of Pd^{2+} onto amine modified surface (Mosai et al., 2021).

hence, the user must specify the surface reactions and the equilibrium constants. The thermodynamic database by Dzombak and Morel (1991), which involves surface reactions is getting pretty old and is only for hydrous ferric oxide surface and does not include PGEs. Fig. 5 shows the PHREEQC input script for the adsorption of palladium using an amine modified adsorbent. The surface master species shows the surface specific sites involved in adsorption. For modified adsorbents, laboratory tests will have to be conducted using the raw and modified surfaces in order to get a good representation of the adsorption process which should be included in the applications. This is because some raw adsorbents can remove some of the analytes from aqueous solutions meaning that it is not only the modified surface that is responsible for adsorption. In Fig. 5, Surf_si and Surf_aa represents the raw and modified surfaces, respectively. Surf_si is a silica surface which have been found to remove significant amounts of palladium from solution. If only the modified surface was included, the adsorption process would have been represented poorly. The surface species shows the reactions of the different species of palladium with the adsorbent surface as well as the corresponding equilibrium constants. When the run is initiated, the equilibrated mass between the dissolved, adsorbed and solid species is computed. Although Fig. 5 represents the PHREEQC geochemical modelling code, other applications also use the same principles i.e. the surface active sites, species and reactions with the corresponding equilibrium constants have to be included in the model in order model the adsorption of elements.

The adsorption of PGEs can be simulated beyond the experimental conditions using PHREEQC. However, this will require a good calibration of the model. When the model is properly calibrated, the user can identify the effect of varying parameters on the recovery of PGEs. Mosai et al. (2021) used PHREEQC coupled with parameter estimation (PEST) software to simulate the adsorption of Pd^{2+} onto amine-functionalised zeolite and found that the PHREEQC model can simulate beyond the given data when calibrated. Currently, PEST has been used because it is a reliable and valuable software that can estimate important parameters as well as computing sensitivities of model outputs to parameters (Welter et al., 2015). Thus, PEST can automate calibration including calibration-constrained uncertainty analysis of numerical models. The interaction of PEST numerical models is through the input and output files of the models. In order for PEST to accurately estimate parameters, it must run a model many times. In order for PEST to run, it must have three important input files (template, instruction, and control files) (Welter et al., 2015). The template file is a replica of the model input file with the exception that the parameters to be estimated are replaced by a sequence of characters. The instruction file contains directions which PEST must follow to read laboratory or field measurements so that the model generated values are as close as possible to the measurements with minimal discrepancies. The PEST control file is known as the master file and is used to bring together all the files involved in numerical modelling (Gallagher and Doherty, 2007). The study showed that changing conditions such as pH, adsorbent mass and concentration of elements can significantly affect the adsorption of Pd^{2+}. The study by Mosai et al. (2021) used synthetic solutions to study the effect of varying conditions on adsorption however, when data is available for real wastewater, the results can be used to calibrate PHREEQC simulations when all the relevant data is included in the model. In this way, the performance of developed adsorbents on the recovery of PGEs from different wastewater can be assessed in a cheaper manner (using previously calibrated PHREEQC simulations). Thus, the mining and other industries involved with the recovery of PGEs can use PHREEQC to determine the potential recovery values of the PGEs from wastewater through geochemical simulation before the implementation of the recovery process in large scale. This can be done using limited experimental data hence, saving costs and time. This step is crucial since the quality of wastewater can change due to different factors such as weather conditions and mineral processing conditions, therefore using PHREEQC coupled to another software e.g. PEST for accuracy will ensure that the actual implementation cost and process is known.

