Development and application of functionalized polymeric materials for heavy metal ions recovery from industrial and mining wastewaters

by

Dalia Saad

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DEDICATION

To my lovely mother .....the most precious gift of heaven

Her sacrifices, love and care made my life worthwhile

Her special support, gave me faith, power and ability to face all difficulties throughout my studies

Without you my life would fall apart

To my father.....his care...., support and love of perfection guided my way through life

To my whole **family** my beautiful sisters and my lovely brother, I cannot express how grateful I am for having you in my life,

To him..... the real treasure in my life.....my beloved husband

There is no single word that could ever express what he did & always does for me and how much appreciation I have for him ... he was & always is there for me and as such my life will go on.

Wherever I go and whatever I do you will always be partly responsible hence this achievement is not only my achievement but yours as well...

To my unborn son .....you made the end of this journey so special to me, full of excitement, satisfaction, wonderful feelings and joy..... being waiting for two lovely dreams to come true

DECLARATION

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

.....

Ms Dalia Saad

School of Chemistry, University of the Witwatersrand, Johannesburg. 2011

This thesis is submitted after examination and approval by the following supervisors

.....

Prof. Ewa Cukrowska

.....

Dr. Hlanganani Tutu

School of chemistry, University of the Witwatersrand, Johannesburg, 2011

ABSTRACT

Water pollution is a serious environmental crisis all over the world hence unsafe water is rated among the top ten risks to health. Heavy metals are among the most threatening water contaminants because of their toxic effects on human health.

This research was dedicated to the development of insoluble polyethylenimine derivatives; with the suitable functionalities for use as adsorbents to abstract specific toxic elements from mining and industrial wastewater. Branched polyethylenimine (PEI), well known for its metal chelating potential, was cross linked by epichlorohydrin in order to convert it into a water-insoluble form. The water-insoluble property gives the advantage of being used in situ and a possibility of regeneration and re-use, making it a more feasible and cost-effective method. Its surface was then modified for selective removal of uranium (U), mercury (Hg, arsenic (As), and selenium (Se).

Three different functional groups were chosen according to the targeted elements namely: the phosphate group for selective removal of U and As; sulphate group for selective removal of Hg and Se, and the thiol group for selective removal of Hg. The adsorption performance of the developed materials was assessed in batch and column experiments.

The selectivity of the synthesized materials as well as their ability to be regenerated for reuse was assessed. The results obtained demonstrated that the phosphonated derivative had a superior selectivity towards U with up to 99% adsorption (at pH 3 and 8) even in presence of competing ions, as well as a very good removal for As showing 88%. However, the removal mechanism of U by phosphonated cross-linked polyethylenimine (PCPEI) was found to be different from that of As in that while U was adsorbed onto PCPEI by complexation with the phosphate, As was adsorbed via anion replacement of the phosphate.

The sulphonated derivative (SCPEI) was found to be very selective towards both Hg and Se giving removal percentages of 87% and 81% respectively (at pH 3 and 8). Interestingly, the performance of SCPEI towards Hg and Se is similar in both single (Hg or Se) or multi removal (Hg and Se), hence the mechanism is totally different.

The thiolated derivative revealed a superior selectivity for Hg with 97% adsorption at pH of 3 and 8. Its adsorption capacity far exceeded that for the sulphonated derivative as a result of high affinity for Hg by the thiol group.

The Langmuir and Freundlich isotherm models were used to interpret the adsorption nature of the metal ions onto the synthesized polymers. The Freundlich isotherm was found to best fit and describe the experimental data, thus implying adsorption onto heterogeneous surfaces.

The kinetic rates were modelled using the pseudo first-order equation and pseudo second-order equation. The pseudo second-order equation was found to explain the adsorption kinetics most effectively, implying chemisorption. This was confirmed by the thermodynamic study which revealed that the adsorption process was accompanied by high activation energies (> 41 kJ mol^{-1}).

Desorption was conducted using 5 mol L^{-1} HNO_3 for Hg and Se on SCPEI; 7 mol L^{-1} for U and As on PCPEI and 5 mol L^{-1} for Hg on TCPEI. The results pointed to a good desorption capacity using this solution and on re-use, the polymers still exhibited commendable adsorption. This desorption-re-use was done in five cycles, with only a small percentage loss in adsorption capacity.

A continuous fixed-bed adsorption study was carried out using PCPEI (as one of the most efficient developed adsorbent) to assess the possibility of using these materials in filter systems for household use. The results obtained demonstrated that the performance of PCPEI in a fixed-bed column is dependent on the inlet concentration, flow rate, and

bed height. Better adsorption results were obtained at lower flow rates and lower concentrations of U and a longer bed height. The Adams–Bohart, Thomas, and Yoon–Nelson models were applied to experimental data to predict the breakthrough curves and to determine the column kinetic parameters. The initial region of the breakthrough curves was defined by the Adams–Bohart model at all inlet concentrations, flow rates and bed height studied while the full description of breakthrough was accomplished by the Thomas and Yoon-Nelson models. The model constants belonging to each model were determined by linear regression and were proposed for use in column design.

The problem of swelling that is usually associated with these resin-types of polymer was overcome by functionalization, a process similar to vulcanisation of rubber. There were no observed changes in the physical aspects of the polymers.

The developed polymeric materials showed good results and potential to be applied for selective remediation of aqueous systems polluted by heavy metals. The study of adsorption in column systems showed that these materials have potential for use in filter systems for household taps, especially for communities accessing polluted drinking water sources.

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Functionalization of cross-linked polyethylenimine for the removal of As from mining wastewater

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These publications are my own work (written by myself), the two co-authors are my project supervisors

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Chapter 1

INTRODUCTION

This introductory chapter gives an overview

of the project, the problem statement and motivation as well as the

key questions related to the study.

1. Introduction

1.1. *General overview*

Water is the most precious element in life. Hegel described it in his famous book (philosophy of nature) by saying: "*Water is the element of selfless contrast, it passively exists for others, water`s existence is, therefore, an existing for others, its fate is to be something not yet specialized and thus it soon came to be called the mother of all that special*". Water is a very important resource for people and the environment since it is essential for everything on our planet to grow and prosper. It covers over 70% of the earth surface and makes up to 65% of human bodies. Therefore, it is the most invaluable natural resource in the planet as without this precious element, life on earth would be nonexistent (Andhale et al., 2011; Asubiojo and Ajelabi, 2009).

Recently, water resources are under a serious threat of over utilization. The world is facing a challenge in meeting rising demands of unpolluted water since the available supplies of freshwater are decreasing due to population growth, extended droughts (climate change), extensive industrialization and improper disposal (Liu et al., 2008; Ruparelia et al., 2008 and Ahmed et al., 2008). This, as a result of demand for economical, industrial, and agricultural development still outweighs the demand for a healthy natural environment. Moreover, the global development raises new challenges in environmental protection and conservation (Ahamed *et al.*, 2008; Erakhrumen, 2007; Hseu, *et al.*, 2010; Pokhrel and Viraraghavan, 2004; WHO, 2002).

Water pollution affects drinking water, rivers, lakes and oceans all over the world. This consequently harms human health, natural environment, and even the economy. It also disrupts the natural food chain. Pollutants such as lead and cadmium are eaten by tiny animals. Later, these animals are consumed by fish and shellfish, and the food chain continues to be disrupted at all higher levels (bioaccumulation and biomagnifications). Eventually, humans are affected by this process as well and they can get diseases such as hepatitis by eating seafood that has been poisoned (Manohar et al., 2006; Pink, 2006; Rajendran et al., 2003;

West, 2006).

One of the most important environmental problems related to water pollution throughout the world is the contamination of water bodies by heavy metal ions because of their toxic effects on the environment and human health (Akpor and Muchie, 2010; Cavus and Gurdag, 2008; Calmano and Förstner, 1983). Although some of them are natural nutrients at trace level, they become very toxic at high concentrations. This is a result of intensive anthropogenic activities including a wide range of industries such as mining, agriculture, and disposal of industrial waste materials (Akpor and Muchie, 2010) As such; removal of heavy metals from environmental systems has become a research priority and subject of uncontained research. (Manohar et al. 2002; Rio and Delebarre 2003; Wahi et al. 2009; Cai and Jia 2010). Several industries generate wastewaters containing heavy metals in excess of discharge limits, thus necessitating treatment of the water before discharge. There are many alternative methods used for the treatment of heavy metal ions from aqueous streams. Conventional techniques for removal of these metals have disadvantages such as poor removal efficiency, high cost, and generation of secondary pollutants. In general, most of these techniques either have the inherent problem of sludge handling and/or are best suited for high metal concentrations (Kar and Misra, 2004).

This research focused on the development of new and improvement/modification of existing polymeric adsorbents for the removal of heavy metals from mining and industrial wastewaters.

1.2. Wastewater

Wastewater is any type of water that has been affected in quality by anthropogenic influence. It is a waste product (end-product or by-product). This encompasses a wide range of potential contaminants and concentrations from different activities, such as domestic wastes, commercial wastes, industrial wastes, and agricultural wastes. In the most common usage, it refers to the municipal wastewater that contains a broad spectrum of contaminants resulting from the mixing of wastewaters from different sources (Ellis, 2004).

The most common wastewaters are the disposal wastewaters from industry because they are difficult and costly to treat. For some industries which produce a lot of wastewaters such as paper and pulp production, handling processes have been developed to recycle water within plants before disposal. Most petroleum refineries, chemical and petrochemical plants, and mining have treatment facilities to make the concentration of pollutants comply with the local and national regulations regarding disposal of wastewaters (Byrd *et al*., 1984; Tchobanoglous, 2003).

1.3. Problem statement and motivation

South Africa is facing a water crisis which is caused by a combination of factors: low rainfall, high evaporation, an expanding economy and a growing population. All these factors are influencing the quantity of water as well as its quality (DWAF, 2001).

First of all, South Africa is a semi arid region with limited fresh water natural resources. It has only 8.6% of the rainfall available as surface water which is considered as one of the lowest conversion ratios in the world (Figure 1.1). Furthermore; the available freshwater resources are already almost fully-utilised and under stress (Davies et al., 1993; Ochieng et al., 2010; Turton et al., 2006).

Figure 1.1 indicates that South Africa has a mean annual precipitation (MAP) to mean annual runoff (MAR) ratio of 8.6%, that is, only 8.6% of the rainfall is available as surface water.

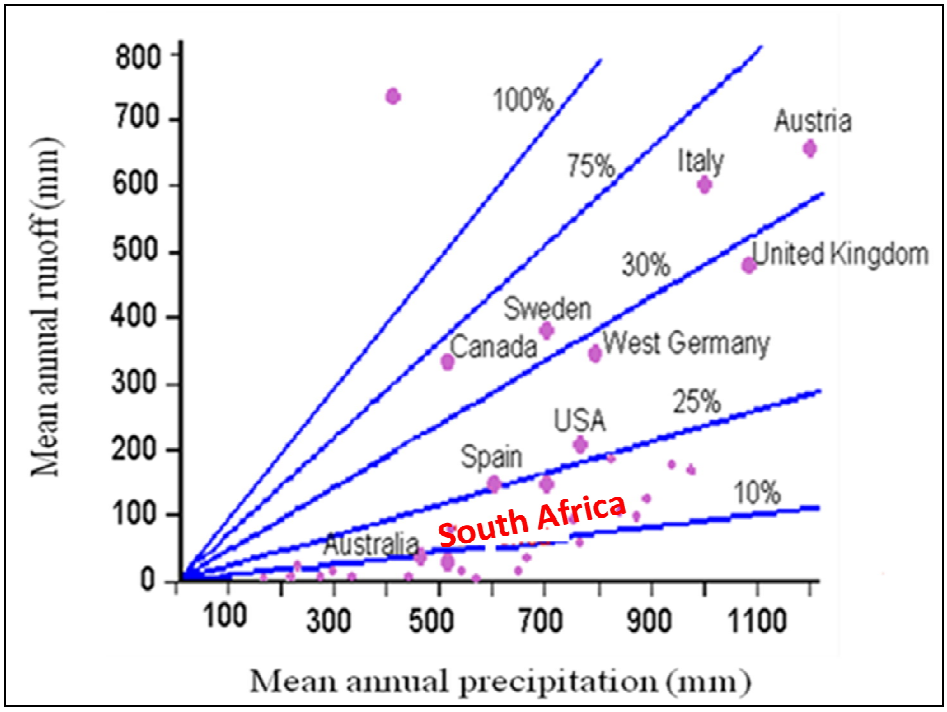


Figure 1.1. Runoff and precipitation state of water in South Africa (Allanson *et al.*, 1990)

In addition to the scarcity of water resources, South Africa faces many problems that affect freshwater quantitatively and qualitatively. Regardless of any unnatural processes, South Africa has poor water resources since the natural conditions particularly climate have been characterised by low rainfall and high evaporation rates resulting in low available run-off. Furthermore, there has been a rapid population growth and expanding economy which leads to greater water demand and increased pollution of available resources. This population growth is accompanied by human activities such as agriculture, industry, and mining which have negative impacts on the ecosystem generally and on water quality particularly (Ashton et al., 2008; DWAF, 2006).

Industrial development has left pronounced effects on the environment generally and on water resource specifically. Many industries generate waste products that contain hazardous materials and chemicals which are discharged directly or indirectly into water systems. Agricultural processes also add pollutants such as fertilizers and to water bodies (Oberholster et al., 2008; Walmsley, 2000).

The mining industry in particular accounts for major environmental threats, as South Africa has the world`s largest reserves of several minerals (Davies et al., 1993; Nisbet, 1981; Ochieng et al., 2010). Gold mining for example represents the largest source of wastes in South Africa, as it has been evaluated to be account for 22 million tons of waste which is about 47 % of all produced mineral wastes (Bell et al., 2001; DWAF, 2001). Wastes from mining represents the most significant source of heavy metals as it contributes by huge amounts of wastes containing heavy metals as well as it facilitates their availability for uptake.

1.3.1. Toxicological aspects of heavy metals

The toxicity of heavy metals depends on many factors such as the type of the exposure whether acute or chronic and the total dose absorbed and the chemical form of the metal. Toxicity of heavy metals also varies significantly according to the oxidation state of metals, the formation of complexes, and the biotransformation of the elemental species (Apostoli, 2006).

Heavy metals can impair numerous body physiology, systems and organs in the body such as: blood and cardiovascular, kidneys, livers, colon, nervous, urinary, enzymatic, gastrointestinal, and energy production. Breathing heavy metal particles can cause serious health problems. Virtually all aspects of animal and human immune system functions are threatened by the inhalation of heavy metals. One of the worst hazards of the heavy metals is that they increase the acidity of the blood, as a result the body draws calcium from the bones to maintain the proper blood pH causing osteoporosis and contributing to hardening of the artery walls with progressive blockage of the arteries due to inflammation in arteries which is also result in more calcium drawn as a buffer (Coppellotti, 1994; Life Extension, 2009; Molinari *et al.*, 2004; Morgan and Lackey, 1958; Soghoian and Sinert, 2009; Steenkampa *et al.*, 2002).

The worst is that the biological half-lives of heavy metals are long, and they readily transferred across the placenta, and then found in breast milk causing detrimental effects on behaviour, intellect, and developing nervous system in

children as a result of natural breast feeding. Generally even trace levels of toxic heavy metals have negative health consequences because they can be gradually built up and reach harmful levels (Life Extension, 2009).

The danger of heavy metal pollutants in water lies in two aspects of their impact. Firstly, heavy metals have the ability to persist in natural ecosystems for an extended period. Secondly, they have the ability to accumulate in successive levels of the biological chain, thereby causing acute and chronic diseases (Boonyapookana *et al.*, 2005; Fuggle, 1983; Jadia and Fulekar, 2009; Johnson and Hallberg, 2005; Khan and Moheman, 2006; Kuzovkina *et al.*, 2004; Lone *et al.*, 2008; Nelson and Campbell, 1991; Nomanbhay and Palanisamy, 2005; Rajendran *et al.*, 2003).

Generally, heavy metals disrupt metabolic function in two ways: firstly, they accumulate and as such they disturb the function of vital organs and glands of human body such as heart, brain, liver, kidney etc. And secondly, heavy metals dislocate nutritional minerals from their original place and as such hinder or change their biological function. Table 2.1 shows few examples for the human effects of some of the most toxic elements, their sources as well as their permissible levels.

Table 1.1 Examples for heavy metals toxicity, sources and permissible levels (Long and Yang, 2002; Martin and Griswold, 2009; Singh, 2011; Zhang et al., 2008)

Metal	sources	toxicity	Permissible level (mg L^{-1})
Mercury	Mining, oil refining, fertilizers, paints, pulp and paper	Affect nervous system, mental retardation, genetic defects (cause chromosome breaking and interference in cell division, chest pain, and dyspnoea.	0.002
Uranium	Mining	Nephrotoxic, neurotoxic, genotoxic (DNA damage), immunotoxic (weakened immune system), disturbs hormone balance.	0.03
Arsenic	Agricultural and industrial sectors (Pesticides, fungicides, algaecides, and herbicides), production of wood preservatives.	Carcinogenic, teratogenic (affects foetuses), and mutagenic (induces chromosomal abnormalities), nasal septum, skin changes, peripheral neuritis.	0.05
Selenium	metal industries, glass industry, pesticides and fertilizers	Neurological damage, cirrhosis of the liver, cancer, cardiovascular disease, cognitive decline, thyroid disease and death.	0.05

Cadmium	Welding, electroplating Cd and Ni batteries, nuclear fission plants, paints and plastics, fertilisers.	Reproduction problems (affects sperm and reduces birth weight), renal dysfunction, lung cancer.	0.06
Lead	Pint, pesticides, automobile, burning coal	Brain damage, anaemia, reduced learning abilities, liver and kidney damage, infertility, cardiotoxic, high blood pressure, congenital paralysis.	0.015
Zinc	Brass manufacture metal plating plumbing	Cause damage to nervous membrane.	15.0
Copper	Mining, pesticide production, metal piping.	Anaemia, hypertension, liver and kidney damage, uraemia.	0.05
Iron	Acid mine drainage, landfill leachate sewage or engineering industries.	Cause tissues damage	0.1
Chromium	Steel and textile industry	Weakened immune system, kidney and liver damage, lung cancer, alteration of genetic material, respiratory problems, irritations and nosebleeds, skin rash.	0.05

Despite the fact that mining has substantial environmental impacts, it also has a significant contribution to the economic growth. It has been the real driving force behind the development of South Africa. This great contribution to the economy and development of South Africa should consider as a motivation to find appropriate waste management alternatives that meet the given environmental regulatory standards in a technological sound (efficiency, applicability and feasibility) and economic (cost-effective) manner (Pinter et al., 1995). All and above, sustainable economic development cannot be accomplished without considering the environmental impacts of mining specially with the growing public awareness of the environmental issues and more stringent environmental legislation. South Africa needs to balance the use of water to create an environment conducive to healthy, social, and economic well-being. However, South Africa`s growing demands for water cannot be met unless wastewater management is revolutionized.

As the contamination of heavy metals has been considered as one of the most significant, difficult, and uncontrollable environmental impacts of mining through acid mine drainage, the removal of these toxic metal ions becomes an important challenge taking into account that the current technologies or remediation methods of contaminated water such as ion-exchange resin, electrolytic or liquid extraction, electro dialysis, chemical precipitation, membrane filtration, and biosorption are inadequate due to the high quantities of these wastes, which might lead to nested problems such as metals bearing sludges which are difficult to dispose of. Furthermore, most of these traditional methods are costly; therefore there is an urgent need for new feasible and cost effective methods (Ahmed *et al.*, 2008; Ghoul *et al.*, 2003). Overall, without a radical improvement in wastewater treatment technologies for removal of heavy metals, progressive worsening of water quality will continue. This research contributes to wastewater management by introducing a promising alternative for removal of heavy metals from mining wastewaters as the most toxic and persistent pollutants found in mining wastewaters (acid mine drainage).

The separation of metal ions present as contaminants in water, is very complicated due to a number of variables that must be considered, including the solution composition, salinity, pH, temperature, and the presence of organic substances. A serious problem encountered in metal ion removal is that the target species are usually present in low concentration and in complex mixtures (Rivas *et al.,* 2003).

Much research is being conducted to develop methods to remove heavy metal ions from wastewater, and many methods have been applied such as precipitation, coagulation, solvent extraction, reduction, neutralization, electrochemical separation through membranes, ion exchange, and adsorption. Among many separation and remediation techniques, polymeric adsorbents are efficient and widely applied. They are comparable to other remediation techniques in terms of technical and economical feasibility as well as green technology (Kwon *et al.,* 2000; Shentu *et al.,* 2007; Wang *et al.,* 2001). Polymeric adsorbents consist of a synthetic polymer and ligand, wherein the metal ions are bound to the polymer ligand by a coordinate bond (Kaliyappan, 2000).

They have a good potential for the recovery of heavy metal ions by having chelating ligands or anchoring sites with functional groups containing donor atoms like nitrogen, oxygen, or sulphur obtained either by polymerization of monomer possessing the coordinating site or by a chemical reaction between a polymer and a low molecular weight compound with coordinating ability that can bind to the metal ions by donating electrons and forming a coordination polymer – metal complex (Rivas *et al.,* 2009; Reddy and Reddy, 2003).

Chapter 2

LITERATURE REVIEW

This chapter presents

a concise review of the literature relating to wastewater

remediation technologies with intensive sight

on polymeric adsorbents.

2. Literature review

2.1. Wastewater remediation methods

Since the environmental contamination due to wastewater discharges containing high concentrations of heavy metals is ubiquitous, the ability to reduce these elevated concentrations below allowable discharge limits has received considerable attention. Many researches are being conducted to develop methods for removal of trace metals from wastewaters. There are many methods used for the recovery of trace metals, some are very simple such as the use of agricultural waste materials and other industrial wastes while some are sophisticated such as: solvent extraction, coagulation, reduction, electrodialysis, ion exchange, phytoremediation, reverse osmosis, electrodeposition, flocculation, crystallization, electrochemical, neutralization, ultrafiltration of ligand-containing polymers, resins containing intricately designed ligands and adsorption.

However, most of these techniques are inadequate because of different reasons in each method such as incomplete metal removal (poor efficiency), high reagent and energy requirements and the large quantities of wastes which are difficult to dispose of, beside generation of toxic waste products. The produced metal hydroxides in the hydroxide precipitation method are a good example of toxic waste products that may be released to the environment upon disposal. Other techniques such as membrane separation methods are quite effective, but are not feasible for large area remediation because of their high cost (Ajayi and Osibanjo, 1981; Fu *et al.*, 2006; Gould *et al.*, 1984; Pagana *et al.*, 2008; Patterson, 1975; Peters *et al.*, 1986; Sauer *et al.*, 2004; Vogel, 1987; Winfield, 1979).

Amongst all these methods, there are some conventional techniques that have been widely applied for heavy metal ions removal with some form of merits and demerits.

2.1.1. Conventional methods

Over the last few decades, several conventional techniques have been used for the removal of heavy metals. Below is a review of properties, advantages, and disadvantages of some of the most commonly used conventional methods.

2.1.1.1. Physiochemical remediation

Chemical precipitation

Chemical precipitation is a known remediation technique that involves transformation of dissolved contaminants into insoluble solids. It has long been used as a primary method for treating metal-laden wastewater. Precipitation of heavy metals in water has been practiced as a prime method of treatment in industrial wastewaters for many years by adding sodium hydroxide or lime as a coagulants or flocculants to increase the particle size. The amount of chemicals that are required for precipitation is dependent on pH and alkalinity of the water. However, the results of this process are far from satisfying. That is why a combination of precipitation with other chemical treatment techniques such as ion exchange has also been used in order to achieve more effective removal. This has been applied to treat acid mine drainage from gold mine in South Africa by precipitation of heavy metals with lime and sulphides, followed by ion exchange (Akpor and Muchie, 2010; Feng *et al.*, 2000).

Chemical precipitation has many disadvantages, making it an unfeasible method. This includes: the high cost of waste disposal due to the large volumes of generated sludge to be disposed of. Hydroxides and carbonates are not always the proper chemicals. Furthermore, each dissolved metal has its own distinct pH level for maximum hydroxide precipitation. Metal hydroxides are increasingly soluble above or below their individual maximum precipitation point, even a slight pH adjustment to precipitate one metal may put another back into solution, and it also requires working with corrosive chemicals, thereby increasing safety concerns (EPA, 2000; METALSORB, 2004).

Ion exchange

Ion exchange is a very similar process to the biosorption method. It is a reversible chemical reaction wherein an ion from wastewater solution is exchanged for a similarly charged ion attached to an immobile solid particle. These solid ion exchange particles are either naturally occurring inorganic zeolites or synthetically produced organic resins (Akpor and Muchie, 2010).

Reverse osmosis

Reverse Osmosis is a membrane process that acts as a molecular filter, wherein the water passes through a membrane; the dissolved and particulate matter is left behind. A significant advantage of reverse osmosis over other traditional water treatment technologies its ability to reduce the concentration of other ionic contaminants, as well as dissolved organic compounds (Akpor and Muchie, 2010; Pawlak *et al.*, 2005; Volesky *et al.*, 2003). It is a very effective method but it is very costly because the membranes are expensive both to procure and operate.

2.1.1.2. Solvent extraction

Solvent extraction of metals from solutions has gained widespread usage in recent years. This process involves an organic solvent to extract the metals and an aqueous solution containing the metals; by which, the metals passes through into the appropriate organic phase. Furthermore, the extracted metals in the organic phase are re-extracted and stripped into stripping aqueous solution contacted with the organic solvent. Thereafter, once the metals have been removed, the organic solvent is recycled for further use. Although solvent extraction seems to be an efficient and simple method for removal of heavy metals but it also has some disadvantages such as the requirement of costly amount of organic solvents as well as the possibility of generation of toxic organic waste. Solvent extraction is also time consuming especially when a multiple extractions is required (Khan et al. 2005).

2.1.1.3. Electrodeposition

Some metals found in waste solution can be recovered by electrodeposition using insoluble anodes. For example, spent solutions resulting from sulphuric acid cleaning of Cu may be saturated with copper sulphate in the presence of residual acid. These are ideal for electro-winning where the high quality cathode copper can be electrolytically deposited while free sulphuric acid is regenerated.

In general, conventional techniques have some disadvantages that limit their usage and there is a crucial need for more alternatives to overcome the complixity of removal of heavy metals. Other recent attractive techniques are the phytoremediation, bioremediation, and microbial remediation as green technologies that are completely environmental friendly; a very critical requirement to be considered for any remediation method.

2.1.2. Advanced methods

2.1.2.1. Phytoremediation

Phytoremediation is a green remediation technology that referred to the use of plants to remediate contaminated soil, sludge, sediment, groundwater, surface water and wastewater. Phytoremediation is broadly categorized into the following main areas:

1- Phytodegradation/phytotransformation,
2- Phytoaccumulation/ phytoextraction,
3- Phytostimulation/rhizostimulation,
4- Phytovolatilization, rhizofiltration
5- Phytostabilisation.

Heavy metal ions removal from wastewater occurs by any of three mechanisms: Phytoextraction, rhizofiltration and phytostabilisation (Lasat, 2000; UNEP, 2010).

Phytoextraction is a phytoremediation process whereby plant roots absorb, translocate and store contaminants along with other nutrients and water. It occurs either naturally using hyperaccumulatotrs or induced through the addition

of chelates to increase bioavailability (Akpor and Muchie, 2010; Utmazian and Wenzel, 2006).

Rhizofiltration is similar to phytofiltration. The only difference is that in rhizofiltration the plants are raised in greenhouses with their roots in water. In this process the contaminants are either absorbed onto the roots of surface or are absorbed by the plant roots. Plants used for rhizofiltration are first acclimated to the pollutants not planted directly in situ. The suitable plants for rhizofiltration can effectively remove toxic metals over an extended period of time, a variety of plant species have been successfully removed toxic metals such as Cu^{2+}, Cd^{2+}, Cr^{6+}, Ni^{2+}, Pb^{2+} and Zn^{2+} from aqueous solutions (Dushenkov and Kapulnic, 2000; Lasat, 2000; Miller, 1996).

In *phytostabilization* the plant roots are using to limit the mobility and bioavailability of contaminants hence they absorb and accumulate pollutants as well as they can precipitate them in the rhizosphere. Many plants are able to uptake significant amounts of heavy metals such as Brassica juncea, Salsola kali, and Prosopis species. Phytoextraction can then be used for the recovery of precious metals such as gold, silver, platinum, and palladium, which indicates the wide possibilities of the phytoremediation technology with regards to mining (Gardea -Torresdey *et al.*, 2005).

2.1.2.2. Bioremediation

Biosorption is a natural physiochemical process that occurs in biological systems. It allows the biomass to passively bind contaminants onto their cellular structure. As a natural passive process it does not require any energy and the amount of contaminants adsorbed onto cellular structure depends on the kinetic equilibrium and the composition of the sorbents cellular surface. Biosorption can be used to remove toxic metals from contaminated water and to trap metals from soil and sediments. A variety of biomasses could be used for this purpose such as bacteria, fungi, algae, and industrial and agricultural wastes (Vijayaraghavan and Yun 2008; Won et al. 2005).

The biosorption process comprise of a solid phase which is the biological material and a liquid phase which is the water containing dissolved metals. Generally, the use of biological materials to remove toxic metals from aqueous solutions has been found to be very interesting as a physiochemical interaction between the metal ions and different functional groups in the cell walls of the biosorbent such as carbonyl, ketones, hydroxyl, and amino groups. But, although biosorption methods have many advantages over the conventional techniques represented in: cost-effectiveness, minimization of chemical and biological sludge, beside the possibility of regenerating the biosorbent. But there are also some drawbacks including early saturation, the biological improvement through genetic engineering of cells is limited hence cells are not metabolizing (Ahluwalia and Goyal 2007; Babarinde et al. 2009; Das et al. 2008). One of the most common biosorption methods is the microbial remediation.

2.1.2.3. Microbial remediation

In this process, microorganisms are used to deal with poisonous chemicals by applying enzymes to convert one chemical into another form and taking energy or utilizable matter from this process. Microbial metal uptake can either occur actively through bioaccumulation or passively through biosorption. Biosorption is much more applicable and effective for the removal of metal ions from contaminated solution in low cost and environmental friendly manner (Akpor and Muchie, 2010; Rani *et al.*, 2009).

Different species of bacteria, fungi and protozoa have been used for removal of high concentration of heavy metals from wastewaters (Munner, 2005).

Microbial remediation system has many advantages including the low cost and low-technology techniques, environmental friendly, no wastes to be generated; it is a self-sustaining system and it can also be used alongside other technologies. But just as it is with other technologies it has several disadvantages such as that it is not always suitable, time consuming, and the residual pollutant levels achievable may not always be appropriate (Humar and Pohleven, 2006; Viladi, 2001).

However, both bioremediation and phytoremediation have been claimed as the most effective methods compared to the conventional techniques taking into account the special advantage of their environmentally friendliness properties. But, despite their efficiency, these methods in general are costly and time consuming. For example, they require maintenance of parameters such as nutrients, energy, and temperature that is required to sustain adequate remediation (Moore and Mahmoudkhani 2011).

Nowadays**,** nanotechnology revolution has resulted in a dramatic increase and a wide possible range of applications of nanomaterials from short-term to medium-term benefits which are contributing to improving the human's life quality (Albrecht *et al.*, 2006). This includes the use of nanomaterials in environmental pollution cleanup specially wastewater treatment. As such, nanomaterials are one of the recent alternatives for removal of heavy metals.

2.1.2.4. Nanomaterials (NMs) for wastewater treatment

Recently, the most advanced technique still under research is using nanomaterials for wastewater treatment generally including removal of heavy metals. However, nanomaterials (materials at the nanometer size) are not new rather, they are common in nature. Biologically, the human body consists of many nanoscale objects such as enzymes, proteins e.g. erritin (a protein which stores excess iron in the body) and DNA. Magnetite is also found in cells and animals. There are also natural resources of nanoparticles including fires and volcanic eruptions. Moreover, nanomaterials were discovered and used very early. Silver and gold nanoparticles, for example, have been used to colour ceramic glazes and stained glass since the 10th century and possibly even earlier (Dowling, 2004; Poole and Owens, 2003).

Nanomaterials can be defined in a number of ways. In general, any material that can be manipulated, measured, and manufactured at the scale of 1-100 nm is a nanomaterial. Therefore, they have unique properties arising from their nanoscale size unlike those of both isolated atoms and bulk material. The nanoscale size demonstrates unusual features which influence a variety of material

properties such as conductivity, heat transfer, melting temperature, optical properties, reactivity, and magnetization (Albrecht et al., 2006; Donaldson and Stone, 2004; Masciangioli and Zhang, 2003).

Despite all these unique properties, the use of nanomaterials in a wide range of applications is limited according to two different points of view. Firstly, their insufficient stability (their tendency to aggregate) and secondly, and most critically, their environmental and health risks, specially that their environmental and health aspects are unknown and still subject to much debate (Macanás *et al.*, 2011; Borm and Berube, 2008; Li *et al.*, 2008).

As a promising technology for a wide range of applications, a massive production of NMs is expected in the near future and this in turn may result in the appearance of the produced NMs and their wastes in the environment. As such, humans could be exposed to these NPs through inhalation, dermal contact absorption or even ingestion. In this sense, a broad knowledge, detection, and prevention should be applied to investigate and assess the safe use of NMs. However, more research is needed before generalize statements can be made regarding NMs eco-toxicology especially because of the potential contribution of NMs in green chemistry processes such as water treatment. Notwithstanding, this has raised concerns for human exposure to NPs contained in treated water (Haverkamp, 2010).

However, it is very important to have a comprehensive knowledge of properties of the materials (chemical and physical properties) in order to investigate the health risks of the material by determining the inherent toxicity and the interaction with living cells as well as the effect of exposure time. It is also very critical to differentiate between free and fixed nanoparticles as the health risks of nanoparticles depend a lot on whether the nanoparticles are fixed or free. Free nanoparticles have a more direct health threat because they easily become airborne and hence can be inhaled. Moreover they can enter and move within the human body whereas the fixed nanoparticles are immobilised and thus cannot be inhaled (Albrecht *et al.*, 2006).

As prevention is always better than cure, it is better to prevent NPs from reaching the environment. It is very easy then to eliminate the possible contamination of natural resources as well as the danger for living organisms. In this sense, the embedding of NPs into organic or inorganic matrices reduces their mobility and hence prevents their availability in the environment (Ajayan *et al.*, 2005; Macanás *et al.*, 2011).

The use of such nanocomposites might be the simplest way to decrease the mobility and availability of nanomaterials and hence their possible health risks as well as to enhance their stability for many applications by preventing their self aggregation. The most promising solution to the issues of nanomaterials health risks and stability is to incorporate the nanomaterials into polymeric matrices. The incorporation of NMs into polymers does not only solve the NMs problems but can also improve the properties of the polymers such as high chemical stability, high permanent selectivity, thermal stability, low electrical resistance, good mechanical stability, surface appearance and electrical conductivity, and decreased permeability to gases, water, and hydrocarbons (Nicolais and Carotenuto, 2005; Vatta *et al.*, 2006).

The most viable class of polymer nanocomposites is the polymer magnetite-nanocomposites where magnetic nanoparticles are used to design the polymer nanocomposite material. Magnetic nanoparticles are of great of interest for a wide range of applications because of their useful properties, most particularly their reaction to a magnetic field. As such, they can be easily recovered when needed in many applications by magnetic traps (Belotelov *et al.*, 2005; Hyeon, 2003).

Polymer nanocomposites are materials having nanoscopic inorganic particles dispersed in an organic polymer matrix in different shapes (platelets, fibers, spheroids). This could be in many dimensions, but at least one dimension must be in the range of 1 to 50 nm. The overall purpose of this combination of the polymers with the nano-particles is to improve the performance properties of the

polymers as well as to overcome undesired properties of the nanoparticles (Biswas and Ray, 2001; Gacitua e*t al.*, 2005; Lagashetty and Venkataraman, 2005; Paul and Robenson, 2008).

The transformation from micro-scale to nano-scale results in an increase in surface area to volume ratio. The surface effect becomes more significant due to the increase in the volume fraction of surface atoms hence the surface area increases as the particles get smaller. This in turn affects the chemical and physical properties of the produced material, such as the interaction properties, the strength, heat resistance and many other factors (Gacitua *et al.*, 2005; Lagashetty and Venkataraman, 2005; Schmidt and Malwitz, 2003; Zhang *et al.*, 2008).

In sum, polymer nanocomposites exhibit remarkably improved properties compared to the pure polymers because of their nanoscale or nanometer size. But the challenge in forming these materials is to understand the chemistry behind this combination. In other words, the chemistry occurring between the polymer and the nanoparticles (guest-host chemistry) is important to understand. As such, good contact between the polymer and the added nanoparticles leads to homogeneous dispersion (Lagashetty and Venkataraman, 2005; Allen *et al.*, 2011; Rosenberg and Kailasam, 2011).

However, both the polymer nanocomposites materials and polymer magnetic-nanocomposites have been largely applied for wastewater treatment processes. The use of magnetic nanoparticles is of special interest. Because of the direct recovery of the loaded material (polymer magnetic-nanocopmosite and the adsorbed metal ions), they can be easily recovered by utilizing magnetic separation (Davis *et al.*, 2011; Liu *et al.*, 2008; Lu *et al.*, 2007; Ponder *et al.*, 2000; Savag and Diallo, 2005).

Many studies reported the promising application of polymer nanocomposites for metal ions removal. Ghorbani *et al.* (2010) applied polyaniline and its nanocomposite derivative (Pan-Fe_3O_4) to remove heavy metal

ions from cotton textile wastewater. Their results demonstrated that the removal of metal ions by polyaniline nanocomposites was much higher than for polyaniline only which emphasises the efficiency of nanoparticles in combination with the polyaniline.

Zhang and co-authors (2008) studied the selectivity of polystyrene nanoparticles towards lead, cadmium and zinc as well as the ability to regenerate the synthesized sorbent for reuse. Their results indicated that (polystyrene-Zr-HPO_3S) is effective and recyclable for selective removal of Pb, Cd, and Zn for five cycles.

Goon *et al.* (2010) reported the successful coating of polyethylenimine onto Fe nanoparticles (PEI-coated Fe_3O_4 NPs) and its application for capturing trace levels of free cobalt ions by controlling the adsorbed amount of PEI onto Fe_3O_4 NPs for optimal performance. They found that the nanoparticles enhanced the performance of the material. The results also highlighted the dependence of the adsorption capacity on the amount of the PEI coated onto nanoparticles where the adsorption of Cu^{2+} reaches a maximum at the same point as maximum adsorption of PEI onto Fe_3O_4.

However, the use of nanoparticles in wastewater treatment is still limited because of the high cost both in synthesis and in separation process. The synthesis of nanoparticles and nano-composites normally involved long and difficult synthesis routes with many factors and variables to be considered. It also requires using advanced techniques such as microwave plasma methods.

All and above, the health risks and environmental impacts also present a major issue because it is very important to ensure that the treatment method is not creating future problems as it has been occurred with many recent technologies.

Another common method for heavy metals removal is the use of polymers as adsorbents. Polymeric adsorbents represent promising materials that

have a great deal of future potential applications as high performance materials. The development of polymers in material research is rapidly growing as a multidisciplinary research resulting in broader applications of polymers. Their properties present them as promising advanced materials for various applications. Furthermore, their simple and cheap routes of synthesis represent them as a reasonable alternative for developing efficient and cost-effective sorbents for heavy metals removal from wastewaters.

2.2. General background on polymers

Polymers are natural or synthetic compounds of usually high molecular weight. They are very large molecules (macromolecules) that are comprised or built up of smaller units or monomers (Painter, 1997).

Polymer science is a rapidly growing area of material science. Polymers are well known for their wide availability and low cost and have been used for a myriad of product applications. They are being used in an increasingly wider range of applications such as wastewater treatment, toxic metal removal and enrichment of precious metals from hydrometallurgical liquids (Moloney, 2008; Reddy and Reddy, 2003).

The structure of a polymer is generally described in terms of its structural units. The structural units are groups having two or more available bonding sites and are linked to one another through covalent bonds in a polymer chain (Style, 1962).

2.2.1. Polymer properties

The structural properties of the polymer play an essential role. The most basic property of a polymer is the identity of its constituent monomers, as these monomers describe its behaviour. The microstructure of the polymer is also an important property because it describes the arrangement of these monomers within the polymer chain.

The bulk physical properties of the polymer describe how the polymer behaves as a continuous macroscopic material. For example, chemical properties at the nano-scale describe how the chains interact through various physical forces whereas at the macro-scale describe how the bulk polymer interacts with other chemicals and solvents (Baeurle, 2009).

The attractive forces between polymer chains play a large part in determining a polymer's chemical properties. Polymer chains are so long and it might contain different side groups that can lend the polymer to ionic bonding or hydrogen bonding between its own chains. For example, polymers containing amide or carbonyl groups can form hydrogen bonds between adjacent chains; the partially positively charged hydrogen atoms in N-H groups of one chain can be attracted to the partially negatively charged oxygen atoms in C=O groups on another chain, these strong interaction forces result in higher tensile strength and higher crystalline melting point. Generally the intermolecular forces in polymers are governed by dipoles in the monomer units (Baeurle, 2009).

2.2.2. Chelating polymers (polymer-metal complex)

A coordination polymer (chelating polymer) is defined as a polymer that contains a metal which coordinates to Lewis base–like ligands, and the coordinate complexes are part of the overall polymer. There is a vast array of structure that has been formed through ligand attachment to metals. There are three main classes of metal-containing coordination polymer synthesis (Abd-El-Aziz, 2005).

i) Complexation with ligands that produce a polymer backbone containing the ligand and metal in the backbone.

In this case, ligands simultaneously attach themselves to two or more metals. There is a vast array of structure that has been formed through ligand attachment to metals. If the complexing groups are somewhat removed from one another, then there is opportunity for larger structures to be formed including macromolecular structures. These ligands can be chelating with several complexing sites acting as bis-chelating agents during the formation of the structure as shown in Figure 2.1 (Abd-El-Aziz, 2005).

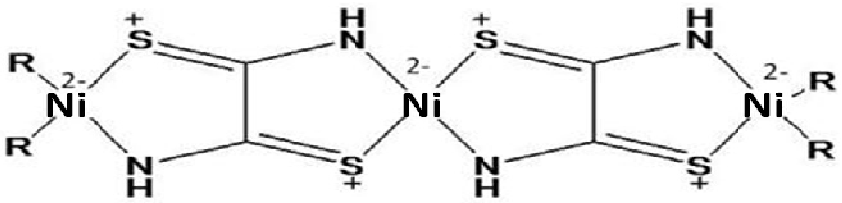


Figure 2.1. Structure of a polymer containing ligands and metal in the backbone.

ii) Chelating to an already formed polymer that contains complexing ligand moieties.

Polymers which have chelating ligands, either in the backbone or pendent to the backbone, can capture metal ions leading to coordination polymers. There are three subclasses of chelating polymers shown below:

A- **A metal ion has been chelated to all ligand sites along the backbone**

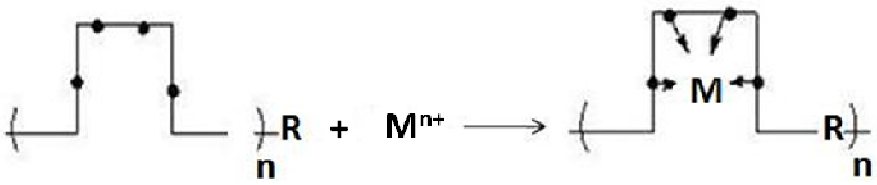


Figure 2.2. Metal chelation along backbone ligands

B- **A cyclic chelating agent in the main chain chelates a metal**

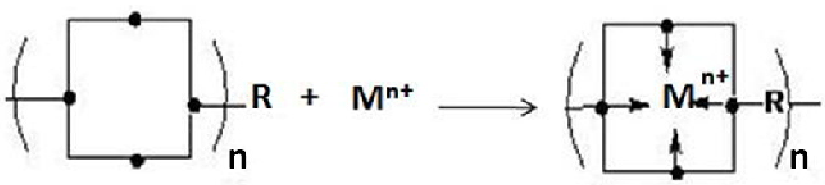


Figure 2.3. Cyclic ligands

C- **A pendent ligand along a polymer chain can capture a metal ion**

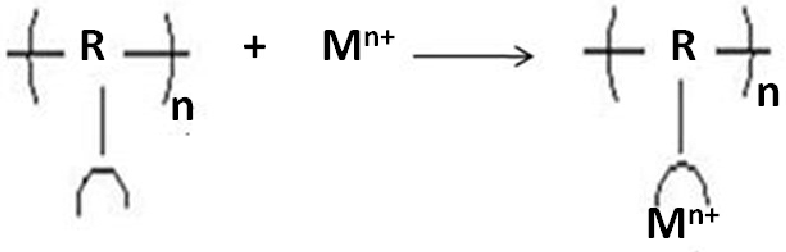


Figure 2.4. Pendent ligands

The ligand could have a variety of types of binding sites. It could have mono-, di-, tri-, tetra-, or other polydenate sites. Furthermore, type A and C subclasses could actually form so as to cross-link different chains together giving network polymers of the types in reactions shown in Figures 2.5 or 2.6 below.