6.2. Isotherm models

The distribution coefficient (K_d) which can be used to predict the interaction of elements with adsorbents and determine the sorption and desorption characteristics of the elements is an important factor that should be considered for adsorption reactions (Bethke and Brady, 2000). In order to use numerical models for predictive adsorption, all the adsorption sites that will have a significant effect on adsorption must be added in the models. Species can be adsorbed using a unique single active site hence uniform adsorption, whereas some can be removed through multiple active sites. Adsorption isotherms can be used to describe the adsorption mechanism (Ayawei et al., 2017). Equilibrium adsorption isotherms can be used to describe the adsorption mechanism or the relationship between the elements and adsorbents. They are referred to as isotherms because they deal with the relationship between equilibrium adsorbate concentrations in the liquid phase and the equilibrium adsorption amount on the solid phase at a particular temperature. The coefficient of determination (R^2) statistical measure is normally used as a validation criterion in the adsorption isotherm modelling. Langmuir adsorption isotherm (Eq. (4) can be used to describe the adsorption of the elements (Langmuir, 1916). It accounts for the surface coverage through balancing the relative rates of adsorption and desorption.

$$q_{eq} = \frac{bq_oC_{eq}}{1 + bC_{eq}} \tag{4}$$

where q_{eq} (mg/g) is adsorbed amount at equilibrium, C_{eq} (mg/L) is adsorbate concentration at equilibrium, b is the Langmuir constant (L/mg) and q_o (mg/g) is the maximum adsorption capacity. Dimensionless constant which is also known as the separation factor (R_L) (Eq. (5) is also used but separately to express the essential characteristics of the Langmuir isotherm (Hall et al., 1966). If R_L=0 it means that the adsorption is reversible, R_L=1 means the adsorption is linear, R_L<1 indicates that the adsorption is unfavourable and when $0 < R_L < 1$ means that the adsorption is favourable.

$$R_L = \frac{1}{1 + K_LC_o} \tag{5}$$

The equilibrium data described by Langmuir isotherm indicates that there is monolayer adsorption, meaning that the elements under consideration are adsorbed through one active site hence a homogeneous surface.

Freundlich isotherm is also a commonly used nonlinear isotherm model (Eq. (6) (Freundlich, 1906). It describes the multilayer adsorption on heterogeneous surface. It also considers the exponential distribution of active sites including their energies. Thus, the adsorption mechanism that follows the Freundlich isotherm indicates that the adsorbate considers multiple active sites of the adsorbent. Therefore, to successfully calibrate the numerical method, all the active sites involved must be specified including the chemical reactions between the adsorbates and adsorbents.

$$logq_e = \log K_F + \frac{1}{n}\log C_e \tag{6}$$

where K_F ($L^{1/n}$ $mg^{1\text{-}1/n}$ g^{-1}) is adsorption capacity and n is adsorption intensity.

Other isotherm models are included in Table 6 and are summarised herein. Temkin and Dubinin-Radushkevich (D-R) isotherm models are also widely used to describe the adsorption data however, they have limitations which should not be ignored (Chu, 2021). The Temkin isotherm assumes that the adsorption of elements is through the multilayer process and very high and very low concentrations of the elements are not considered (Chu, 2021). The D-R isotherm is based on the

Table 6
Isotherm models and corresponding equations.