If two pendent chelating ligands are required, cross-linking can give structure in Figure 2.5 whereas structure which is given in Figure 2.6 is formed if the chelating sites are along the main chains of two polymer molecules.

Figure 2.5. Network polymer (pendent ligands)

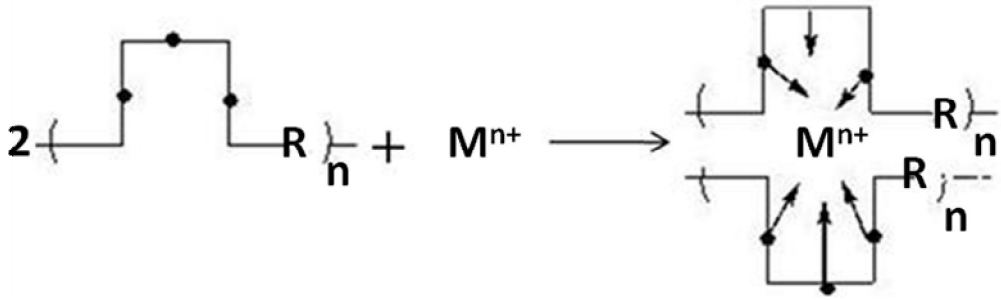


Figure 2.6. Network polymer (attached ligands)

iii) Polymerization of ligand groupings that already complex the metal (Abd-El-Aziz, 2005).

Here the polymer is composed of a group of ligands that have already complexed with the metals. In this case the complexation is done before the polymerization.

2.2.2.1. Chelating polymers as remediation agents

Chelating polymers have a good potential for removal of heavy metal ions from wastewaters and they are widely and effectively used for recovery of heavy metal ions from waste streams. The importance of the synthetic polymers has increased because of their high efficiency due to their physical and chemical properties represented in their high selectivity, thermal stability, sensitivity to the high concentration of ions, easy and cheap route of synthesis, chemical stability, high capacity for the metals, fast kinetics and rapid equilibration with metal-containing solutions and high mechanical strength and toughness of the exchanger particles (Pang and Rosenberg, 1997; Ahmed *et al.*, 2008; Kiefer, 2001; Rivas *et al.*, 2006; Rivas *et al.*, 2004; Shin *et al.*, 2004; Zander, 2009).

A polymer metal complex is composed of synthetic polymer and metal ions. The metal ions are bound to the polymer ligand by coordinate bond. The polymer ligands contain anchoring sites like nitrogen, oxygen, or sulphur obtained either by polymerization of monomer or by chemical reaction between the polymer and low molecular weight compound having coordinating ability. These results in an organic polymer with inorganic functions attached to the polymer

backbone which leads to exhibit characteristic catalytic behaviour (Kaliyappan, 2000; Hughes *et al*., 2008).

The key mechanism of the remediation of the wastewater using coordination polymers depends on the ligands or chelating groups with functional groups containing donor atoms (O, N, S, P) capable of coordinating to several metal ions (Caihua *et al.*, 2001; Samal *et al.*, 2000; Shin *et al.*, 2004). Figure 2.7 demonstrate the complexation mechanism.

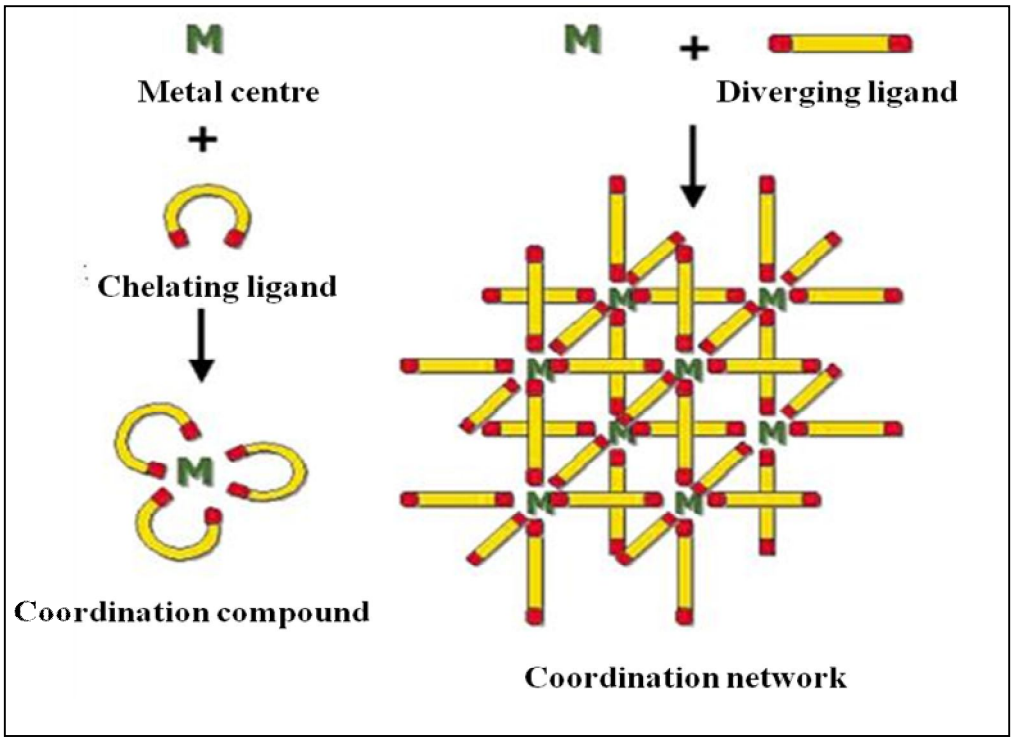


Figure 2.7. Polymer-metal interaction

There are some critical factors that significantly influence the polymer-metal complexation as a remediation process; including metal ligand affinity, metal ligand selectivity, effect of pH, and the regeneration of the polymeric materials for reuse.

❖ ***Metal ligand affinity***

The interaction of the metal and ligand is influenced by many factors including the functionality of the chelating group, the density of chelating groups in the polymer, oxidation state and electronic configuration of the metal and stereochemistry. The chelating functionality usually consists of some type of mono-, bi-, or polydentate moiety with donor groups contain atoms like nitrogen and charged or neutral oxygen that can act as a Lewis base and donate electron density to the metal.

When the donor groups are closed together on the polymer chain, this leads to steric hindrance between chains as several monodentate ligands can act as polydentate ligands hence the metal ion can induce local folding or cross linking of the polymer chains. Thus the spacing between the functional groups on the polymer can play an important role in how the ligands chelate. The nature of the intervening groups is also important. For example small, flexible spacing groups aid in the folding of the polymer chains, while rigid or bulky groups prohibit such activity. As well as the bulkiness of the functional group it also determines the steric constraints on metal ligation (Micio *et al.*, 2007).

The pKa of the polymeric backbone and ligands also has a significant effect on the metal-ligand interaction. Many of the polymers bearing nitrogen functionalities experience very weak binding to metal cations at low pH due to protonation of the amine; hence loss of electron donation ability. On the other hand, increasing the pH above the pKa for carboxylic acid functional groups leads to deprotonation and increased electron donating ability. In addition, charge repulsion between similarly charged groups on the polymer can cause electrostatic repulsion which can impact the ligation efficacy as well. (Li *et al.*, 2008; Rivas, 2007; Zander, 2009).

There are several factors affecting the coordination geometry and number such as size, electronic configuration, and oxidation state of the metal. Metals with large ligand field stabilization energies such as d6 low spin prefer octahedral arrangements whereas metals such as Zn^{2+} with d10 configurations tend to have

tetrahedral geometry. Furthermore, the electro negativity, and hence polarizability of the metal affects the strength of the metal ligation (Atkins *et al.*, 2006).

❖ ***Metal ligand selectivity***

The ability of the polymeric ligand to discriminate binding of metal ions (selectivity) plays an important role in successful remediation because most of wastewaters contain a complex mixture of metallic ions. Thus, separation of target ions allows for proper waste disposal or recycling of these materials. Furthermore, most of the waste streams contain competing ligands such as ethylenediaminetetraacetic acid (EDTA) which can compete with the chelating group in the polymer to bind target metals, and acids (H^+) which result in protonation hence inactivation of the donating ability of the polymer (Fu *et al.*, 2006; Li *et al.*, 2008).

There are several parameters that can be controlled for selective metal ion removal. In case of competing ligand, the pH of the solution can be altered to reduce the affinity between the metal and the competing ligand. For competing metal ions, ligand substitution kinetics can be taken into account in the design of the chelate group, as well as the experimental conditions such as reaction time and temperature. Furthermore, depending on the relative size of the target ion, encapsulating ligand functional groups can be utilized to create a size specific cage to trap the target ion (Micio *et al.*, 2007. & Fu *et al.*, 2006).

❖ ***The pH effect***

One of the main factors and most influential is the pH of the polymer, and hence protonation state for acidic and basic polymers, which play an important role in controlling the chelation properties. Figure 2.8 displays results for retention of various metal ions using poly(2-acrylamido glycolic acid) at three different pHs. In all cases, metal ion retention increased with pH, although the extent varied with the particular metal. At low pH, the polymer is in a fully protonated form; thus the nitrogen atoms are positively charged and cannot donate electron density to the metal cations. In addition, the carboxylic acids are also

protonated and are less effective donors (Li *et al.*, 2008; Shin *et al.*, 2004; Zander, 2009).

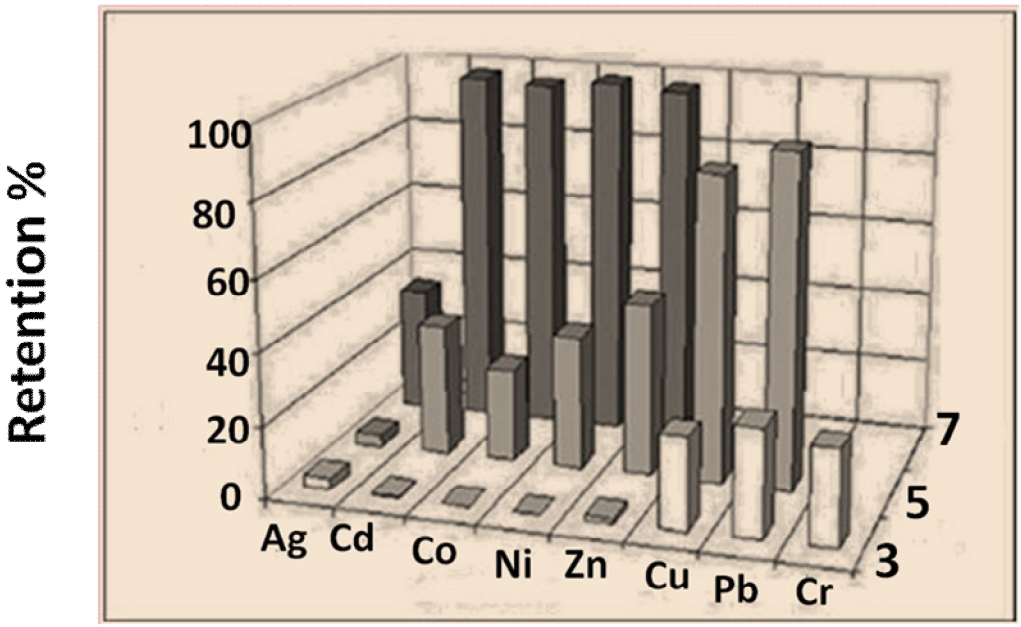


Figure 2.8. Metal ion retention of poly (2-acrylamido glycolic acid) at pH 3, 5, and 7 (Li et al., 2008).

❖ ***Regeneration***

The possibility to regenerate the synthesized polymer for reuse is one of the most important factors to be considered to achieve much more feasibility and cost effectiveness. On the other hand, the regeneration in the ion recycling process limits waste disposal costs and reduces the environmental impacts. Regeneration also recovers the metals so they can be disposed of properly or purified for reuse (Zander, 2009).

There are three major methods to regenerate polymer chelating groups: chemical regeneration, electrochemical regeneration, and thermal regeneration. Among the three methods; chemical is the simplest and most cost-effective one (Geckeler, 2001).

1. Chemical regeneration

Chemical regeneration involves three main methods:

i) Protolysis

This method can be effectively applied in case of acidic and basic polymers by changing the pH of the solution in order to cleave the polymer-metal bonds as a result of the protonation, and then pass the metals into the solution.

ii) Transcomplexation

This method involves addition of another ligand with stronger affinity for the target metal. Simply, it is a competitive binding process using an agent with a higher stability constant for the target metal or metals such as ethylenedieminetetraacetic acid (EDTA) in case of some transition metals.

iii) Redox reactions

The third chemical regeneration method is the redox reaction where the metal ions can be reduced, for example the reduction of Cr^{6+} with sodium sulfide to form chromium hydroxide ($Cr(OH)_3$) which precipitates out of the aqueous solution (Geckeler, 2001).

2. Electrochemical regeneration

The electrolysis of the retentate results in a deposition of the metal on an electrode, while the polymer reagent remains in the solution. No further separation of the polymer from metal ions is necessary as the metals are recovered in a very pure form. Although electrolysis is a very effective regeneration method, it consumes a lot of energy and as such is more costly than chemical regeneration methods.

3. Thermal regeneration

This method can be applied when the polymer–metal bond can be broke by heating. Then thermal regeneration becomes a good alternative, but this method seems to be restricted to few cases (Geckeler, 2001).

Generally, chelating polymers have two main key properties that make them significantly distinguished adsorbents. Firstly, on mass bases they have large surface area. Secondly, on functional basis they have the ability to be modified with different functional groups to increase their affinity towards targeted elements (Savage and Diall, 2005).

However, the use of polymeric adsorbents for the removal and recovery of toxic elements from industrial and mining wastes has been gaining popularity because of their efficiency and environmental friendliness relative to other methods (Hughes *et al.*, 2006; Rosenberg and Fischer, 2006). The polymeric materials for this purpose comprise a polymer chain that has a terminal functional groups or ligands that capable of coordinating to several metal ions. The strength and unique of this method is not only the ability to modify the polymer chain by introducing different functional groups but furthermore, a combination of two or more materials having different physical and chemical properties is also possible to produce a finished structure with desired properties (Rosenberg *et al*., 2013).

In sum, among the separation and remediation techniques, polymeric adsorbents are some of the most efficient and widely applied in separation processes (Kwon et al. 2000; Shentu et al. 2007; Wang et al. 2001; Hughes and Rosenberg, 2007). They can be of varying configurations, but mainly consist of a polymer backbone and a ligand pendent on the backbone. Metal ions are usually bound to the polymer ligand by a coordinate bond (Kaliyappan 2000). The advantage of this chemistry is that, a selective removal can be achieved by choosing a suitable functionality for a specific metal.

Moreover, Polymeric adsorbents can be used for a multi-removal as well as a selective removal by choosing the suitable functionality. Many studies reported the successful use of polymeric adsorbents to remove toxic metal ions from aqueous solutions. Below is a review of some reported literature for this purpose, some for multi-removal and others for selective (single) removal. On the selective removal we focus on specific elements of interest for this research (mercury, uranium, arsenic, and selenium).

Multi-removal

Ali et al. (2003) studied the chelating properties of poly(vinylpyrrolidone/acrylic acid) copolymer in removal of Fe, Cu, and Mn based on batch equilibration technique. The result of this work demonstrated high removal capacity followed the following order: Fe > Cu > Mn. The prepared adsorbent also exhibited high thermal stability up to 400 ^{o}C as well as a good potential for reuse after regeneration by 2 M HCl. The removal process was found to be fully dependent on the carboxylic groups in the polymer surface which are responsible for the interaction of the metal ions and the polymer and the adsorption behaviour was pH dependent.

In another work by Ali (2012), a synthetic polymeric material (polychelatogen composed of 2-acrylamido-2-methyl propane sulfonic acid (AMPS) and carboxymethyl cellulose (CMC), was employed to recover some toxic metal ions from aqueous solutions. The prepared polymer showed a great capability to recover some metal ions such as: Mn, Co, Cu, and Fe. The obtained results revealed that the chelating ability of the synthesized polymer is mainly dependent on their internal composition as well as the physical properties of the metal ion solution such as pH and metal ion concentration. The obtained data approved that the adsorption behavior of the prepared material increases with increasing the pH of the solution and the metal concentration. Furthermore, the synthesized polymer exhibited good reusability for five times as an advantage of its chemical stability.

Kesenci et al. (2002) studied the uptake of mercury, lead and cadmium using poly(ethyleneglycol dimethacrylate-co-acrylamide) (poly(EGDMA-co-AAm)) copolymer beads by batch equilibration technique. Their results suggested that the adsorption of metals occurs mainly at the polymer surface hence a fast uptake was observed (the largest amount of the metal ions was adsorbed within the first 10 min after which, the adsorption rate became very slow until gradual saturation was reached after 30 min), showing removal order of: Pb > Cd > Hg. The developed copolymer was found to be highly selective towards

Pb and the adsorption capacity for all three metals was increased with pH until it reached the plateau value around pH value of 6. Their findings also include the high reusability of the polymer for three cycles with high efficiency.

Masotti et al. (2010) investigated the performance of PEI for metal ions removal and obtained adsorption percentages of: Cr 99%, Ni 86%, Mn 77%, Pb 66%, and Zn 77%.

Selective removal: U

A new active polymeric material for the treatment of uranium contaminated groundwater from mine tailings was developed by Bryant and his co-workers (2003). The developed material works based on a ligand system that selectively removes uranium from solutions. The active medium in this material is a polyacryloamidoxime polymer derived from polyacrylonitrile. Their results revealed that the investigated material forms strong complex with uranium and effectively removes it at pH range of 5 – 8. The removal capacity was found to be dependent on the surface area that coated with the polymer where a removal capacity of 4mg g^{-1} was achieved when the dissolved uranium concentration was greater than 300 mg L^{-1}.

Leroy and his co-authors (2000), also, reported the complexation of uranium using polyacrylamide, polyacrylamidoglycolic acid, and polyacrylamidomethylpropanesulfonic acid with efficiencies of 89%, 92%, and 88%, respectively.

In another work by St John et al. (2010), the extraction of uranium from acidic sulphate solution was studied using polyvinylchloride (PVC) as a base polymer containing Alamine 336, Cyanex 272, Aliquat 336, di-(2-ethylhexyl) phosphoricacid (D2EHPA), and tri-n-butyl phosphate (TBP) as extractants, where the di-(2-ethylhexyl) phosphoricacid (D2EHPA) is found to be the most effective in the quantitative extraction and back extraction of uranium.

Selective removal: Hg

A study by Sreedhar and Anirudhan (1999) showed that poly-acrylamide grafted onto sawdust had a superior removal capacity for mercury; the removal was dependent on the pH (less removal efficiency was observed at pH below 5.5). Moreover, the removal procedure was time consuming where 5 h was needed to reach the optimum removal.

Another study by Liu and Guo (2006), reported the successful use of polyacrylamide grafted attapulgite (APM-ATP) for removal of mercury in which a high adsorption capacity was achieved.

Selective removal: As & Se

Suzuki et al. (2000) investigated the removal of oxo-anions As and Se using the Zr(IV)-chelated polymer. According to their findings, the adsorption of oxo-anions on the Zr(IV)-chelated polymer complex has been interpreted by a ligand substitution reaction. The adsorption characteristics of As and Se onto polymer surface have been examined with respect to the removal percentage, pH effect, equilibrium adsorption, and the effect of co-existing ions. Where they found that the presence of common anions including SO3 2-, Cl-, NO3- and acetate ions did not interfere with the adsorption of As and Se. the optimal pH for mixed complex formation of As and Se lies at around pH 3.5 - 4.5. The result also revealed that the synthesized polymer is reusable hence a remarkable stability was observed.

Eisazadeh H. (2008) reported the performance of polypyrrole and its composites for removal of arsenic from water. The conductive polypyrrole composites were prepared using different surfactants such as sodium dodecylbenzenesulfonate, ydroxypropylcellulose, poly(vinyl alcohol) and poly(ethylene glycol). The obtained results demonstrated that the great effect of the surface active agents on the removal process.

A very recent study by Awual and his co-authors (2012) reported the development of bifunctional polymeric adsorbents contained both phosphonate

and sulfonate groups by graft polymerization of chloromethylstyrene onto polyethylene coated polypropylene by electron irradiation graft polymerization technique followed by further modification (phosphorylation and sulfonation) to introduce phosphonate and sulfonate groups. The modified polymer was used as an adsorbent for arsenic removal where the removal was carried out using column method. The removal process showed a slight change with pH change between 3 - 7; with a high breakthrough capacity observed at highly acidic condition below pH of 2. Furthermore, the modified adsorbent was found to be very selective to As in presence of competing ions as well as its reusability for many cycles without deterioration to be observed.

Bleiman and Mishael (2010) reported the use of designed Polymer–clay composites to adsorb selenium from water, where the adsorption of Se onto chitosan–clay composites was found to be very high and increased with polymer loading on the clay. The reason behind the increase of the adsorption with the increase of the polymer content is that at such high loadings the composites are positively charged and that a bi-layer and partial clay exfoliation structures are formed. This structure can account for high Se adsorption due to internal anion-exchange sites. They achieved very high removal below the WHO limit (0.01 mg L^{-1}). Moreover, the designed polymer showed high selectivity for selenium even in the presence of sulfur as well as pH independency.

Another study by Khajeh and co-workers (2007) introduced polymeric adsorbents for selective removal and preconcentration of selenium from aqueous solutions. Where they used o-phenylenediamine as complexing reagent, 2-vinylpyridine as monomer, ethyleneglycom dimethacrylate as cross-linker, and 2,2-azobisisobutyronitrile as initiator. In their results, first of all, the developed polymer was found to be remarkably stable against elevated temperature, mechanical stress, and high pressure. The results also showed high resistant against treatment with acid and base, as well as the possibility of storing it for several years without change in its performance. Furthermore, the polymer showed high efficiency and selectivity and most importantly very good reusability.

In brief, the reviewed literature highlights the main advantages of using polymeric materials as adsorbents for removal of toxic heavy metal ions in the following:

- They have simple and cheap synthesis route.
- They have long usable lifetimes.
- They are re-usable
- They are feasible and cost-effective.
- They can be used at high temperatures (chemical and thermal stability)
- They have good mass-transfer kinetics and rapid equilibrium with metal-containing solutions.
- They have high selectivity and high capacity.

Although the reviewed literature demonstrated the high efficiency of polymeric adsorbents for the removal of heavy metals, still there are some gaps to be filled in order to introduce this type of materials as an ideal solution for such application. For instance, most of the applied polymers in the above mentioned studies were used in a liquid form (water soluble polymers). This makes them unfeasible, time consuming and very costly as they require additional treatment such as addition of doping agents, ultra filtration, membrane support, etc. Another gap is the lack of selectivity for some adsorbents which has been experienced in means of high competition between some elements.

This study, therefore, seeks to fulfil those gaps and to enhance the performance of polymeric adsorbents for the removal of heavy metals in order to introduce them as an efficient, feasible and cost-effective method.

Chapter 3

RESEARCH OBJECTIVES AND APPROACH

This chapter presents the

general aim of the research, specific objectives and a general

background of the research approach.

3.1. Aim of the research

The general aim of the research was the development, modification, characterization, and application of polymeric materials that would be feasibly used as ameliorants and remediation agents for aqueous systems polluted by heavy metals, notably mining and industrial wastewaters.

This general aim was achieved by addressing the following specific objectives:

- Development and functionalization of cross-linked polyethylenimine to target uranium, mercury, selenium and arsenic in solution.
- Investigating the effectivemess of the developed polymers by using batch bench top experiments at varying pH, ion concentration and temperature.
- Modelling the adsorption process (isothermic, kinetic and thermodynamic models) based on the second objective.
- Investigating the design parameters for fixed-bed columns packed with the polymers to assess their potential for use in filter systems and faucets.

These objectives were realised by adopting the following research approach.

3.2. Research process

In this research branched polyethylenimine (Figure 3.1) was used as one of the most common co-ordination polymers. It is an aliphatic polyamine chelating polymer (Zhu *et al.*, 2006) available in a broad range of molecular weights. It is available in two different structures: linear form and branched form.

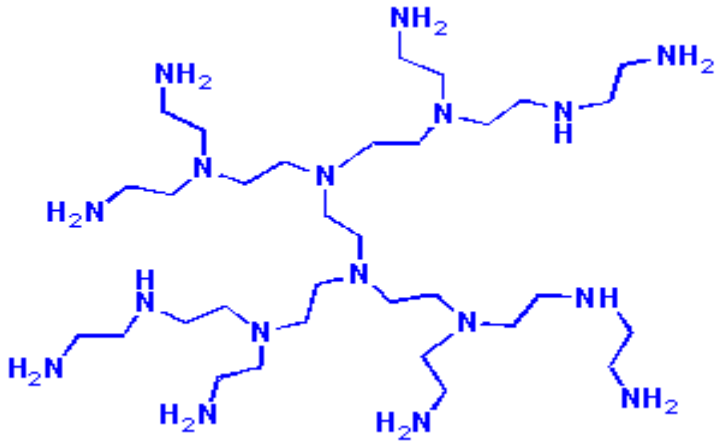


Figure 3.1. Branched polyethylenimine

Polyethylenimine (PEI) is well known for its metal chelating potential (Leroy et al. 2003) owing to the presence of amino groups. It has been widely used for the retention of metal ions, but largely as a water soluble polymer (Gohdes et al. 2001; Taylor et al. 2003; Masotti, Giuliano, and Ortagi 2010) which requires additional techniques for effective removal such as membrane support or ultrafiltration (Molinari et al. 2004; Molinari et al. 2005; Molinari et al. 2006; Cojocaru et al. 2009; Masotti et al. 2010; Leroy et al. 2003) making it difficult to work with (unfeasible and costly).

According to the above mentioned desired properties; PEI has been chosen as the most suitable polymer to be modified by introducing different functional groups for selective removal of U, Hg, As, and Se. The functionalization of polyethylenimine produces different derivatives of polyethylenimine that have same polymer chain and only differ in their functional groups and accordingly in their chelating properties including affinity and selectivity. This has been achieved by following the below procedures.

3.2.1. *Synthesis and functionalization of polyethylenimine*

❖ ***Cross-linking***

Cross-linking is a process of chemically joining two or more molecules by covalent bonds. Cross linking reagents contain two or more reactive ends that are capable of attaching to specific functional groups (primary amines, sulfhydryls, etc.). The most common cross linkers which contain at least two functional groups are dihaloalkanes such as 1,2-dichloroethane, 1,2-dichloropropane, 1,3-dichloropropane,and 1,4-dichlorobutane, and glycidyl halides such as epichlorohydrin, polyepoxides (Steuerle *et al.*, 2000).

In this research branched polyethylenimine was cross-linked to achieve the water-insoluble form, which gives the advantages of being used *in situ* and possibility of regeneration and re-use making it a more feasible and cost-effective adsorbent.

❖ ***Modification***

The surface characteristics of the polymers are of substantial importance because many critical interactions between the polymer and its environment occur at the surface. So the surface composition plays a significant role in the performance of the polymers (Kumagai *et al*., 2007).

Polymer surface modification improves the properties of the polymers hence the specific desired properties can rarely be achieved with one homogenous material since their surface properties are often less than optimal for desired application.

The modification of polymers by coating (laminating) one material onto another, or by functionalization (introducing different functional groups) gives new materials whose properties combine the desired properties of each component. The change in the surface characteristic could be achievable without changing the bulk properties of the polymer such as the mechanical strength. This gives the advantages of manipulating the macroscopic properties and surface

characteristic to maintain favoured surface properties of the polymer to suit the given application (Kumagai *et al.*, 2007; Moloney, 2008; Rivas *et al.*, 2009).

A growing demand for more selective chelating polymers is evident in many applications. This can be achieved by functionalization. Functionalized polymers are used for many different applications including organic syntheses, metal ion separation, pollution control, polymer drug grafts, wastewater treatment, and uptake of trace metal ions. The modification of the polymers by functionalization is a preferred process of enhancing metal selectivity since polymer surface grafting offers versatile means for providing existing polymers with new functionalities (Reddy and Reddy, 2003).

So, overall purposes of modification (functionalization) is to obtain the optimum removal efficiency of the synthesized polymers by combining the water-insoluble properties of cross-linked polyethylenimine together with the good chelating properties of polyethylenimine and the high selectivity of its functionalized derivatives.

3.2.2. Optimization and application of developed materials

The developed polymers were applied to abstract certain elements from standard synthetic solutions and mining wastewater samples. The applications involved both batch experiments and column method to assess the feasibility of these materials. According to this, **paper I** discussed the selective removal of uranium by the phosphonated derivative of cross-linked polyethylenimine, where the influence of pH, contact time, initial concentration, and competing ions has been all studied. Whereas, in **Paper II**, the performance of the sulphonated derivative of cross-linked polyethylenimine towards mercury has been assessed.

Paper III and **IV** from the other hand, were dedicated to investigate the selective removal of oxo-anions using phospnonated cross-linked polyethylenimine for As and sulphonated derivative for Se, respectively.

In **paper V**, a further study on selective removal of mercury was reported by developing other derivative rather than the sulphonated one, where Se was

found to be competitive. This study revealed a superior selective removal for mercury using a developed method to introduce thiol group (which produced a thiolated derivative) as the most selective chelating group for mercury.

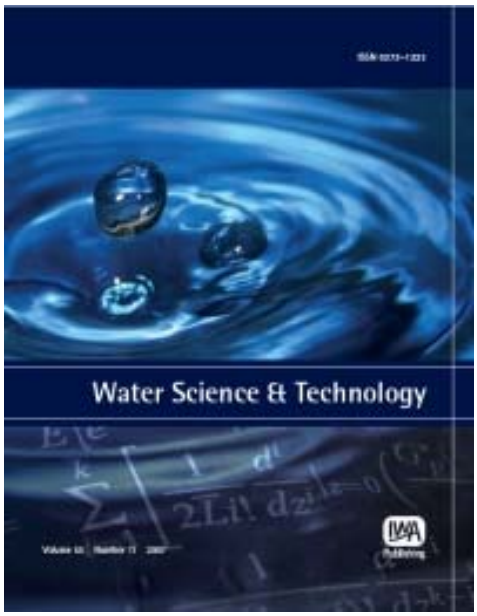
Paper VI reported the use of the developed materials in fixed-bed mode in order to assess the possibility of designing an industrial adsorption column using PCPEI as an example for the developed materials. The fixed-bed column study is to assess the performance of the materials for possible use for water purification in household filter systems.

Chapter 4

PAPER I

This paper addressed

The selective removal of uranium by the phosphonated cross-linked polyethylenimine. The influence of pH, contact time, initial concentration, and competing ions were demonstrated.



Phosphonated cross-linked polyethylenimine for selective removal of uranium ions from aqueous solutions

Dalia M. G. Saad, Ewa M. Cukrowska and Hlanganani Tutu

ABSTRACT

Among many remediation techniques for metal ion removal, polymeric adsorbents are efficient and widely applied. This has made them comparable with other remediation techniques in terms of technical and economic efficiency, feasibility as well as green technology. This study was dedicated to the development of an insoluble modified chelating polymer for use as an adsorbent for abstraction of uranium from wastewaters. Cross-linked polyethylenimine (CPEI) was phosphonated by phosphorous acid for selective removal of uranium ions. The binding affinity of the phosphonated cross-linked polyethylenimine (PCPEI) to uranium ions was assessed as well as its ability to be regenerated for reuse. It exhibited high removal percentage for uranium ions up to 99% with high selectivity even in the presence of competing ions (Mn, Ni, As). The Freundlich isotherm was found to be the best fit describing the adsorption process of uranyl ions onto the PCPEI. The pseudo-second-order equation was found to better explain the adsorption kinetics, implying chemisorption. The thermodynamic study of the adsorption revealed high activation energies which confirmed the chemisorption as the mechanism of adsorption.

Key words | adsorption, phosphonated cross-linked polyethylenimine, polymeric adsorbent, uranyl ions

Dalia M. G. Saad (corresponding author)
Ewa M. Cukrowska
Hlanganani Tutu
Molecular Science Institute,
School of Chemistry,
University of the Witwatersrand,
Johannesburg,
South Africa
E-mail: *dalianono@gmail.com*

INTRODUCTION

Chelating polymers are some of the most effective adsorbents for remediation of polluted water. They have a good potential for metal ions recovery as they have chelating ligands or anchoring sites with functional groups containing donor atoms such as nitrogen, phosphorus, oxygen or sulfur that can donate electrons to metal ions, thus forming a coordination polymer – metal complex (Kaliyappan & Kannan 2000).

Many studies have reported the successful application of different polymers for the removal of U such as sulfonated polyethylenimine, phosphonated polyethylenimine, polyvinylimidazole, polyacrylamide, polyacrylamidoglycolic, and polyacrylamidomethylpropanesulfonic acid (Martinot *et al.* 1997; Leroy *et al.* 1999, 2003). However, all these polymers are soluble in water, which requires additional treatment such as addition of doping agents (Leroy *et al.* 2000, 2003) or addition of polyanions (Leroy *et al.* 1999; Martinot *et al.* 1997) to precipitate the uranyl complexes, making it an unfeasible, time consuming and more costly process.

This study was aimed at using a cross-linked phosphonated polymer as an adsorbent for the removal of uranium from aqueous solutions. The influence of pH, contact time, initial concentration, and competing ions on adsorption behaviour has been investigated. These factors are important in assessing the potential for use of the polymer in filters for household taps in areas where communities in the vicinity of some mining areas inevitably have to consume polluted water. This is the intended application of the polymer.

The water-insoluble polymer has the advantage of being used *in situ* and the possibility of regeneration and re-use, making it a more feasible and cost-effective method. Functionalization enhances the selectivity and as such the surface composition plays a significant role in the performance of the polymers. The specific desired properties can rarely be achieved with homogenous materials as their surface properties are often less than optimal for desired application (Rivas *et al.* 2009).

The insoluble property of the polymer was achieved by cross-linking in the previous study by the authors (Saad *et al.* 2011) and the selectivity has been explored in this study by functionalizing the polymer with phosphorous acid.

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MATERIALS AND METHODS

Materials

All chemicals were obtained from Sigma Aldrich (South Africa) without further purification. For the functionalization, cross-linked polyethylenimine (CPEI) (Saad *et al.* 2011), H_3PO_3, formaldehyde 38% (CH_2O), and 6 mol L^{-1} (HCl) were used. $UO_2(NO_3)_2 \cdot 6H_2O$ was used to prepare the solutions. Competing metal ion solutions were prepared from their nitrate salts. As and Se solutions were prepared from $NaAsO_2$ and Na_2SeO_3, respectively. Adjustments of pH for the adsorption experiments were conducted using 1 mol L^{-1} solutions of HNO_3 and NaOH. Deionized water was used for the preparation of all solutions.

Synthesis of phosphonated cross-linked polyethylenimine

CPEI, 2.5 g, was placed in 80 mL of 6 mol L^{-1} HCl. Phosphorous acid, 19.31 g, was added and the mixture was heated under reflux at 90 °C. Formaldehyde, 38 mL, was added dropwise over a period of an hour, and the reaction was left over night. A pale powdery yellow solid was obtained, washed with abundant deionized water before drying in an air oven at 30 °C. The solid was then pulverized and sieved. The phosphonation reaction is shown in Figure 1.

Batch adsorption studies

The batch adsorption experiments were conducted using a 1,000 mg L^{-1} stock standard solution of $UO_2(NO_3)_2 \cdot 6H_2O$ from which the 40 mg L^{-1} working standard solutions were obtained by serial dilution. This concentration was arbitrarily chosen as it represents a 'worst-case' scenario of uranium pollution in mining-impacted waters in the Witwatersrand Basin goldfields (Tutu *et al.* 2009).

A 1,000 mg L^{-1} stock solution of multi-component standard metal nitrate salts and salts of oxo-anions Se and As was prepared from which the 40 mg L^{-1} multi-component working standard solutions were obtained by serial dilution.

Adsorption experiments were performed in 50 mL flasks at room temperature. One gram of synthetic phosphonated cross-linked polyethylenimine (PCPEI) (an optimal adsorbent amount according to preliminary optimization of the solid:liquid ratio) was weighed out into each flask; 40 mL of 40 mg L^{-1} solution of $UO_2(NO_3)_2 \cdot 6H_2O$ standard was then added to each flask and stirring done by means of a magnetic stirrer. Adsorption at pH 3 and pH 8 was assessed. At equilibrium, the solutions were filtered and the equilibrium concentrations determined using a Genesis inductively coupled plasma optical emission spectroscope (ICP-OES) (Spectro, Germany). The same procedure was followed using the multi-component solution to assess the effect of competing ions. The amount of ions adsorbed per unit mass of adsorbent was calculated on the basis of the mass balance equation:

$$\text{Capacity}(\text{mg metal g}^{-1}\text{ polymer}) = \frac{(C_i - C_f) \times V}{1{,}000 \times P}$$

where: C_i (mg L^{-1}) is the initial concentration of U in the solution; C_f (mg L^{-1}) is the concentration of U in the filtrate; V(mL) is the volume of initial solution; P(g) is the amount of polymer used.

Effect of contact time

Contact time adsorption experiments were conducted at room temperature in order to obtain the optimal time required for adsorption. Adsorption was studied at various time intervals (10–120 min) and fixed concentration (40 mg L^{-1}). The concentration of uranium was determined at the end of each time. The obtained equilibrium capacities (q_e) were then plotted against the equilibrium time for kinetic modelling.

Desorption studies

The regeneration of the synthesized polymers plays an essential role in achieving more feasibility and cost

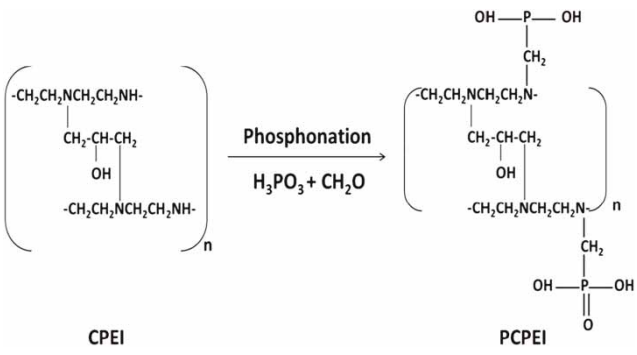

Figure 1 | Phosphonation reaction scheme.

effectiveness as it reduces waste disposal costs and environmental impact.

The regeneration of PCPEI was carried out by the treatment of previously loaded polymer with an excess of extracting reagent. HNO_3 at different concentrations, namely: 2, 3, 5, and 7 mol L^{-1}, was used as an extractant. During regeneration, the mixtures were stirred for 1 h, filtered and the polymer washed with de-ionized water and dried prior to re-use.

Application of the developed polymer to wastewater samples

The synthesized polymer was applied for the removal of uranium from wastewater samples collected in the vicinity of gold mining activities in the Central Rand goldfield, Johannesburg.

Four samples were used (one pit water and three surface water samples) collected from the Natalspruit, an acid mine drainage-impacted stream (26°13′07.15″ S and 28°07′52.74″ E). Sampling was done according to standard water sampling protocols (Hermond & Fechner-Levy 2000) and geochemical parameters (pH, redox potential and electrical conductivity) recorded in the field using field-meters. The samples were filtered in the laboratory prior to application in the adsorption experiments. The field measurements were carried out with a portable kit Multi Line F/Set 3 of the Wissenschaftlich- Technische Werkstatten, Weilheim (WTW, Germany) equipped with a pH electrode, an integrated temperature probe (Sen Tix 41), a standard conductivity cell (Tetra Con 375) and an oxidation-reduction potential probe (Sen Tix ORP). The pH electrode was calibrated according to IUPAC recommendations against two buffer solutions pH 4 and pH 7 and an uncertainty of ±0.1 units. Metal analysis was carried out using ICP-OES. Anion concentrations were determined by ion chromatography (IC) (761 Compact, Metrohm, Switzerland).

In each analytical technique, the limit of detection (LOD) was calculated as 3 × standard deviation of the blank and the method quantitation limit (MQL) was calculated as 10 × standard deviation of the blank.

Modelling of analytical results

The results from adsorption studies were modelled using kinetic, equilibrium (isotherms), and thermodynamic models.

Kinetic models

Table 1 shows the kinetic models that were used to fit the experimental data.

Isotherm models

Adsorption isotherms describe the nature of the adsorbent–adsorbate interaction as well as the specific relation between the concentration of adsorbate and its degree of accumulation onto the adsorbent surface (Gupta *et al*. 2003; Li *et al*. 2008). In order to understand the adsorption mechanism of uranium onto the PCPEI surface, two adsorption isotherm models, Langmuir and Freundlich, were used to fit the experimental data.

Langmuir model

The Langmuir model is valid for monolayer localized physical adsorption onto a homogeneous surface with a finite number of identical sites. In monolayer adsorption, there is no transmigration of adsorbed molecules at the maximum adsorption, meaning that the adsorbed molecules do not deposit on each other, but are only adsorbed on the free surface of the adsorbent (Hamdaoui & Naffrechoux 2007). The Langmuir model is given by the following equation:

$$q_e = \frac{q_m b C_e}{1 + b C_e}$$

where: q_e (mg g^{-1}) is the amount adsorbed per unit weight of adsorbent at equilibrium, C_e (mg L^{-1}) is the equilibrium concentration of the adsorbate, and q_m (mg g^{-1}) is the maximum adsorption capacity, and b (L mg^{-1}) is the constant related to the free energy of adsorption. The values of maximum capacity (q_m) and Langmuir constant (b) were calculated from the intercept and the slope of the plots.

Table 1 | Kinetic models

Model	Equations	Linearized equation
Pseudo-first-order model	$\text{Log}\ (q_e - q_t) = \log q_e - (k/2.303)$	Log $(q_e - q_t)$ vs t. (to obtain K)
Pseudo-second-order model	$1/q_t = (1/k_2 q_e^2) + (1/q_e)t$	t/q_t vs t (to obtain K_2)

Where: q_e (mg g^{-1}) is the adsorption capacity at equilibrium, q_t (mg g^{-1}) is the adsorption capacity at time t, and K and K_2 (1/min) are the rate constants for the pseudo-first-order and pseudo-second-order models, respectively.

Freundlich model

The Freundlich model is an empirical formula for heterogeneous adsorption given by the following equation:

$$q_e = K_F C_e^{1/n}$$

where: K_F ($mg^{1-(1/n)}$ $L^{1/n}$ g^{-1}) is a constant correlated to the relative adsorption capacity of the adsorbent and n is a constant indicative of the intensity of the adsorption.

As the Freundlich model is an exponential equation, it assumes that the adsorption capacity of the adsorbent increases with increasing concentration of the adsorbate. The values K_F and $1/n$ can be correlated to the adsorption capacity and intensity (Freundlich 1926).

Thermodynamic studies

The thermodynamic study was done by conducting the adsorption experiments at two different temperatures (15 and 27 °C). The concentrations obtained after adsorption were then used to calculate the activation energy (E_a) according to the Arrhenius equation:

$$E_a = \frac{R.T_1.T_2 \,.\ln K_1/K_2}{T_1.T_2}$$

where: E_a is the activation energy; R is the gas constant; T_1 and T_2 are the two different temperatures; K_1 and K_2 are constants for the two temperatures.

The constants K_1 and K_2 could be calculated as follows:

$$K = \frac{C_i - C_e/M}{C_e}$$

where: C_i is the initial concentration; C_e is the concentration at equilibrium for each temperature; M is the atomic number for each element.

The magnitude of the activation energy gives an idea about the type of adsorption. There are two main types of adsorption: chemisorption and physisorption. Physisorption is usually rapidly attained and easily reversible, because of the small amount of energy required. It is usually no more than 4.2 kJ mol^{-1} as the forces involved are weak. On the other hand, chemisorption involves forces much stronger than those for physisorption. Therefore, the activation energy for chemisorption is higher (Klekamp & Urnbac 1993; Özcan *et al.* 2006).

RESULTS AND DISCUSSION

Effect of contact time

Figure 2 shows the effect of contact time on the adsorption of U onto PCPEI.

The adsorption was fast within the first 30 min, slowing down between 30 and 60 min and with no further increase beyond 60 min. This could be attributed to the unavailability of reaction sites which decreases with time. Thus, despite an increase in adsorption after 45 min being low, the minimum required time for adsorption to be completed was 60 min.

Effect of pH

The results for the adsorption of uranium from synthetic solutions are presented in Table 2. The table shows the final uranium concentration obtained (C_f) after 60 min, adsorption capacity, percentage as well as the relative standard deviation (RSD).