Isotherm model	Equation	Reference
Temkin	$q_e = \frac{RT}{b_T} lnK_T + \frac{RT}{b_T} lnC_e$ where K_T is the Temkin isotherm constant, b_T is the Temkin constant, R is gas constant (8.314 $Jmol^{-1}K^{-1}$) and T (K) is temperature.	Johnson and Arnold, 1995; Chu, 2021
Dubinin-Radushkevich (D-R)	$q_e = q_o exp\left\{-\beta\left[RTln\left(\frac{C_s}{C_e}\right)\right]^2\right\}$ where β is D-R constant and Cs is the solubility concentration.	Wang and Guo, 2020
Sips	$q_e = \frac{q_o K_s C_e^{ns}}{1 + K_S C_e^{ns}}$ where ns and Ks are the Sips constants.	Ko et al., 2005
Redlich-Peterson (R-P)	$q_e = \frac{K_{RP} C_e}{1 + a_{RP} C_e^{g}}$ where KRP and ɑ are R-P constants and g is the exponent between 0 and 1.	Redlich and Peterson, 1959)
Hill-Deboer (H-D)	$ln\left[\frac{C_e(1-\theta)}{\theta}\right] - \frac{\theta}{1-\theta} = -lnK_1 - \frac{K_2\theta}{RT}$ Where K_1 is the H-D constant and K_2 energetic constant of the interaction between the adsorbed elements and θ if fractional coverage.	Ayawei et al., 2017
Fowler-Guggenheim (F-G)	$ln\left[\frac{C_e(1-\theta)}{\theta}\right] = -lnK_{FG} - \frac{2\omega\theta}{RT}$ where K_{FG} is the F-G equilibrium constant and ω is the interaction energy between the adsorbed elements.	Hamdaoui and Naffrechoux, 2007)
Flory-Huggins (F-H)	$ln\left(\frac{\theta}{C_o}\right) = lnK_{FH} + nln(1-\theta)$ where KFH is the F-H constant, n is the number of adsorbates and θ is the degree of surface coverage.	Padmesh et al., 2006
Aranovich	$q_e = \frac{q_o C_A \frac{C_e}{C_{sA}}}{\sqrt{\left(1-\frac{C_e}{C_{sA}}\right)\left(1+C_A\frac{C_e}{C_{sA}}\right)}}$ where C_A is the Aranivich constant and C_{sA} is the elements monolayer saturation concentration.	Aranovich (1992)
Hills	$q_e = \frac{q_{SH} C_e^{nH}}{K_D + C_e^{nH}}$ Where n_H is the Hill cooperative coefficient of the binding interaction, q_{SH} is the Hill isotherm maximum uptake saturation and K_D is the Hill isotherm constant.	Al-Ghouti and Da'ana, 2020

Polanyi's potential theory and is used to describe the adsorption mechanism with Gaussian energy distribution onto a heterogeneous surface (Wang and Guo, 2020). Others such as the Sips and Redlich-Peterson models are hybrid models which combine the Langmuir and Freundlich models which can be applied in the homogeneous and heterogeneous adsorption processes (Redlich and Peterson, 1959; Ko et al., 2005). These models use certain conditions to determine whether the adsorption data follows the Langmuir or the Freundlich isotherm models. The Hill-Deboer model which fits data that indicate mobile adsorption and lateral interaction among elements attached onto adsorbents (Ayawei et al., 2017). The Fowler-Guggenheim model also indicates lateral interactions between the adsorbed elements (Hamdaoui and Naffrechoux, 2007). The data from these models will also help build the input file of the numerical model and lead to a successful calibration of the model. The Flory-Huggins isotherm model expresses the degree of surface coverage characteristics of the elements attached onto the adsorbent (Padmesh et al., 2006). It can indicate whether the adsorption process will be feasible or spontaneous. The Aranovich isotherm model is a physical adsorption model that can be used to model adsorption data with broad range of element concentrations. It can also be used in the determination of surface areas of porous adsorbents. It can also be used to solve the problem which is caused by ignoring the possibility of lateral interactions between elements attached onto adsorbents as well as prohibiting the vacancies in the elements (Aranovich, 1992). The Hills isotherm model is used to express the binding of different elements onto homogeneous sites and the assumption made is that the elements selectively adsorb onto one active site on the adsorbent whilst affecting other binding sites of the same adsorbent. The model will be able to specify whether the binding of the elements is positive cooperative, negative cooperative or non-cooperative Al-(Ghouti and Da'ana, 2020). As indicated, the R^2 value can be used to determine the isotherm model that best fits the adsorption data. The suitable isotherm model will also be important in setting up the input script of the numerical method. For example, if the data is fitted well by the Langmuir isotherm, the adsorption occurs on a homogeneous surface, meaning that one active site is responsible for the uptake of elements (Alafnan et al., 2021). Moreover, there is monolayer adsorption which makes it easy to specify the sites and all the possible reactions in the input script. Other isotherms indicate multilayer adsorption onto a heterogeneous surface. For such cases, the important active sites should be identified and added in the input script so that the calibration of the numerical model can be successful. The possible interactions of the elements with each other should also be known and included in the model.