The adsorption percentages showed high removal efficiency even at low pH. The mechanism of metal (in this case uranium) binding onto the polymer is based on the hard–soft Lewis acid–base theory, in which the phosphorus

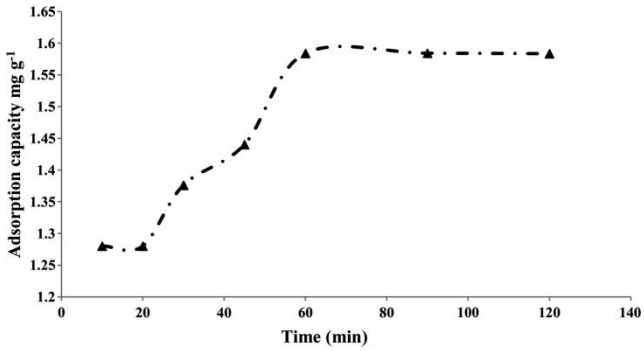

Figure 2 | Effect of contact time on the adsorption process.

Table 2 | Removal of uranium from synthetic solutions by PCPEI

	C_f (mg L^{-1})	RSD	Adsorption capacity (mg g^{-1})	Adsorption efficiency (%)
pH 3	0.770	6.227	1.569	98%
pH 8	0.600	0.333	1.576	99%

Initial concentration of the ions = 40 mg L^{-1}; C_f : final concentration after adsorption; RSD: relative standard deviation ($n = 3$); LOD: limit of detection in mg L^{-1} = 0.078; MQL: method quantitation limit in mg L^{-1} = 0.260.

atom on the chelating group ($-PO_3H_2$) acts as a Lewis base and donates electrons to uranium which is considered a Lewis acid.

Effect of initial concentration

The results for the dependence of adsorption on U concentrations are shown in Figure 3.

The adsorbed amount of U increased with increasing concentration. This could be attributed to the availability of the U to be complexed.

Effect of competing ions

To investigate the possibility of competition between uranium and other ions such as Mn, Pb, As, Zn, Fe, Cr, Hg, Se and Ni, adsorption experiments were performed using multi-component standard solutions with initial concentrations of 40 mg L^{-1}. The amount of uranium adsorbed in the presence of these ions was determined to investigate the selectivity of PCPEI toward uranium. Table 3 shows the removal percentages of elements in a multi-component solution.

Although, some ions such as Mn, Ni and As showed good removal percentages, the amount of uranium adsorbed was still high. In the article on CPEI by the authors (Saad *et al*. 2011), nitrogen was a donor atom and exhibited poor removal of U, especially in the presence of competing ions. U has a higher affinity for phosphate-containing groups than for nitrogen-containing groups. On the other hand, hydrogen and metals such as Fe, Zn, and Ni have a high affinity for the latter and would preferentially be bound. This renders them more competitive than U for nitrogen-containing groups. This demonstrates the role of functionalization on the adsorption process and implies that the difference in the selectivity is attributed to the functionality of the adsorbent. Another proof of the role of the functional group in the removal efficiency is the far lower removal of selenium compared with other elements. In addition to the fact that selenium is a soft acid that prefers soft bases to be complexed with, it is also a metalloid and exists in solution as an oxo-anion in which other mechanisms of removal are expected such as chemical replacement in which the affinity for the functional group to be replaced is an essential factor.

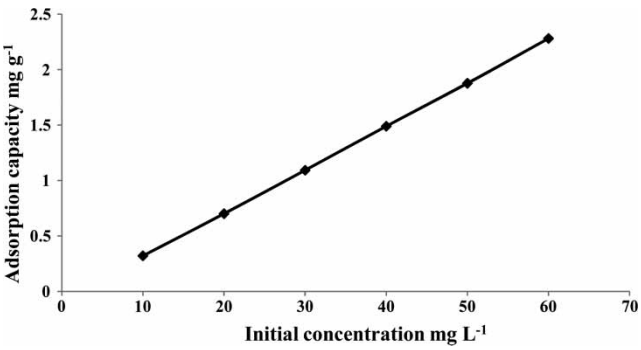

Figure 3 | Effect of initial concentration on the adsorption process.

Kinetic modelling of adsorption process

The plot of the linearized form of pseudo-second-order model (t/q_t vs t) is given in Figure 4. A good correlation ($R^2 = 0.998$) can be observed, implying that the adsorption occurs via a chemisorption process (Antures *et al*. 2003).

Adsorption isotherms

The calculated Langmuir constants (b and q_m) and Freundlich constants (n and K_f) as well as the coefficients of correlation (R^2) for both isotherms are given in Table 4.

The results suggest that the Freundlich model best fits the data as shown by the correlation coefficient >0.95, whereas that for the Langmuir correlation coefficient is <0.95. This result demonstrates adsorption on a heterogeneous surface. It also assumes that the adsorption capacity of the adsorbent increases with increasing concentration of the adsorbate, in this case U, which is in agreement with the results obtained for the effect of initial concentration on adsorption.

Thermodynamic studies

The calculated activation energy value (E_a) for the adsorption of U onto the PCPEI surface, as well as the calculated constants K_1 and K_2, are presented in Table 5.

Table 3 | Removal percentages of elements in a multi-component solution

Element	Cr	Mn	Fe	Hg	Zn	Pb	U	Se	Ni	As
Removal %	68	90	62	57	71	61	98	26	84	76

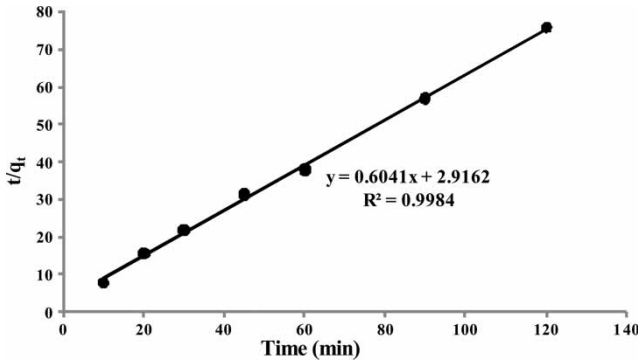

Figure 4 | Pseudo-second-order plot for the adsorption process.

Table 4 | Langmuir and Freundlich parameters for the adsorption of uranium onto PCPEI

	b	Langmuir R^2	q_m	K_f	Freundlich R^2	n
U	0.220	0.0.942	15.00	4.317	0.957	0.222

The elevated value of activation energy implies that the uranium is adsorbed onto the PCPEI via a chemisorption process. This is consistent with the results obtained for kinetic modelling as discussed previously.

Desorption studies

Optimal recovery and regeneration of PCPEI was achieved at a concentration of 7 mol L^{-1} of the regeneration acid solution. Subsequently, regeneration of the used polymer was carried out using 7 mol L^{-1} acid concentration. The desorption percentage was 81%. The adsorption percentages for the recovered polymer (regenerated PCPEI) on the same synthetic solutions are given in Table 6.

Adsorption percentages, though lower compared with those for the fresh PCPEI, still portrayed good recoveries. The adsorption at pH 3 dropped by 3% and at pH 8 dropped by 4%.

Serial desorption was conducted in order to assess the amount of intractable U that would remain bound to the polymer. For example, after a cycle of five desorptions (Figure 5), the adsorbed U on PCPEI was decreased by 20.1 mg L^{-1} (from 22.46 mg L^{-1} after the first desorption to 2.37 mg L^{-1} after the fifth desorption).

Table 5 | Activation energy for the adsorption of U by PCPEI

Element	K_1	K_2	E_a kJ mol^{-1}
U	0.004	0.003	56.90

Table 6 | Removal of uranium from synthetic solutions by regenerated PCPEI

	C_f (mg L^{-1})	RSD	Adsorption capacity (mg g^{-1})	Adsorption efficiency (%)
pH 3	2.200	1.797	1.512	95%
pH 8	1.970	3.335	1.521	95%

Initial concentration of the ions = 40 mg L^{-1}; C_f : final concentration after adsorption; RSD: relative standard deviation ($n = 3$); LOD: limit of detection in mg L^{-1} = 0.090; MQL: method quantitation limit in mg L^{-1} = 0.001.

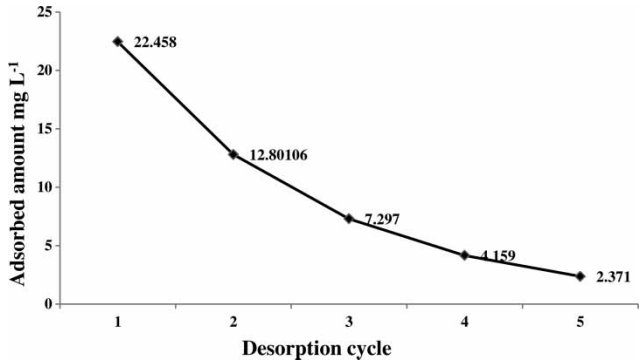

Figure 5 | Desorption cycle of uranium from PCPEI using 7 mol L^{-1} HNO_3.

The results obtained showed that the performance of PCPEI is comparable with that of other adsorbents. Leroy *et al.* (1999), for example, reported the complexation of uranium using polyacrylamide, polyacrylamidoglycolic acid, and polyacrylamidomethylpropanesulfonic acid with efficiencies of 89, 92, and 88%, respectively, which are quite similar to the results of this study. On other hand, some differences in terms of efficiency, selectivity, influencing of different conditions such as pH and initial concentration, as well as cost-effectiveness, were demonstrated.

A study by Sprynskyy *et al.* (2011) showed that talc had a superior removal capacity, but this was more dependent on the pH and initial concentration. While the removal efficiency was 80% at pH 4–7, it decreased to below 7% at lower pH values. There was also a decrease in removal efficiency with an increase in initial concentration. This limits the use of talc for U recovery from low pH solutions e.g. AMD-impacted waters in which pH can be lower than 3.

The superior adsorption of U at these low pH values hinges on its high affinity for the phosphates and as such outperforms the hydrogen ions. To corroborate this, the dissociation of H^+ from phosphoric acid can be used as a proxy. The dissociation of H^+ gives a log β value of 0.007 for pure phosphoric acid and when a uranyl ion is introduced, the value of log β is 1.12 (Sandino & Bruno 1992).

Table 7 | Removal of uranium from mining wastewater samples

Samples	Metals	C_i (mg L^{-1})	RSD ($n = 3$)	C_f (mg L^{-1})	RSD ($n = 3$)	Ads %
Pit water	Ni	10.70	7.968	2.030	1.860	81%
pH (3)	U	0.161	6.700	0.001	5.048	99%
SO_4^{2-} (1,669 mg L^{-1})	Mn	136.4	7.990	4.400	4.727	96%
SW 1, pH (7.2)	As	0.117	2.590	0.020	2.946	83%
SO_4^{2-} (19.80 mg L^{-1})	Ni	1.500	5.281	0.372	2.164	75%
SW 2	As	0.280	2.056	0.024	6.245	91%
pH (4)	Ni	1.790	1.722	0.859	1.387	57%
SO_4^{2-} (819.4 mg L^{-1})	Mn	22.00	8.823	3.360	2.395	85%
SW 3	Ni	4.670	3.531	0.88	2.061	81%
pH (5.6)	Zn	7.650	7.073	1.76	2.078	77%
SO_4^{2-} (653.6 mg L^{-1})	Mn	179.2	2.707	19.05	5.638	90%

SW – surface water, C_i – initial concentration before adsorption, C_f – final concentration after adsorption.
LOD (mg L^{-1}): As – 0.014; Ni – 0.007; Mn – 0.002; U – 0.035; SO_4^{2-} – 0.01 (by ion chromatography).
MQL (mg L^{-1}): As – 0.047; Ni – 0.023; Mn – 0.007; U – 0.117; SO_4^{2-} – 0.03 (by ion chromatography).

This implies that the uranyl ion easily displaces H^+. Thus, at low pH it is still possible to adsorb U. Also, it should be noted that H^+ binds to both amine and phosphate sites while U preferentially binds to phosphates.

Application of the developed polymer to wastewater samples

The results for the adsorption of uranium and other elements in the collected samples onto fresh PCPEI are given in Table 7.

U was only detected in the pit water sample with Mn and Ni. The adsorption trend was similar to that observed for the synthetic standard solutions. Percentage removal followed the order U > Mn > As > Ni.

CONCLUSIONS

In this study, PCPEI was successfully employed for the removal of uranium under optimal conditions (contact time of 60 min, pH of 8, and adsorbent amount of 1 g). The removal mechanism of uranium hinges on the functional groups present in the polymer, largely the phosphate group.

The Freundlich isotherm was found to be the best fit describing the experimental data, suggesting that adsorption occurred on a heterogeneous surface.

The pseudo-second-order model was found to explain the adsorption kinetics most effectively. This model and the results of the thermodynamic study showed that uranium adsorption occurred via chemisorption.

There was no significant difference in adsorption performance in the presence of competing ions, indicating that PCPEI is more selective for uranium.

The synthesized polymer exhibited commendable potential for re-use through regeneration by 7 mol L^{-1} HNO_3, which is a very significant factor influencing the cost of the removal process as well as the waste disposal.

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Chapter 5

PAPER II

This paper studied

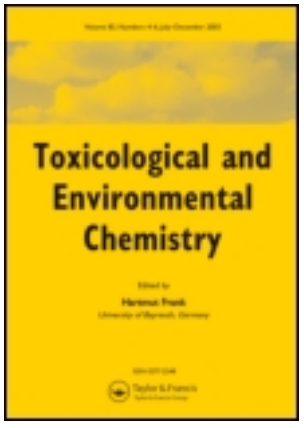
The adsorption performance of the

sulphonated cross-linkedpolyethylenimine towards mercury.

The study covers the thermodynamic, kinetics and isotherm

modelling as well as the effect of pH, time, concentration and competing

ions on the removal process.



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Sulfonated cross-linked polyethylenimine for selective removal of mercury from aqueous solutions

Dalia M.G. Saad [a], Ewa M. Cukrowska [a] & Hlanganani Tutu [a]

[a] School of Chemistry, University of the Witwatersrand, Johannesburg, South Africa

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Sulfonated cross-linked polyethylenimine for selective removal of mercury from aqueous solutions

Dalia M.G. Saad*, Ewa M. Cukrowska and Hlanganani Tutu

School of Chemistry, University of the Witwatersrand, Johannesburg, South Africa

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Polymeric materials are among the most promising, effective, and increasingly important adsorbents for the removal of toxic metals from wastewater. This study was dedicated to the development of an insoluble, modified chelating polymer for use as an adsorbent for abstraction of Hg from aqueous solutions. Cross-linked polyethylenimine (CPEI) was sulfonated by 3-chloropropanesulfonyl chloride for selective removal of Hg. The binding affinity of the sulfonated CPEI (SCPEI) to Hg was assessed as well as its ability to be regenerated for reuse. It exhibited high removal percentage for Hg up to 87% in synthetic solutions, with high selectivity even in the presence of competing ions: ''Mn, Ni, Fe, Pb, Zn, and Cr.'' The removal mechanism followed was observed to be adsorption and precipitation at pH 3 and 8, respectively. High adsorption capacities were also observed for wastewater to which the polymer was applied. The Freundlich isotherm was found to be the best fit describing the adsorption process of Hg onto the SCPEI. The pseudo second-order equation was found to better explain the adsorption kinetics, implying chemisorption. The thermodynamic study of the adsorption revealed high activation energies which confirmed the chemisorption as the mechanism of adsorption. The polymer exhibited up to 72% removal efficiency after regeneration, thus showing potential for re-use.

Keywords: polymeric adsorbents; sulfonated polyethylenimine; functionalization; adsorption; mercury

Introduction

Extensive industrialization has caused many water bodies to receive loads of toxic metals which affect the quality of drinking water (Akpor and Muchie 2010). Mercury (Hg) is known as one of the most toxic elements for human health, mostly because of its high volatility and bioaccumulation properties. It is released into the aqueous environment through different sources, including microelectronics, effluents from plastics, metal smelters, textiles, as well as fertilizers and pesticides. Hg exposure could affect the central nervous system, kidney functions and the mental system as it can easily pass through the blood-brain barrier. As such, removal of Hg from environmental systems has become a research priority (Manohar, Krishnan, and Anirudhan 2002; Rio and Delebarre 2003; Wahi, Ngaini, and Jok 2009; Cai and Jia 2010).

Many studies have reported the use of different methods for the removal of Hg from aqueous solutions and these include precipitation, ion exchange, electrodeposition,

*Corresponding author. Email: dalianono@gmail.com

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adsorption, iron coagulation, and activated carbon. Among these methods, activated carbon is very efficient, but most studies demonstrated the high dependency of the removal of Hg on the pH, initial concentration, and time (Cai and Jia 2010).

The aim of this work was to study the removal of Hg in aqueous solutions using sulfonated cross-linked polyethylenimine (SCPEI). The influence of pH, contact time, initial concentration and competing ions on adsorption behavior have been investigated. The ultimate objective was to assess the potential of this polymer for use in filters for household taps. These are intended for households (e.g., small plot holdings) that use contaminated groundwater as their source of water. Such households draw water (through boreholes) from aquifers that have been impacted by mine water, for instance. The filtration system will thus enable removal of Hg from the water before use, which is the ultimate intended application of this polymer.

The insoluble property of the polymer was achieved by cross-linking in the previous study by the authors (Saad, Cukrowska, and Tutu 2011) and the selectivity has been explored in this study by functionalizing the polymer with 3-chloropropanesulfonyl chloride. In most other work, the solubilised forms of polyethyleneimine were used with the challenge by the recovery of the polymer at the end. Techniques such as ultrifiltration and membrane support have been reported as ways of polymer recovery from solution (Molinari, Argurio, and Poerio 2006; Cojocaru, Zakrezewska, and Jaworska 2009; Masotti, Giuliano, and Ortagi 2010). These make the process expensive and time-consuming. Thus, cross-linking was observed to be a better option in dealing with challenges of recovering the solubilised polymer. This way, the removal process becomes cost-effective. Notwithstanding, such an application requires specific desired properties which are rarely achieved with homogenous materials since their surface properties which are often less than optimal for the desired application (Rivas et al. 2009).

Experimental protocol

Materials

All chemicals were obtained from Sigma Aldrich (South Africa) and were used without further purification. For the functionalization, cross-linked polyethylenimine (CPEI; Saad, Cukrowska, and Tutu 2011), 3-chloropropanesulfonyl chloride, and tetrahydrofuran were used. $Hg(NO_3)_2$ was used to prepare the Hg^{2+} solutions. Competing metal ion solutions were prepared from their nitrate salts, namely: $Zn(NO_3)_2$, $Pb(NO_3)_2$, $Cr(NO_3)_3$, $Mn(NO_3)_2$, $Fe(NO_3)_3 \cdot H_2O$, and $Ni(NO_3)_2$. Adjustments of pH for the adsorption experiments were conducted using $1\,mol\,L^{-1}$ solutions of HNO_3 and NaOH. Deionized water was used for the preparation of all solutions.

Synthesis of SCPEI

Cross-linked polyethylenimine, 2.5 g, was distributed in tetrahydrofuran (C_4H_8O). A volume of 2.4 mL of 3-chloropropanesulfonyl chloride ($C_3H_6Cl_2O_2S$) was added and the mixture was heated under reflux at 70°C over night. Optimal sulfonation was achieved by conducting sulfonation at different temperatures and times followed by infra red spectroscopic measurements on the different products. Thus, a temperature of 70°C and allowing the reaction to proceed over night were found to be optimal conditions. A pale rubbery brownish solid was obtained, washed with water (4 L) three times and dried in an air oven at 30°C to yield 4.8 g. The sulfonation reaction scheme is shown in Figure 1.

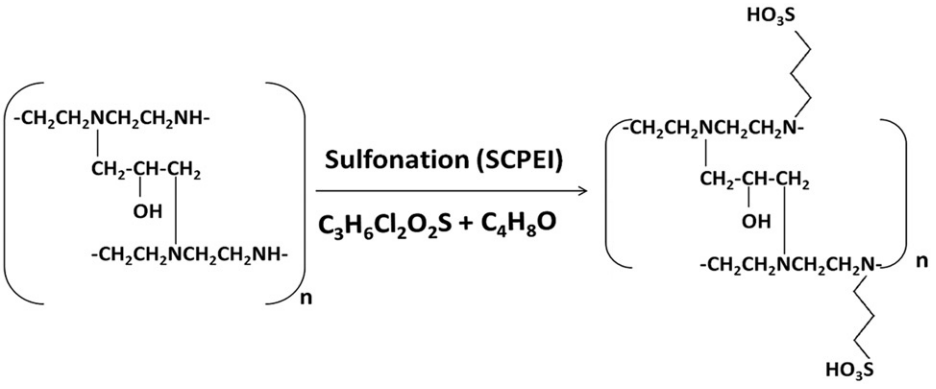

Figure 1. Sulfonation reaction scheme.

Batch adsorption studies

The batch adsorption experiments were conducted using a 1000 mg L^{-1} stock standard solution of $Hg(NO_3)_2$ from which the 40 mg L^{-1} working standard solutions were obtained by serial dilution. This concentration was arbitrarily chosen as it represents a "worst-case" scenario of pollution by most toxic elements (e.g., Hg, U, As, and V) in mining-impacted waters in the Witwatersrand Basin goldfields (Tutu et al. 2009).

Adsorption experiments were performed in 50 mL flasks at room temperature. 1 g of synthetic SCPEI (an optimal adsorbent amount according to preliminary optimization of the solid : liquid ratio) was weighed out into each flask; 40 mL of 40 mg L^{-1} solution of $Hg(NO_3)_2$ standard was then added to each flask and stirring done by means of magnetic stirrer. Adsorption at acidic (pH 3) and basic (pH 8) conditions was assessed. At equilibrium, the solutions were filtered and the equilibrium concentrations determined using a Genesis inductively coupled plasma optical emission spectroscopy (ICP-OES) (Spectro, Germany). The same procedure was followed using the multi-component solution to assess the effect of competing ions. The amount of ions adsorbed per unit mass of adsorbent was calculated on the basis of the mass balance equation:

$$q_e = \frac{(C_i - C_f) \times V}{1000 \times P}, \tag{1}$$

where q_e (mg metal g^{-1} polymer) is the adsorption capacity; C_i (mg L^{-1}) is the initial concentration of Hg in the solution; C_f (mg L^{-1}) is the concentration of Hg in the filtrate; V (mL) is the volume of initial solution; and P (g) is the amount of polymer used.

Effect of contact time

Contact time adsorption experiments were conducted at room temperature in order to obtain the optimal time required for adsorption. Adsorption was studied at various time intervals (10–120 min) using seven solutions of (40 mg L^{-1}) each. The concentration of Hg was determined at the end of each time. The obtained equilibrium capacities (q_e) were then plotted against the equilibrium time for kinetic modeling.

Desorption studies

The regeneration of SCPEI was carried out by the treatment of previously loaded polymer with an excess of extracting reagent. HNO_3 at different concentrations, namely, 2, 3, 5, and 7 mol L^{-1}, was used as an extractant. During regeneration, 1 g of loaded SCPEI was dispersed in 40 mL of the acidic solution, the mixtures were then stirred for one hour, filtered and the polymer washed with de-ionized water and dried prior to re-use.

Application of SCPEI to wastewater samples

The synthesized SCPEI was applied for the removal of Hg from wastewater samples collected in the vicinity of gold mining activities in the Central Rand goldfield, Johannesburg. Gold tailings in this area are known to contain some Hg as a result of the mercury amalgamation method that was used prior to extract gold from ores (Tutu, McCarthy, and Cukrowska 2008). As such, Hg tends to find its way into water systems in the area and poses a potential threat to humans and animals that use this water.

Three samples were used (one pit water and two surface water samples) collected from the Natalspruit, an acid mine drainage-impacted stream (26°13/07.15″S and 28°07/52.74″E). Sampling was done according to standard water sampling protocols (Hermond and Fechner-Levy 2000) and geochemical parameters (pH, redox potential and electrical conductivity) recorded in the field using field-meters. The samples were filtered in the laboratory prior to application in the adsorption experiments. The field measurements were carried out with a portable kit Multi Line F/Set 3 of the Wissenschaftlich-Technische Werkstatten, Weilheim (WTW, Germany) equipped with a pH electrode, an integrated temperature probe (Sen Tix 41), a standard conductively cell (Tetra Con 375) and an oxidation-reduction potential probe (Sen Tix ORP). The pH electrode was calibrated according to IUPAC recommendations against two buffer solutions pH 4 and pH 7 and an uncertainty of ±0.1 units. Metal analysis was carried out using ICP-OES. Anion concentrations were determined by ion chromatography (IC) (761 Compact, Metrohm, Switzerland).

In each analytical technique, the limit of detection (LOD) was calculated as $3 \times$ standard deviation of the blank and the method quantitation limit (MQL) was calculated as $10 \times$ standard deviation of the blank. Analytical results had uncertainties $< 10\%$.

Modeling of analytical results

The results from adsorption studies were modeled using kinetic, equilibrium (isotherms), and thermodynamic models. Medusa software (Department of Chemistry, KTH Royal Institute of Technology, Sweden).

Kinetic models

The kinetic models that were used to fit the experimental data are as follows.

The pseudo first-order model was defined by the equation

$$\log(q_e - q_t) = \log q_e - (k_1/2.303) \tag{2}$$

The plot of $\log(q_e - q_t)$ *versus* t gives a straight line.

The pseudo second-order model was defined by the equation

$$1/q_t = \left(1/k_2 q_e^2\right) + (1/q_e)t \tag{3}$$

The plot of t/q_t *versus* t gives a straight line.

The parameters in the above equations are defined as follows: q_e ($\mathrm{mg\,g^{-1}}$) is the adsorption capacity at equilibrium, q_t ($\mathrm{mg\,g^{-1}}$) is the adsorption capacity at time t, and k_1, and k_2 ($\mathrm{1\,min^{-1}}$) are the rate constants for the pseudo first-order and pseudo second-order models, respectively. These are obtained from the slope of the plot of log $(q_e - q_t)$ *versus* t.

Isotherm models

Adsorption isotherms describe the nature of the adsorbent–adsorbate interaction as well as the specific relation between the concentration of adsorbate and its degree of accumulation onto the adsorbent surface (Gupta et al. 2003; Li et al. 2008). In order to understand the adsorption mechanism of Hg onto the SCPEI surface, two adsorption isotherm models, Langmuir and Freundlich were used to fit the experimental data. The experimental data for isotherm modeling were obtained by conducting the adsorption experiments using 1 g of SCPEI and 40 mL solutions of different Hg concentrations under continuous stirring. At equilibrium, the solutions were filtered and the non-desorbed mercury was determined.

Langmuir model. The Langmuir model is valid for monolayer localized physical adsorption onto a homogeneous surface with a finite number of identical sites. In monolayer adsorption, there is no transmigration of adsorbed molecules at the maximum adsorption, meaning that the adsorbed molecules do not deposit on each other, but are only adsorbed on the free surface of the adsorbent (Hamdaoui and Naffrechoux 2007). The Langmuir model is given by the following equation:

$$q_e = \frac{q_m b C_e}{1 + bC_e}, \tag{4}$$

where q_e ($\mathrm{mg\,g^{-1}}$) is the amount adsorbed per unit weight of adsorbent at equilibrium, C_e ($\mathrm{mg\,L^{-1}}$) is the equilibrium concentration of the adsorbate, and q_m ($\mathrm{mg\,g^{-1}}$) is the maximum adsorption capacity, and b ($\mathrm{L\,mg^{-1}}$) is the constant related to the free energy of adsorption. The values of maximum capacity (q_m) and Langmuir constant (b) were calculated from the intercept and the slope of the plots.

Freundlich model. The Freundlich model is an empirical formula for heterogeneous adsorption given by the following equation:

$$q_e = K_F C_e^{1/n} \tag{5}$$

where K_F ($\mathrm{mg^{1-(1/n)}\,L^{1/n}\,g^{-1}}$) is a constant correlated to the relative adsorption capacity of the adsorbent and n is a constant indicative of the intensity of the adsorption.

Since the Frendlich model is an exponential equation, it assumes that the adsorption capacity of the adsorbent increases with increasing concentration of the adsorbate. The values K_F and $1/n$ can be correlated to the adsorption capacity and intensity (Freundlich 1926).

Thermodynamic modeling

The thermodynamic study was done by conducting the adsorption experiments at two different temperatures (15°C and 27°C). The concentrations obtained after adsorption were then used to calculate the activation energy (E_a) according to the Arrhenius equation:

$$E_a = \frac{R \cdot T_1 \cdot T_2 \cdot \ln K_2/K_1}{T_1 - T_2}, \tag{6}$$

where E_a is the activation energy; R is the gas constant; T_1 and T_2 are the two different temperatures; and K_1 and K_2 are constants for the two temperatures.

The constants K_1 and K_2 could be calculated as follows:

$$K = \frac{C_i - C_e/M}{C_e} \tag{7}$$

where C_i is the initial concentration ($mg\,L^{-1}$); C_e ($mg\,L^{-1}$) is the concentration at equilibrium for each temperature; and M is the atomic mass for each element.

The magnitude of the activation energy gives an idea about the type of adsorption. There are two main types of adsorption: chemisorption and physisorption. Physisorption is usually rapidly attained and easily reversible, because of the small amount of energy required. It is usually no more than $4.2\,kJ\,mol^{-1}$ since the forces involved are weak. On the other hand, chemisorption involves forces much stronger than those for physisorption. Therefore, the activation energy for chemisorption is higher (Klekamp and Urnbac 1993; Özcan et al. 2006).

Results and discussion

Characterization of SCPEI

Fourier Transform Infra Red spectroscopy was used to characterize the SCPEI in order to confirm the introduction of the $–SO_3H$ chelating group. The FTIR spectrum is given in Figure 2.

The absorption bands at 1038.29; 1165.42; and $589.71\,cm^{-1}$ confirmed the sulfonation reaction, as they refer to the presence of S=O sym; S=O asym; and S–O bonds, respectively. The difference in the absorption bands strength for the stretching vibration of N–H could be observed, with the sulfonated polymer yielding lower band strength. This could be attributed to the closure of some secondary amine sites during sulfonation of the polymer. The sulfonated polymer thus contains less secondary amine groups due to the reaction between these groups in CPEI and ($–SO_3H$) groups in chloropropanesulfonyl chloride.

Effect of contact time

Figure 3 shows the effect of contact time on the adsorption of Hg onto SCPEI at pH 3. The initial concentration had a concentration of $40\,mg\,L^{-1}$.

The adsorption was fast within the first 20 min, slowing down between 20–50 min, showing a noticeable jump from 50–60 min, with no further increase beyond 60 min. This could be attributed to the unavailability of reaction sites which decreases with time. Thus, despite an increase in adsorption after 45 min being low, the minimum required time for adsorption to be completed was 60 min.

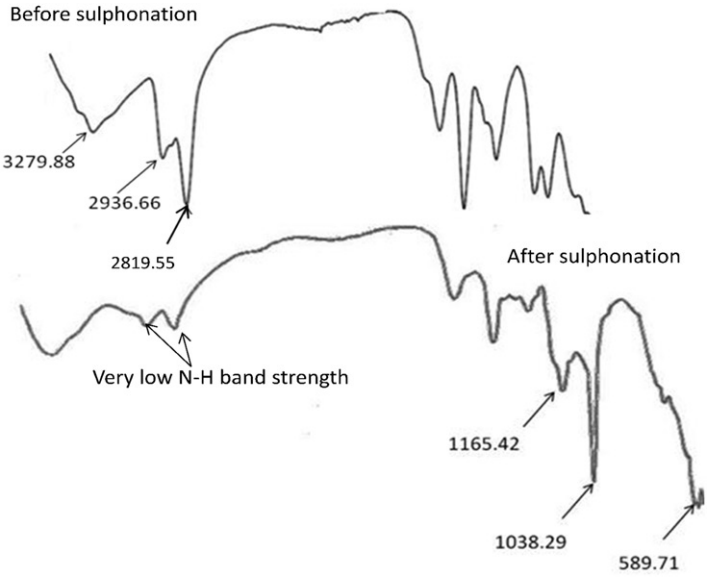

Figure 2. FTIR spectrum of CPEI and SCPEI.

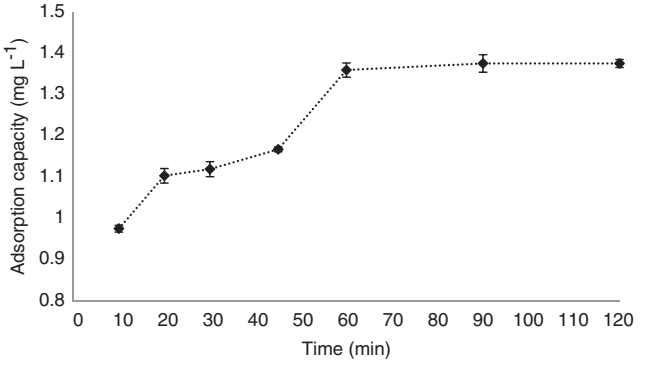

Figure 3. Effect of contact time on the adsorption process.

Effect of pH

The results for the adsorption of Hg from synthetic solutions are presented in Table 1. The table shows the final Hg concentration obtained (C_f) after 60 min, adsorption capacity, percentage as well as the relative standard deviation (RSD).

The adsorption percentages showed high removal efficiency and the adsorption performance was found to be a function of pH. From speciation modeling using Medusa, Hg was found to exist as Hg^{2+} at pH 3 and Hg(OH)2 at pH 8. This implies that at low pH, the mechanism of Hg binding onto the polymer is based on the hard–soft Lewis acid-base theory, where the sulfur atom on the chelating group ($–SO_3H$) acts as a Lewis base and donates electrons to Hg^{2+} which is considered Lewis acid. At high pH, Hg removal proceeds by precipitation. The model predicts that at pH values higher than 12,

Table 1. Removal of Hg from synthetic solutions by SCPEI.

	C_f (mg L^{-1})	RSD	Adsorption capacity (mg g^{-1})	Adsorption efficiency (%)
pH 3	5.4	2.6	1.38	87%
pH 8	5.2	1.3	1.39	87%

Notes: Initial concentration of the ions = 40 mg L^{-1}; C_f: final concentration after adsorption; RSD ($n = 3$); LOD (mg L^{-1}) = 0.018; MQL (mg L^{-1}) = 0.060.

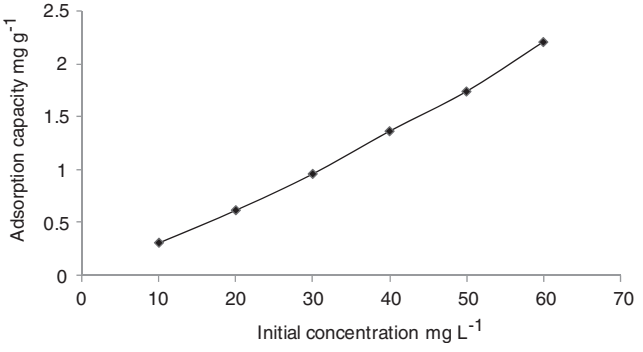

Figure 4. Effect of initial concentration on the adsorption process.

$Hg(OH)_3^-$ becomes the dominant species. This may mean that Hg is not adsorbed beyond pH 12.

Effect of initial concentration

The results for the dependence of adsorption on Hg concentrations are shown in Figure 4. The adsorbed amount of Hg increased with increasing concentration. This could be attributed to the availability of sites for Hg adsorption. The saturation of the polymer could not be established in this work.

Effect of competing ions

To investigate the selectivity of SCPEI toward Hg, adsorption experiments were performed in the presence of competing ions by using multi-component standard solutions containing Mn, Pb, Zn, Fe, Cr, and Ni with initial concentrations of 40 mg L^{-1}. Table 2 shows the removal percentages of elements in a multi-component solution.

Although, some ions such as Pb, Ni, and Zn showed good removal percentages, the removal of Hg was still the highest showing almost similar removal efficiency to that observed in the single-component Hg solution which indicates that SCPEI has high efficiency to remove Hg even in presence of competing ions. The selectivity orders are: Hg > Pb > Ni = Zn > Cr = Mn > Fe at pH 3, and Hg > Zn > Pb > Ni > Cr > Mn > Fe at pH 8. Moreover, the removal of these ions was dependent on pH, whereas the removal

Table 2. Removal percentages of elements in a multi-component solution.

Element	Cr	Mn	Fe	Zn	Pb	Ni	Hg
pH 3	53%	53%	49%	67%	68%	67%	84%
pH 8	59%	54%	53%	74%	71%	70%	85%

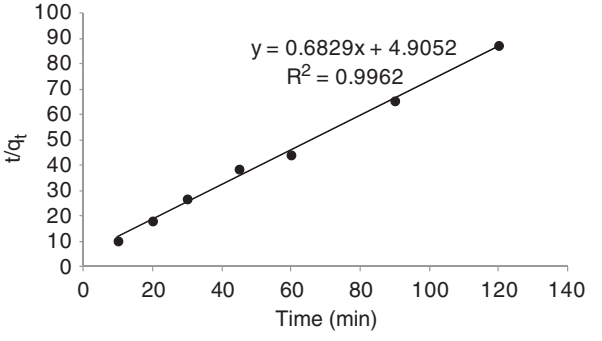

Figure 5. Pseudo second-order plot for the adsorption process.

of Hg appeared to be independent of pH. In the article on CPEI by Saad, Cukrowska, and Tutu (2011), nitrogen was a donor atom and exhibited poor removal of Hg especially in the presence of competing ions, where the removal percentages were 54% at pH 3 and 55% at pH 8. This difference in the adsorption behavior could be attributed to the functionality of the polymer. In this case, Hg as (a soft acid) preferably binds to sulfur (a soft base) and not to nitrogen which is a hard base. In the article on phosphonated cross-lined polyethylenimine by Saad, Cukrowska, and Tutu (2012), where phosphorous was the donor atom, the removal of Hg was also very poor compared to U, which is also consistent with the mechanism since phosphorous is a hard base and U is a hard acid. Same trend was observed in the article on CPEI by Saad, Cukrowska, and Tutu (2011), where nitrogen was the donor atom. This demonstrates the role of functionalization on the adsorption behavior and selectivity of the adsorbent.

Kinetic modeling of adsorption result data

The high correlation obtained by plotting the linearised form of pseudo second-order model ($R^2 = 0.996$) compared to that of pseudo first-order model ($R^2 = 0.931$) demonstrated that pseudo second-order gives the best fit, implying that the adsorption occurs via a chemisorption process (Antures et al. 2003). A plot of the linearized form of pseudo second-order model (t/qt *vs.* t) is given in Figure 5.

Adsorption isotherms

The calculated Langmuir constants (b and q_m) and Freundlich constants (n and K_f) as well as the coefficients of correlation (R^2) for both isotherms are given in Table 3.

Table 3. Langmuir and Freundlich parameters for the adsorption of Hg onto SCPEI.

	Langmuir			Freundlich		
	b	R^2	q_m	K_f	R^2	n
Hg	1.381	0.258	8.869	4.072	0.951	0.339

Table 4. Activation energy for the adsorption of Hg by SCPEI.

Element	K_1	K_2	E_a (k J mol^{-1})
Hg	0.004	0.003	56.89

The results suggest that the Freundlich model best fits the data as shown by the correlation coefficient >0.95 whereas that for the Langmuir correlation coefficient is <0.95. This result demonstrates adsorption on a heterogeneous surface or sites of different energy. It also assumes that the adsorption capacity of the adsorbent increases with increasing concentration of the adsorbate in this case Hg which is in agreement with the results obtained for the effect of initial concentration on adsorption.

Thermodynamic studies

The calculated activation energy value (E_a) for the adsorption of Hg onto SCPEI surface as well as the calculated constants K_1 and K_2 are presented in Table 4. The elevated E_a value further corroborates the occurrence of adsorption through a chemisorption process.

Desorption studies

Optimal recovery and regeneration of SCPEI was achieved at a concentration of 5 mol L^{-1} of the regeneration acid solution. Subsequently, regeneration of the used polymer was carried out using 5 mol L^{-1} acid concentration. The adsorption percentages for the recovered polymer (regenerated SCPEI) on the same synthetic solutions discussed previously are given in Table 5.

Adsorption percentages, though lower compared with those for the fresh SCPEI, still portrayed good recoveries. Adsorption at pH 3 dropped by 18% and at pH 8 dropped by 13%.

Serial desorption was conducted in order to assess the amount of intractable Hg that would remain bound to the polymer. For example, after a cycle of five desorptions (Figure 6), the adsorbed Hg on SCPEI was decreased by 1.182 mg g^{-1} (from 1.360 to 0.178 mg g^{-1} after the fifth desorption).

Generally, the results obtained from this study showed that the performance of SCPEI is comparable to that of other reported methods. Rio and Delebarre (2003), for example studied the removal of Hg using silico-aluminous fly ashes and sulfo-calcic fly ashes. They obtained removal efficiencies of 54% and 81%, respectively. According to their

Table 5. Removal of Hg from synthetic solutions by regenerated SCPEI.

	C_f (mg L^{-1})	RSD	Adsorption capacity (mg g^{-1})	Adsorption efficiency (%)
pH 3	13.8	5.2	1.05	66%
pH 8	11.2	1.3	1.15	72%

Notes: Initial concentration of the ions = 40 mg L^{-1}; C_f: final concentration after adsorption; RSD ($n = 3$); LOD (mg L^{-1}) = 0.093; MQL (mg L^{-1}) = 0.93.

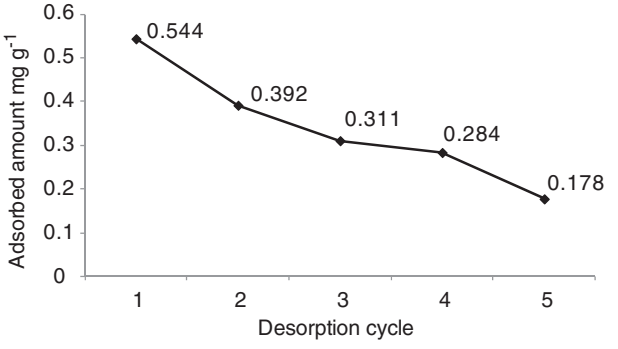

Figure 6. Desorption cycle of Hg from SCPEI using 5 mol L^{-1} HNO_3.

explanation, the difference on the removal efficiency is based on the chemical composition of two fly ashes, in which the one with high removal efficiency contains more sulfur than the other one with poor removal. However, in both cases, the removal process was time consuming, taking 72 h to reach the equilibrium while in our case this was achieved in 1 h.

Generally, the results obtained showed that the performance of SCPEI is comparable to that of other adsorbents. Liu and Guo (2006), for example, reported the removal of Hg using poly-acrylamide grafted attapulgite with removal capacity of 1.12 mg g^{-1}, which is quite similar to the results of this study. On other hand, some differences in terms of efficiency, selectivity, influencing of different conditions such as pH, time and initial concentration were demonstrated.

A study by Sreedhar and Anirudhan (1999) showed that poly-acrylamide grafted onto sawdust had a superior removal capacity, but this was more dependent on the pH (less removal efficiency was observed at pH below 5.5). This limits the use of the adsorbent for Hg recovery from low pH solutions e.g. AMD-impacted waters in which pH can be lower than 3. Moreover, the removal procedure was time consuming where 5 h was needed to reach the optimum removal. Another study by Kesenci, Say, and Denizli (2002) demonstrated very fast adsorption procedure using poly (ethyleneglycol dimenthacrylate-co-acrylamide) beads, where the largest amount of Hg was attached to the adsorbent within the first 10 min with saturation gradually reached within 30 min. But beside the advantage of the fast kinetics it also showed some demerits such as the high dependency on the pH as well as the poor selectivity towards Hg in presence of Pb. In this sense, SCPEI represents a good alternative for Hg removal considering its high selectivity and independency of pH, as well as the re-usability.

Table 6. Removal of Hg from mining wastewater samples (1 g SCPEI in 40 mL wastewater).

Samples	Metals	C_i (mg L^{-1})	RSD ($n=3$)	C_f (mg L^{-1})	RSD ($n=3$)	Ads (%)
Pit water	Cr	0.038	7.7	0.02	3.6	42
pH (3)	Fe	0.6	3.5	0.4	7.0	41
SO_4^{2-} (1669 mg L^{-1})	Mn	136.4	7.9	66.0	5.3	52
	Hg	0.3	1.8	0.004	1.7	99
	Ni	10.7	7.9	2.2	6.3	79
	Zn	14.8	8.4	5.6	1.8	62
S W 1, pH (7.2)	Fe	6.1	0.1	4.5	3.1	26
SO_4^{2-} (19.80 mg L^{-1})	Ni	6.0	7.0	2.9	3.2	52
	Zn	4.3	9.9	1.9	0.2	56
	Mn	111.7	3.8	50.0	2.9	55
S W 2	Ni	4.7	3.5	1.2	3.2	74
pH (5.6)	Zn	7.7	7.1	2.8	2.9	64
SO_4^{2-} (653.6 mg L^{-1})	Mn	179.2	2.7	89.0	6.3	50
	Fe	5.8	8.9	4.0	5.0	32

Notes: SW: surface water, C_i: initial concentration before adsorption, C_f: final concentration after adsorption.
LOD (mg L^{-1}): Cr: 0.003; Fe: 0.002; Hg: 0.001; Ni: 0.007; Zn: 0.008; Mn: 0.002; SO_4^{2-}: 0.01 (by ion chromatography).
MQL (mg L^{-1}): Cr: 0.010; Fe: 0.007; Hg: 0.003; Ni: 0.023; Zn: 0.027; Mn: 0.007; SO_4^{2-}: 0.03 (by ion chromatography).