The PGEs cannot be recovered from wastewater using any adsorbent since they require specific functional groups in order for adsorption to occur. Thus, most adsorbents that can remove other elements such as Cd, Cr, Hg and As with high efficiency (>99 %) are not suitable for the removal of PGEs from aqueous solutions due to the absence of important functional groups. Adsorbents with amine groups are normally successful with the adsorption of PGEs including other nitrogen containing adsorbents. As a result, isotherms such as the Freundlich and the D-R models which are concerned with heterogeneous surfaces for adsorption always show lower coefficient of determination (R^2) on the adsorption of PGEs which prefer specific groups. Thus, the Langmuir isotherm almost always describes the PGEs adsorption process (Asere et al., 2019; Chen et al., 2021) Moreover, most of the adsorbents used, are functionalised or modified with ligands containing groups and the majority is used as support for the ligands since very few naturally occurring adsorbents have significant amount of nitrogen containing groups.

6.3. *Kinetic models*

Adsorption kinetics can also be very important for geochemical modelling. The current thermodynamic databases incorporated in the numerical models include kinetics for mineral dissolution/precipitation. Thus, adsorption kinetics should also be included as they can provide crucial information on the adsorption of the elements. Adsorption kinetic studies have been conducted using various kinetic models to determine the type of adsorption between the adsorbent and the elements. The uptake of elements can be through bulk diffusion, external mass transfer and sorption onto active sites which are distributed on adsorbents (Kumar and Gaur, 2011). These studies have many advantages since they provide other important information such as the controlling mechanism of the adsorption process, adsorption rate, mass transfer mechanism and the efficiency of the adsorption process which is important for the numerical models. Pseudo first-order (PFO) and pseudo second-order (PSO) models are the widely used kinetic models. The PFO kinetic model which is known as the Lagergren PFO model assumes that the rate of adsorption of the elements onto active sites is directly proportional to the number of available sites and can be expressed as follows (Babarinde and Onyiaocha, 2016):

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{7}$$

where q_t (mg/g) is the amount of adsorbates attached onto the adsorbent per unit mass of the adsorbent at time t (min) and k_1 (min^{-1}) is PFO rate constant. The kinetic data that is best described by the PFO model indicates that the interaction of the elements and the adsorbents is through physisorption. The pseudo second-order kinetic model (Eq. (8) indicates the strong interaction between the elements and the adsorbent. The data described by PSO shows a chemisorption behaviour.

$$\frac{d}{dt}q_t = k_2(q_e - q_t)^2 \tag{8}$$

where k_2 (g $mg^{-1}h^{-1}$) is the PSO equilibrium rate constant. The model determined adsorbed amounts at equilibrium can be compared with experimental adsorbed amounts at equilibrium and can be used along with R^2 value to determine the model that best fits the kinetic data.

The Elovich kinetic model is also widely used and has the assumption that the adsorption energy increases with adsorption time and that the adsorption occurs on different active sites hence a heterogeneous surface (Elovich and Larinov, 1962). The Elovich model can be described by Eq. (9):

$$\frac{dq_t}{dt} = ae^{-bq_t} \tag{9}$$

Where α (mg $g^{-1}h^{-1}$) is the initial adsorption rate of the Elovich model and b (g mg^{-1}) is the desorption rate constant. The uptake of elements can also be through intra-particle diffusion into macro, meso and micropores of adsorbents. As a result, intra-particle diffusion model is also used to describe the kinetic data because it considers the diffusion of elements since the models mentioned above do not identify the diffusion mechanism (Eq. (10) (Xu et al., 2009).

$$q_e = k_p t^{1/2} + C \tag{10}$$

where kp (mg (g $min^{0.5})^{-1}$) is rate coefficient and C is the intercept. The intraparticle diffusion can be used to determine the rate of adsorption of adsorbents (Kumar and Gaur, 2011). The Boyd's intraparticle diffusion model is known as an external diffusion model which assumes that the diffusion of elements in a bounding liquid film around the adsorbent occurs very slowly (Eq. (11).