Application of the developed polymer to wastewater samples

The results for the adsorption of Hg and other elements in the collected samples onto fresh SCPEI are given in Table 6. Hg was only detected in the pit water sample. The adsorption trend was similar to that observed for the synthetic standard solutions. Percentage removal followed the same order, namely: Hg > Ni > Zn > Mn > Cr > Fe. The most noticeable trend is the considerable increase in the removal of some metals which could be attributed to the availability of chelating sites as there is low or no Hg to compete with other metals. This confirms the high selectivity of SCPEI towards Hg.

Conclusion

In this study, SCPEI was successfully employed for the removal of Hg. The removal mechanism of Hg hinges on the functional groups present in the polymer largely the sulfate group. The Freundlich isotherm was found to be the best fit describing the experimental data, suggesting that adsorption occurred on a heterogeneous surface. The pseudo-second-order model was found to explain the adsorption kinetics most effectively. This model and the results of the thermodynamic study showed that Hg adsorption occurred *via* chemisorption.

The high removal of Hg in presence of competing ions confirmed the selectivity of SCPEI to Hg. The synthesized polymer exhibited commendable potential for re-use through regeneration by 5 mol L^{-1} HNO_3 which is a very significant factor influencing the feasibility and cost-effectiveness of the removal process as it reduces waste disposal and environmental impact.

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Chapter 6

Paper III

This paper investigated

The removal of As using phosphonated

cross-linked polyethylenimine. The removal mechanism was also

studied in order to highlight the deference in the mechanism between

metals and metalloids.

Functionalisation of cross-linked polyethylenimine for the removal of As from mining wastewater

Dalia M Saad, Ewa M Cukrowska and Hlanganani Tutu*

Molecular Science Institute, School of Chemistry, University of the Witwatersrand, Private Bag X3, WITS 2050, Johannesburg, South Africa

ABSTRACT

Cross-linked polyethylenimine (CPEI) was phosphonated by reaction with phosphorous acid and formaldehyde. The functionalised polymer was used as an adsorbent for the removal of arsenic as an oxo-anion. The binding affinity of the synthesised polymer to abstract As from synthetic solutions and wastewater samples was assessed, as well as its ability to be regenerated for re-use. The PCPEI demonstrated an elevated loading capacity, removing up to 88% of As. The kinetic rates were modelled using pseudo first-order and pseudo second-order equations. The pseudo second-order equation was found to explain the adsorption kinetics most effectively, implying chemisorption. The Langmuir and Freundlich isotherms were used to interpret the adsorption of As onto PCPEI. The Freundlich isotherm was found to best fit and describe the experimental data. The thermodynamic study of the adsorption process indicated high activation energies (55.91 kJ mol^{-1}) which confirms chemisorption as a mechanism of interaction between As and PCPEI.

Keywords: Adsorption; arsenic; phosphonated cross-linked polyethylenimine, functionalisation

INTRODUCTION

Water pollution is an increasingly pressing problem. The world is facing a challenge in meeting rising demands for unpolluted water, since the available supplies of freshwater are decreasing due to population growth, extended droughts, extensive industrialisation and improper disposal. Water contamination by trace elements is a global environmental concern as it affects the quality of drinking water and hence human health. Although some elements are natural nutrients at trace level, they become very toxic at high concentrations. High concentrations of toxic elements result from intensive anthropogenic activities, including mining, agriculture, and disposal of industrial waste materials (Akpor and Muchie, 2010; Liu et al., 2008; Savage and Diallo, 2005; Ruparelia et al., 2008; Ahmed et al., 2008; Madoni and Giuseppa, 2005; Bhattacharya et al., 2007). Arsenic (As) is one of the most toxic elements. It is a naturally occurring metalloid and a micronutrient in small quantities. Elevation of As concentration in natural water is a major concern because of its toxicity, posing a threat to aquatic life if left untreated. Long-term drinking of arsenic-polluted water causes bladder, kidney, skin, and lung cancer, as well as other effects such as loss of appetite, muscular weakness, pigmentation changes, and nausea. Arsenic is mobilised naturally by weathering reactions, biological activity, geochemical reactions and volcanic emissions, as well as anthropogenic activities. Mining activities account for some of the most serious additional sources (Carvalho and Martin, 2001; Mohan and Pittman, 2007).

Several different methods have been reported to remove toxic elements from wastewaters, such as chemical-, physical-, and bio-remediation (Sauer et al., 2004). Among the remediation techniques for metal ion removal, polymeric adsorbents are some of the more efficient in terms of technical and economic efficiency, feasibility, and environmental impact.

Polyethylenimine (PEI) is one of the most popular polymeric adsorbents and well-known for its metal-chelating properties (Leroy et al., 2003). It has been widely applied for the retention of toxic elements. PEI is more effective for the removal of metals than metalloids (Saad et al., 2011). The aim of this study, therefore, was to develop a water-insoluble form of polyethylenimine with suitable functionality to facilitate selective removal of As. The insoluble property of PEI was achieved by cross-linking, as reported in a previous study by the authors (Saad et al., 2011).

MATERIALS AND METHODS

Materials

All chemicals were obtained from Sigma Aldrich (South Africa) without further purification. Cross-linked polyethylenimine (Saad et al., 2011), phosphorous acid, formaldehyde 38% (CH_2O), and 6 mol·ℓ^{-1} HCl were used. The solutions were prepared from $NaAsO_2$. Adjustments of pH for the adsorption experiments were conducted using 1 mol·ℓ^{-1} solutions of HNO_3 and NaOH. Deionised water was used for the preparation of all solutions.

Synthesis of PCPEI

The synthesis of PCPEI was carried out according to the method reported by Saad et al. (2012a); cross-linked polyethylenimine, 2.5 g, was placed in 80 mℓ of 6 mol·ℓ^{-1} HCl. Phosphorous acid, 19.31 g, was added and the mixture was heated under reflux at 90°C. Formaldehyde, 38 mℓ, was added drop-wise over a period of an hour, and the reaction was left overnight. A pale powdery yellow solid was obtained, and was washed with abundant deionised water before drying in an air oven at 30°C. The solid was then pulverised and sieved.

* To whom all correspondence should be addressed.
☎ +27 11 717 6771; e-mail: Hlanganani.tutu@wits.ac.za
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Batch adsorption studies

The batch adsorption experiments were conducted using a 1 000 mg·ℓ$^{-1}$ standard stock solution of $NaAsO_2$ from which the 40 mg·ℓ$^{-1}$ working standard solutions were obtained by serial dilution. Adsorption experiments were performed in 50 mℓ flasks at room temperature. 1 g of synthetic PCPEI (an optimal adsorbent amount according to preliminary optimisation of the solid: liquid ratio) was weighed out into each flask separately; 40 mℓ of 40 mg·ℓ$^{-1}$ standard solutions were then added to each flask and stirring done by means of magnetic stirrer. This concentration was arbitrarily chosen as it represents a 'worst-case' scenario of pollution by most toxic elements (e.g. Hg, U, As and V) in mining-impacted waters in the Witwatersrand Basin goldfields (Tutu et al., 2009). Adsorption at pH 3 and pH 8 was assessed to investigate the effect of pH. At equilibrium, the solutions were filtered and the equilibrium concentrations determined using a Genesis inductively coupled plasma optical emission spectroscopy (ICP-OES) (Spectro, Germany). The amount of ions adsorbed per unit mass of adsorbent was calculated on the basis of the mass balance equation:

$$\text{Capacity (mg metal·g}^{-1}\text{ polymer)} = \frac{(C_i - C_f) \times V}{1\,000 \times P}$$

where:

C_i (mg·ℓ$^{-1}$) is the initial concentration of As in the solution
C_f (mg·ℓ$^{-1}$) is the concentration of As in the filtrate
V (mℓ) is the volume of initial solution
P (g) is the amount of polymer used.

Effect of contact time

Adsorption experiments were conducted at room temperature in order to obtain the optimal time required for adsorption. Adsorption was studied at various time intervals (10–120 min) and fixed concentration (40 mg·ℓ$^{-1}$). The concentration of As was determined at the end of each time period. The obtained equilibrium capacities (q_e) were then plotted against the equilibrium time for kinetic modelling.

Desorption studies

The regeneration of the synthesised polymer was carried out by the treatment of previously loaded polymer with an excess of extracting reagent. HNO_3 at different concentrations, namely, 2 mol·ℓ$^{-1}$, 3 mol·ℓ$^{-1}$, 5 mol·ℓ$^{-1}$, and 7 mol·ℓ$^{-1}$, was used as an extractant. During regeneration, the mixtures were stirred for 1 h, filtered and the polymer washed with de-ionised water and dried prior to re-use.

Application of the developed polymer to wastewater samples

The synthesised polymer was applied for the removal of As from wastewater samples collected in the vicinity of gold-mining activities in the Central Rand Goldfield, Johannesburg.

Five samples were used (1 pit water and 4 surface water samples) collected from the Natalspruit, an acid mine drainage impacted stream (26°13'07.15" S and 28°07'52.74" E). Sampling was done according to standard water sampling protocols (Hermond and Fechner-Levy, 2000) and geochemical parameters (pH, redox potential and electrical conductivity) recorded in the field using field-meters. The samples were filtered in the laboratory prior to application in the adsorption experiments. The field measurements were carried out with a portable kit Multi Line F/Set 3 of the Wissenschaftlich- Technische Werkstatten, Weilheim (WTW, Germany) equipped with a pH electrode, an integrated temperature probe (Sen Tix 41), a standard conductivity cell (Tetra Con 375) and an oxidation-reduction potential probe (Sen Tix ORP). The pH electrode was calibrated according to IUPAC recommendations against 2 buffer solutions, pH 4 and pH 7, and with an uncertainty of ±0.1 units. Metal analysis was carried out using ICP-OES. Anion concentrations were determined by ion chromatography (IC) (761 Compact, Metrohm, Switzerland).

In each analytical technique, the limit of detection (LOD) was calculated as 3 x standard deviation of the blank and the method quantitation limit (MQL) was calculated as 10 x standard deviation of the blank.

Modelling of analytical results

The results from adsorption studies were modelled using kinetic, equilibrium (isotherms), and thermodynamic models.

Kinetic models

The kinetic models that were used to fit the experimental data were as follows:

The pseudo first-order model was defined by the equation:

$$\log (q_e - q_t) = \log q_e - (k_1/2.303)t$$

The plot of $\log (q_e - q_t)$ vs. t gives a straight line.

The pseudo second-order model was defined by the equation:

$$1/q_t = (1/k_2 q_e^2) + (1/q_e)t$$

The plot of t/q_t vs. t gives a straight line.

The parameters in the above equations are defined as follows: q_e (mg·g^{-1}) is the adsorption capacity at equilibrium, q_t (mg·g^{-1}) is the adsorption capacity at time t, and k_1 and k_2 (1/min) are the rate constants for the pseudo first-order and pseudo second-order models, respectively. These are obtained from the slope of the plot of $\log (q_e - q_t)$ vs t.

The experimental data for kinetic modelling were obtained by conducting the adsorption experiments using 1 g of PCPEI and 40 mℓ of 40 mg·ℓ$^{-1}$ standard solutions at different time intervals under continuous stirring at pH 3.

Isotherm models

Adsorption isotherms describe the nature of the adsorbent–adsorbate interaction as well as the specific relation between the concentration of adsorbate and its degree of accumulation onto the adsorbent surface (Gupta et al., 2003; Li et al., 2008). In order to understand the adsorption mechanism of As onto the PCPEI surface, two adsorption isotherm models, Langmuir and Freundlich, were used to fit the experimental data. The experimental data for isotherm modelling were obtained by conducting the adsorption experiments using 1 g of PCPEI and 40 mℓ solutions of different As concentrations under continuous stirring. At equilibrium, the solutions were filtered and the non-desorbed arsenic was determined.

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Langmuir model

The Langmuir model is valid for monolayer localised physical adsorption onto a homogeneous surface with a finite number of identical sites. In monolayer adsorption, there is no trans-migration of adsorbed molecules at the maximum adsorption, meaning that the adsorbed molecules do not deposit on each other, but are only adsorbed on the free surface of the adsorbent (Hamdaoui and Naffrechoux, 2007). The Langmuir model is given by the following equation:

$$q_e = \frac{q_m b C_e}{1 + b C_e}$$

where:

q_e (mg·g^{-1}) is the amount adsorbed per unit weight of adsorbent at equilibrium
C_e (mg·ℓ$^{-1}$) is the equilibrium concentration of the adsorbate
q_m (mg·g^{-1}) is the maximum adsorption capacity
b (ℓ·mg^{-1}) is the constant related to the free energy of adsorption.

The values of maximum capacity (q_m) and Langmuir constant (b) were calculated from the intercept and the slope of the plots.

Freundlich model

The Freundlich model is an empirical formula for heterogeneous adsorption given by the following equation:

$$q_e = K_F C_e^{1/n}$$

where:

K_F (mg$^{1-(1/n)}$ ℓ $^{1/n}$ g^{-1}) is a constant correlated to the relative adsorption capacity of the adsorbent
n is a constant indicative of the intensity of the adsorption.

Since the Freundlich model is an exponential equation, it assumes that the adsorption capacity of the adsorbent increases with increasing concentration of the adsorbate. The values K_F and 1/n can be correlated to the adsorption capacity and intensity (Freundlich, 1926).

Thermodynamic modelling

The thermodynamic study was done by conducting the adsorption experiments using the abovementioned procedure at 2 different temperatures (15°C and 27°C). The concentrations obtained after adsorption were then used to calculate the activation energy (*Ea*) according to the Arrhenius equation:

$$E_a = \frac{R \cdot T_1 \cdot T_2 \cdot \ln K_2 / K_1}{T_1 - T_2}$$

where:

E_a is the activation energy
R is the gas constant
T_1 and T_2 are the two different temperatures
K_1 and K_2 are constants for the two temperatures.

The constants K_1 and K_2 could be calculated as follows:

$$K = \frac{C_i - C_e / M}{C_e}$$

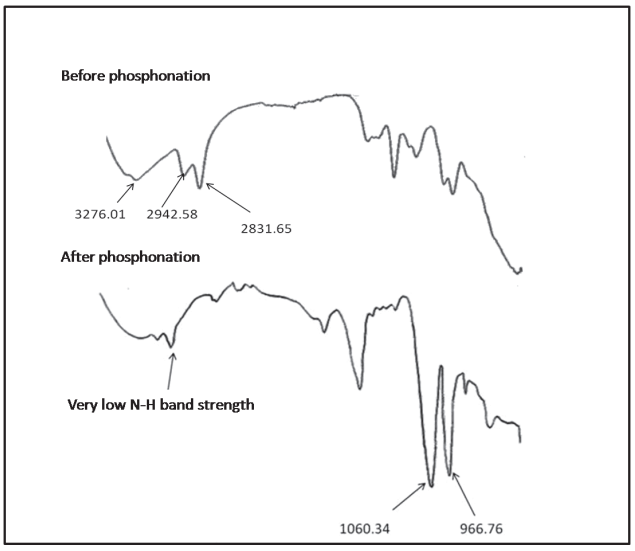

Figure 1
FTIR spectrum of CPEI and PCPEI

where:

C_i is the initial concentration (mg·ℓ$^{-1}$)
C_e (mg·ℓ$^{-1}$) is the concentration at equilibrium for each temperature
M is the atomic mass for each element.

The magnitude of the activation energy gives an indication of the type of adsorption. There are two main types of adsorption: chemisorption and physisorption. Physisorption is usually rapidly attained and easily reversible, because of the small amount of energy required, usually no more than 4.2 kJ·mol^{-1} since the forces involved are weak. Chemisorption involves much stronger forces and the activation energy is therefore higher (Klekamp and Urnbac, 1993; Özcan et al., 2006).

RESULTS AND DISCUSSION

Characterisation of phosphonated cross-linked polyethylenimine

Fourier transform infrared spectroscopy was used to characterise the phosphonated derivative of cross-linked polyethylenimine (PCPEI) in order to confirm the introduction of the $-PO_3H_2$ chelating group. The FTIR spectrum is given in Fig. 1.

The major peaks of importance on the IR spectrum of PCPEI are: 966.76 cm^{-1} indicating the presence of P–OH bond; 1 060.34 cm^{-1} corresponding to the presence of the P–O bond; and 2 803.31 cm^{-1} signifying the presence of the PO–H bond. The difference in absorption band strength for the stretching vibration of N–H before and after the phosphonation could be observed, with the phosphonated polymer yielding lower band strength. This could be attributed to the closure of some secondary amine sites during phosphonation of the polymer. The phosphonated polymer thus contains fewer secondary amine groups due to the reaction between these groups in CPEI and ($-PO_3H_2$) groups in phosphorous acid.

Effect of contact time

Figure 2 shows the effect of contact time on the adsorption of As onto PCPEI.

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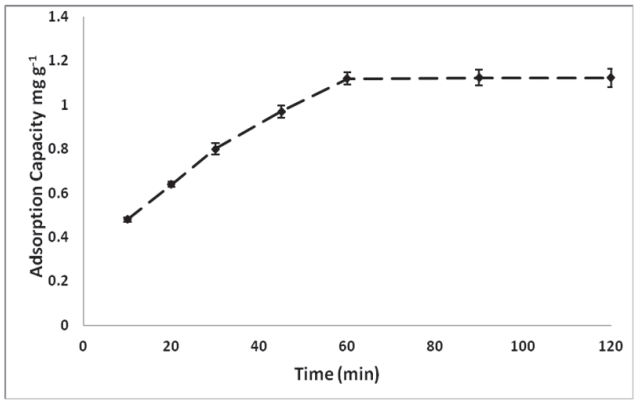

Figure 2
Effect of contact time on the adsorption process

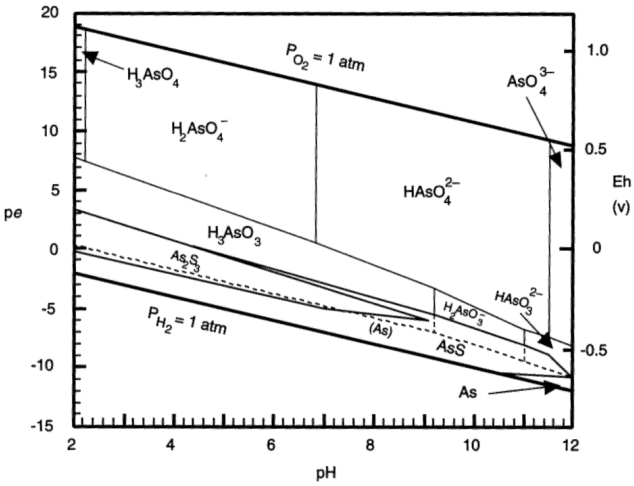

Figure 3
Pourbaix diagram for As

The adsorption was rapid within the first 30 min, slowing down between 30–60 min and with no further increase beyond 60 min. This could be attributed to the unavailability of reaction sites, as availability decreases with time. Thus, despite the increase in adsorption after 45 min being low, the minimum required time for adsorption to be completed was 60 min.

Effect of pH

The results for the adsorption of As by PCPEI from synthetic solutions are presented in Table 1. The table shows the final concentrations obtained (C_f) after 60 min, adsorption capacity, percentage as well as the relative standard deviation (RSD).

The adsorption percentages showed high removal efficiency. Moreover, the performance of PCPEI in removal of As was found to be independent of the pH. As can be seen from the Pourbaix diagram (Fig. 3), As in aqueous systems is soluble across a wide pH range (2–12), as $H_2AsO^-_4$ and $HAsO_4^{2-}$.

Effect of initial concentration

The results for the dependence of adsorption of As onto PCPEI on initial concentration are given in Fig. 4.

The adsorption increased with increasing concentration. It should be noted that, at each concentration, adsorption increases and reaches a maximum after 60 min, as shown in Fig. 2.

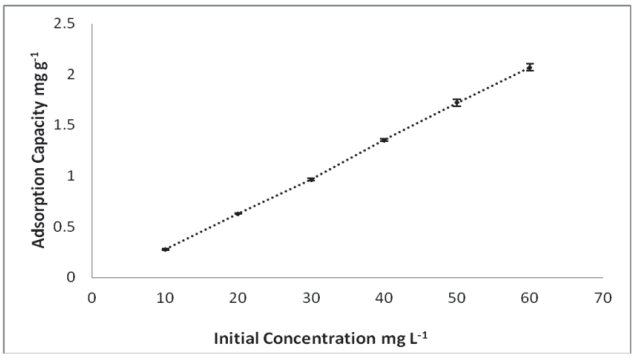

Figure 4
Effect of initial concentration on the adsorption process

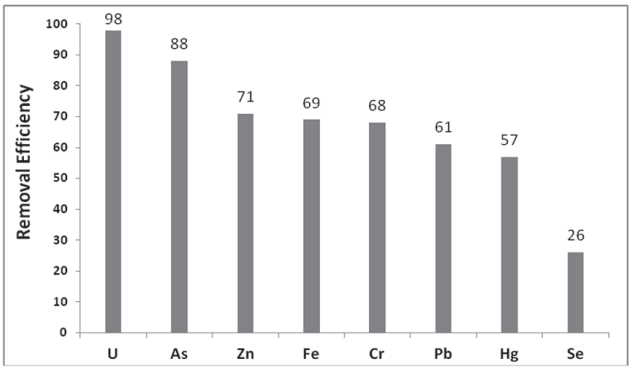

Figure 5
Removal efficiency for elements in a multi-component solution (at RSD < 10%)

TABLE 1
Removal of As from single-component synthetic solution by PCPEI

	C_f (mg·ℓ$^{-1}$)	RSD	Adsorption capacity (mg·g^{-1})	Adsorption efficiency (%)
pH 3	4.97	0.226	1.401	88%
pH 8	4.71	0.786	1.412	88%

Initial concentration of the ions = 40 mg·ℓ$^{-1}$; C_f – final concentration after adsorption; RSD – relative standard deviation (n=3); LOD– limit of detection in mg·ℓ$^{-1}$ = 0.018; MQL – method quantitation limit in mg·ℓ$^{-1}$ = 0.06

Effect of competing ions

To investigate the possibility of competition between As and other ions such as Pb, U, Zn, Fe, Cr, Hg, and Se, the adsorption experiments were performed using multi-component standard solutions of 40 mg·ℓ$^{-1}$ at pH 3. The amount of As adsorbed in the presence of these ions was determined to investigate the selectivity of PCPEI toward As. Figure 5 shows the removal efficiency of As in the presence of these elements.