$$\frac{dq_t}{dt} = R(q_\infty - q_t) \tag{11}$$

where $q_\infty = 4\pi r_0^3 C^l k/3$ (k is the distribution coefficient)

7. Future suggestions

1. There is a need to come up with databases that include all or most of the PGEs at different conditions including temperature, concentration, ionic strength and pH. The databases should be suitable for the different available numerical modelling techniques and should incorporated the different possible surface reactions. This will ensure that the speciation of PGEs is easily attainable, and that the adsorption is quickly, easily and successfully simulated.
2. Most of the available prediction modelling techniques work better when the ionic strength of the solution under consideration is low or moderate. Thus, they fail at higher ionic strengths. There is therefore a need to develop suitable databases that can simulate and predict the adsorption of PGEs at higher ionic strengths.
3. It would be ideal to incorporate parameter estimation (PEST) in the different available numerical modelling techniques so that the models can be easily calibrated with available crucial data. In addition, there is limited information on the availability of other model calibration techniques besides PEST.
4. The predictive adsorption modelling techniques should have the capability of simulating the desorption of the elements from different adsorbents using different desorbing agents at different conditions. This capability should be included in the PGEs databases. In addition, the models should have the capability of simulating the adsorption efficiency with the resulting quality of desorbed adsorbent. Thus, the performance of the adsorbent should be simulated at different cycles.
5. It would be beneficial for the modelling techniques to have ability to calculate/estimate the cost of treating a particular amount and quality of wastewater. Thus, the models should have cost analysis option in order to determine the potential economic value and applicability of the adsorption process under consideration.

8. Conclusion

Platinum group elements (PGEs) are crucial for the development of the world due to their unique properties physical and chemical properties which are required for many current products and technologies. PGEs are mainly used in the automotive (>50& consumption), jewellery, electrical, chemical, medical and petroleum industries. However, studies have indicated that supply and demand have not been in balance due to very high demand and readily depleting natural resources which can lead to scarcity. There is therefore a need to recover PGEs from secondary sources including spent automotive catalysts and industrial wastewater. Large amount of wastewater is released during the processing of PGEs minerals and significant concentrations of PGEs have been detected. Thus, mining wastewater can be considered a good source of PGEs. Different techniques using hydrometallurgy, pyrometallurgy, solvometallurgy, liquid–liquid extraction, polymer inclusion membranes and leaching with organic acids have been developed for the recovery of PGEs but, they are known to be expensive. The adsorption technique has been found to be efficient and cheap for the recovery of PGEs from wastewater, however, large scale applications are lacking. Thus, the mining industry still seeks efficient and affordable technologies for the recovery of PGEs from wastewater. Thus, more research should still be conducted on the development of such technologies and/or techniques which can be applied in large scale. Predictive adsorption using numerical models such as PHREEQC, Geochemist's workbench, MINEQL+, MINTEQA2 and Windermere Humic Aqueous Model (WHAM) coupled with parameter estimation (PEST) software can be used to determine the performance of the developed adsorbents beyond the available data since they have capabilities of modelling surface reactions when important data such as the concentrations of elements involved, chemical reactions between elements and the adsorbent, number of moles of active sites and surface area as well as the mass of adsorbents are available. This will help determine the efficiency of the adsorbents in wastewater with different qualities. Thus, saving money and time required to perform experiments. Moreover, some experimental conditions are challenging to achieve using laboratory experiments, hence the importance of computational modelling. The thermodynamic database files incorporated in the models do not usually have all the PGEs and their reactions in different conditions hence, the need for the user to modify the database by including the PGEs as well as their surface reactions and the equilibrium constants.

CRediT authorship contribution statement

Alseno K. Mosai: . **Raymond H. Johnson:** Writing – review & editing, Writing – original draft, Visualization, Validation, Conceptualization. **Hlanganani Tutu:** Writing – review & editing, Visualization, Supervision, Investigation, Conceptualization.

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.

Data availability

No data was used for the research described in the article.

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