PCPEI showed a similar performance to that observed in the single-component solution (88%) which indicates that PCPEI displays a high efficiency in removing arsenic even in the presence of competing ions. The high selectivity of PCPEI

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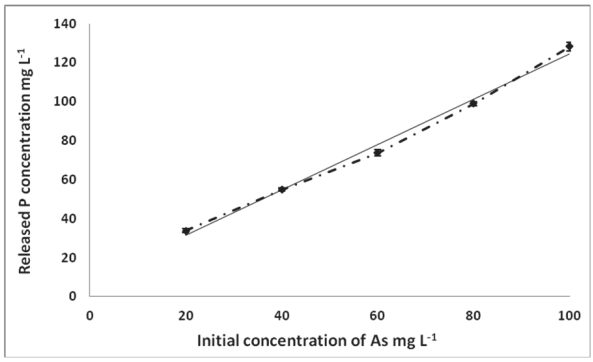

Figure 6
As concentration versus P concentration

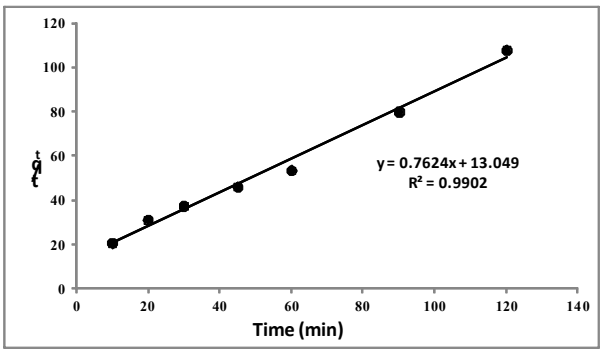

Figure 8
Pseudo second-order plot for the adsorption process

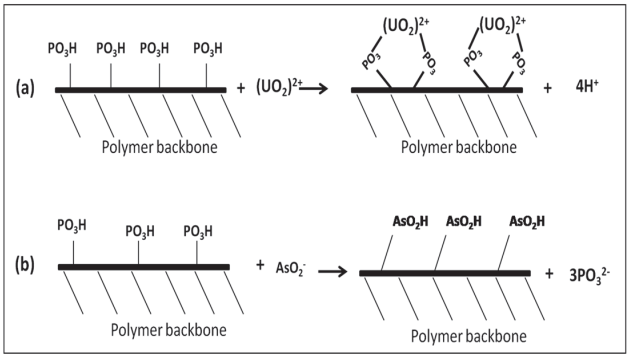

Figure 7
The mechanism of U removal (a) and As removal (b) by PCPEI

towards As could be attributed to the functional group in the polymer. For example, in the previous study by the authors on cross-linked polyethylenimine (CPEI) (Saad et al., 2011), nitrogen was a donor atom and CPEI exhibited low removal of As especially in the presence of competing ions, where the removal percentage was 54%. Another study by the authors (Saad et al., 2012b) where sulphur was the donor atom, also resulted in poor removal of As compared to other elements like Se and Hg. This confirms the role of the functionality of the polymer in selectivity behaviour and introduces the phosphate group as a most suitable functional group for removal of As. The results also showed that PCPEI has high affinity towards U; as such, U is highly competitive against As. However, the removal mechanism is completely different, taking into account the fact that As is a metalloid whereas U and the other elements (except Se) are metals. The mechanism of metal binding onto the polymer is based on the hard-soft Lewis acid-base theory, in which the P atom on the chelating group ($–PO_3H$) acts as a Lewis base and donates electrons to metals which are Lewis acids. According to this mechanism, the high removal achieved for U is understandable since U is a hard acid and P a hard base.

To investigate the mechanism of As removal, the concentration of P was measured before and after adsorption. Figure 6 shows the concentration of the released P versus the initial concentration of As.

The increase of P concentration with the increase of As adsorption indicates the mechanism of As removal to be substitution of HPO_3, because of the group similarities between As and P. Metals, e.g., U, are removed via interaction with the phosphate group on the polymer (complexation). Thus, the chemisorption adsorption of As is by reaction of As with the polymer backbone,

TABLE 2
Langmuir and Freundlich parameters for the adsorption of As onto PCPEI

	Langmuir			Freundlich		
	b	R^2	q_m	K_f	R^2	n
pH 3	0.749	0.824	13.88	3.575	0.981	0.483

while that for U is a metal-ligand complexation process ($U\text{-}HPO_3H$). Figure 7 demonstrates this mechanism.

Since As exists as a base in solutions, anion replacement could occur. Because As is in the same group in the periodic table as P, they share some similarity in their chemical behaviour. This similarity allows them to replace each other (the As adsorbed onto the polymer surface and P released into the solution). Unlike the complexation reaction, protonation at low pH in this case does not affect chemical replacement.

Kinetic modelling of adsorption process

The high correlation obtained by plotting the linearised form of the pseudo second-order model ($R^2 = 0.990$) when compared to that of pseudo first-order model ($R^2 = 0.756$) demonstrated that pseudo second-order gives the best fit, implying that the adsorption occurs via a chemisorption process (Antures et al. 2003). A plot of the linearised form of pseudo second-order model (t/qt vs. t) is given in Fig. 8.

Adsorption isotherms

The calculated Langmuir constants (b and q_m) and Freundlich constants (n and K_f) as well as the coefficients of correlation (R^2) for both isotherms are given in Table 2.

The results suggest that the Freundlich model best fits the data as shown by the correlation coefficient of > 0.95, whereas that for the Langmuir correlation coefficient is < 0.95. This result demonstrates adsorption on a heterogeneous surface. It also assumes that the adsorption capacity of the adsorbent increases with increasing concentration of the adsorbate, which is in agreement with the results obtained for the effect of initial concentration on adsorption.

Thermodynamic studies

The calculated activation energy value (E_a) for the adsorption of As onto PCPEI surface as well as the calculated constants K_1

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TABLE 3 Activation energy for the adsorption of Se by PCPEI		
K_1	K_2	*Ea* kJ·mol^{-1}
0.011	0.008	55.91

TABLE 4 Removal of As from single-component synthetic solution by regenerated PCPEI			
Cf (mg·ℓ$^{-1}$)	RSD	Adsorption capacity (mg·g^{-1})	Adsorption efficiency (%)
10.61	1.983	1.176	73%

Initial concentration of the ions = 40 mg·ℓ$^{-1}$; C_f – final concentration after adsorption; RSD – relative standard deviation (n=3); LOD – limit of detection in mg·ℓ$^{-1}$ = 0.003; MQL – method quantitation limit in mg·ℓ$^{-1}$ = 0.010

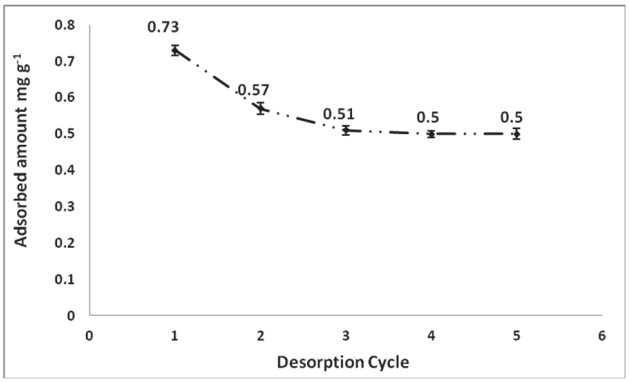

Figure 9
Desorption cycle of As from PCPEI using 7 mol·ℓ$^{-1}$ HNO

TABLE 5 Removal of As from mining wastewater samples						
Samples	**Metals**	C_i (mg·ℓ$^{-1}$)	RSD (n = 3)	C_f (mg·ℓ$^{-1}$)	RSD (n =3)	Ads %
SW 1 pH (3.8) SO_4^{-2} (383.2 mg·ℓ$^{-1}$)	Fe	6.10	0.09	1.62	5.507	73%
	Ni	6.00	7.00	0.83	1.885	86%
	Zn	4.30	9.87	1.22	3.487	72%
	Mn	111.70	3.78	17.08	1.956	85%
SW 2 pH (7.2) SO_4^{-2} (19.80 mg·ℓ$^{-1}$)	**As**	**0.12**	**2.59**	**0.02**	**2.946**	**83%**
	Se	0.09	5.84	0.06	5.456	14%
	Ni	1.50	5.28	0.37	2.164	75%
SW 3 pH (4) SO_4^{-2} (819.4 mg·ℓ$^{-1}$)	Cr	0.25	6.89	0.11	1.458	56%
	As	**0.28**	**2.06**	**0.02**	**6.245**	**91%**
	Fe	4.48	6.51	1.38	2.056	69%
	Ni	1.79	1.72	0.86	1.387	57%
	Zn	1.57	5.02	0.51	1.585	67%
	Mn	22.00	8.82	3.36	2.395	85%
SW 4 pH (5.6) SO_4^{-2} (653.6 mg·ℓ$^{-1}$)	Fe	5.84	8.97	1.50	6.765	74%
	Ni	4.67	3.53	0.88	2.061	81%
	Zn	7.65	7.07	1.76	2.078	77%
	As	**7.34**	**2.09**	**0.87**	**1.92**	**88%**
Pit water pH (3) SO_4^{-2} (1 669 mg·ℓ$^{-1}$)	Cr	0.04	7.75	0.02	2.395	61%
	Fe	0.60	3.54	0.14	3.707	77%
	Hg	0.28	1.84	0.12	1.817	56%
	Ni	10.70	7.97	2.03	1.860	81%
	U	0.16	6.70	0.001	5.048	99%
	As	**0.89**	**1.31**	**0.10**	**0.564**	**89%**
	Se	0.05	8.66	0.03	1.304	30%

SW – surface water, C_i – initial concentration before adsorption, C_f – final concentration after adsorption.
LOD (mg·ℓ$^{-1}$): Cr – 0.003; As – 0.014; Fe – 0.002; Hg - 0.001; Ni – 0.007; Zn – 0.008; Mn – 0.002; U – 0.035; Pb – 0.065; Se – 0.017; SO_4^{2-} – 0.01 (by ion chromatography).
MQL (mg·ℓ$^{-1}$): Cr – 0.010; As – 0.047; Fe – 0.007; Hg – 0.003; Ni – 0.023; Zn – 0.027; Mn – 0.007; U – 0.117; Pb – 0.217; Se – 0.057; SO_4^{2-} – 0.03 (by ion chromatography).

and K_2 are presented in Table 3.

The elevated value of activation energy implies As is adsorbed onto the PCPEI via a chemisorption process. This is consistent with the results obtained for kinetic modelling as discussed previously.

Desorption studies

Optimal recovery and regeneration of PCPEI was achieved at a concentration of 7 mol·ℓ$^{-1}$ of the regeneration acid solution (HNO_3). Subsequently, regeneration of the used polymer was

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carried out using 40 mℓ of 7 mol·ℓ$^{-1}$ acid. The adsorption efficiency for the recovered PCPEI with the same synthetic solutions is given in Table 4.

Adsorption efficiency, though lower than that for the fresh polymer, still indicated good recovery. The adsorption efficiency dropped by 15%.

Serial desorption was conducted in order to assess the amount of intractable As that would remain bound to the polymer. For example, after a cycle of 5 desorptions (Fig. 9), the adsorbed amount of As onto PCPEI dropped by 0.912 mg·g^{-1} (from 1.412 mg·g^{-1} to 0.5 mg·g^{-1} after the fifth desorption).

Application of the developed polymer to wastewater samples

The results for the adsorption of As and other elements in the collected samples onto fresh PCPEI are given in Table 5.

The adsorption trend of As onto PCPEI was similar to that observed for the synthetic solutions. The removal order was U > As > Mn > Ni > Zn > Fe > Hg > Se.

CONCLUSIONS

In this study PCPEI was successfully employed for the removal of As under optimal conditions (contact time of 60 min, initial concentration of 40 mg·ℓ$^{-1}$, and adsorbent amount of 1 g). The removal mechanism hinges on the existence of the chelating group present in the PCPEI; largely, the –PO_3H which facilitates the removal of oxo-anions. PCPEI exhibited commendable potential for re-use through regeneration at 7 mol·ℓ$^{-1}$, this is a significant factor influencing the cost of the removal process as well as waste disposal. The Freundlich isotherm was found to best describe the experimental data, suggesting that adsorption occurred on a heterogeneous surface. The pseudo second-order model was found to explain the adsorption kinetics most effectively. This model and the results of the thermodynamic study showed that As adsorption occurred via chemisorption. The study has shown, overall, that PCPEI can be used for the abstraction of As from wastewaters and can perform comparably to other remediation techniques.

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Chapter 7

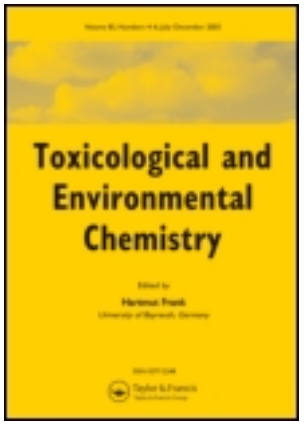
Paper IV

This paper dedicated to

Study the removal of Se by sulphonated

cross-linked polyethylenimine and to compare the

mechanism of the removal by that of Hg.



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Modified cross-linked polyethylenimine for the removal of selenite from mining wastewaters

Dalia M.G. Saad[a], Ewa M. Cukrowska[a] & Hlanganani Tutu[a]
[a] Molecular Science Institute, School of Chemistry, University of the Witwatersrand, Johannesburg, South Africa
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Molecular Science Institute, School of Chemistry, University of the Witwatersrand, Johannesburg, South Africa

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Cross-linked branched polyethylenimine (CPEI) was sulfonated by reaction with 3-chloropropanesulfonyl chloride. The functionalized polymer was used as an adsorbent for the removal of SeO_3^{2-} from aqueous solutions, particularly mining wastewaters. The binding affinity of the synthesized polymer to abstract SeO_3^{2-} from synthetic solutions and wastewater samples has been assessed as well as its ability to be regenerated for reuse. The process demonstrated that sulfonated cross-linked polyethylenimine (SCPEI) exhibited good affinity to SeO_3^{2-} with removal efficiency up to 81%. The kinetic rates were modeled using pseudo first-order and pseudo second-order equations. The pseudo second-order equation was found to explain the adsorption kinetics most effectively implying chemisorption. The Langmuir and Freundlich isotherms were used to interpret the adsorption of SeO_3^{2-} onto the modified polymer. The Freundlich isotherm was found to best fit and describe the experimental data. The thermodynamic study of the adsorption process revealed high activation energies >41 kJ mole^{-1} which confirm chemisorption as a mechanism of interaction between the adsorbate (SeO_3^{2-}) and adsorbent (SCPEI).

Keywords: adsorption; selenium; sulfonated cross-linked polyethylenimine

1. Introduction

Selenium (Se) is a naturally occurring metalloid which, in small quantities, is a micronutrient.

Elevated Se concentration in natural water has become a worldwide problem because of its toxicity, which will pose a threat to aquatic life if left untreated since the permissible level of Se concentration is 0.05 mg L^{-1} (Carvalho and Martin 2001).

The chemical speciation of Se is very important as the bioavailability and toxicity of Se are greatly affected by its chemical forms. However, the most dominant species in water systems are selenates and selenites. Selenites are the most bioavailable form of Se, which makes its removal more urgent. Furthermore, selenites have greater affinity for sulfhydryl groups and, therefore, it may be retained in animal protein longer than selenates (Maider 1993; Painter 1941; Skorupa 1998).

Many methods have been reported for the removal of Se including chemical, physical, and bioremediation (Moore and Mahmoudkhani 2011). Physical treatment includes simple filtration through sand, clay, and titanium dioxide. The problem with filtration is the huge amount of wastes. Moreover, these types of methods are also sensitive to other anions such as nitrate, sulfates, and chlorides. Ion exchange resins could be a good

*Corresponding author. Email: dalianono@gmail.com

alternative, but in some cases the resin cannot distinguish between ions due to their chemical similarity. For instance, it is quite difficult to separate sulfates and selenates because of their similar chemical nature and reactivity (Carvalho and Martin 2001).

Bioremediation has been claimed as the most effective methods. But, despite the efficiency of bioremediation there are some disadvantages. Bioremediation methods in general are costly and time consuming. For example, they require maintenance of parameters such as nutrients, energy, and temperature that is required to sustain adequate remediation (Moore and Mahmoudkhani 2011).

Polymeric adsorbents represent a good alternative for this purpose as they have a good potential for metal and metalloid ions recovery. Polyethylenimine (PEI) is among those polymers and is well known for its metal and metalloid chelating properties (Leroy et al. 2003). It has been widely applied for the retention of toxic elements, but as a water soluble polymer which requires additional techniques for effective removal such as membrane support or ultrafiltration making it unviable and costly method (Cojocaru, Zakrewska, and Jaworsksa 2009; Molinari, Gallo, and Poerio 2004; Molinari, Poerio, and Argurio 2005; Molinari, Argurio, and Poerio 2006). It is also more effective for the removal of metals than metalloids which are present in solution as oxoanions. The aim of this study, therefore, was to develop a new water-insoluble form of polyethylenimine with suitable functionality to facilitate selective removal of oxoanions, particularly SeO_3^{2-}.

The insoluble property of PEI was achieved by cross-linking in the previous study by the authors (Saad, Cukrowska, and Tutu 2011) and the selectivity to oxoanions has been explored in this study by introducing new functional group.

For simplicity, the term selenium (Se) will be used to refer to selenite ions.

2. Materials and methods

2.1. Materials

All chemicals were obtained from Sigma Aldrich (Johannesburg, South Africa) and were used without further purification. CPEI (Saad, Cukrowska, and Tutu 2011), 3-chloropropanesulfonyl chloride (98%), and tetrahydrofuran were used for sulfonation. The selenite solutions were prepared from Na_2SeO_3. Adjustments of pH for the adsorption experiments were conducted using 1 mol L^{-1} solutions of HNO_3 and NaOH. Deionized water was used for the preparation of all solutions.

2.2. Synthesis of sulfonated cross-linked polyethylenimine (SCPEI)

CPEI, 2.5 g, was dispersed in tetrahydrofuran. A volume of 2.4 mL of 3-chloropropanesulfonyl chloride was added and the mixture was heated under reflux at 70°C over night. Sulfonation was conducted at different temperatures and times and followed by infrared spectroscopy. Reaction at 70°C over night was found to be optimum. A pale brownish solid was obtained, washed with water three times, and dried in an air oven at 30°C to yield 4.8 g. The sulfonation reaction scheme is shown in Figure 1. The obtained polymer was characterized using Fourier Transform Infra Red (FTIR).

2.3. Batch adsorption studies

Batch adsorption experiments were conducted using a 1000 mg L^{-1} stock standard solution of Na_2SeO_3 from which 40 mg L^{-1} working standard solutions (as Se) were obtained by

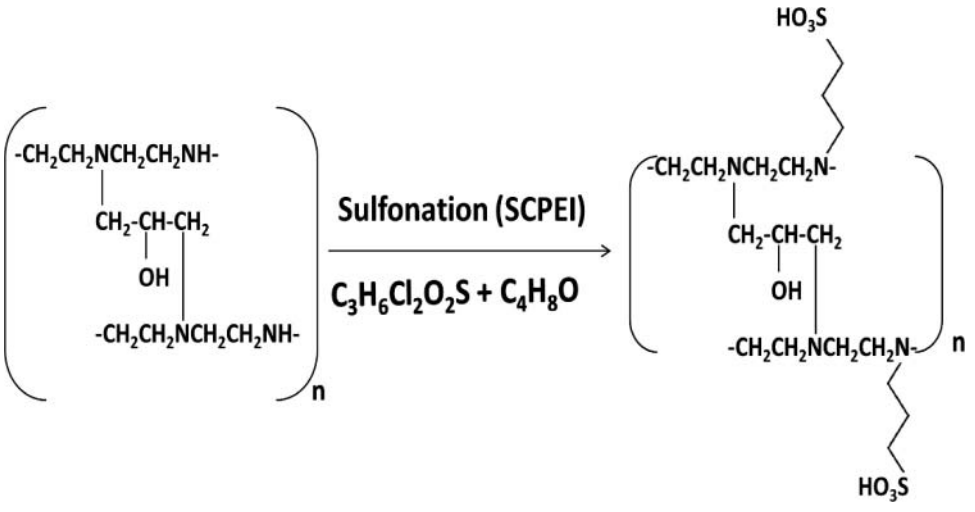

Figure 1. Sulfonation reaction scheme.

serial dilution. Adsorption experiments were performed in 50 mL flasks at room temperature. One gram of synthetic SCPEI (an optimal adsorbent amount according to preliminary optimization of the solid: liquid ratio) was weighed out into each flask separately; 40 mL of 40 mg L^{-1} standard solutions were then added to each flask and stirring done by means of magnetic stirrer. The concentration of 40 mg L^{-1} was arbitrarily chosen as it represents a "worst-case" scenario of pollution by most toxic elements (e.g., Hg, Se, U, As, and V) in mining-impacted waters in the Witwatersrand Basin goldfields (Tutu et al. 2009). Adsorption at pH 3 and pH 8 was assessed. The pH values represent the pH regime in which Se is soluble and are also representative of the pH expected of mining wastewaters which have high pH when they are disposed and tend to have low pH after some time of exposure due to sulfide oxidation. At equilibrium, the solutions were filtered and the equilibrium concentrations determined using a Genesis inductively coupled plasma optical emission spectroscopy (ICP-OES) (Spectro, Germany). The amount of Se adsorbed per unit mass of adsorbent was calculated on the basis of the mass balance equation:

$$q_e = \frac{(C_i - C_f) \times V}{(1000 \times P)},$$

where q_e (mg Se g^{-1} polymer) is the adsorption capacity; C_i (mg L^{-1}) is the initial concentration of Se in the solution; C_f (mg L^{-1}) is the concentration of Se in the filtrate; V (mL) is the volume of initial solution; P (g) is the amount of polymer used.

2.4. Desorption studies

Desorption of Se from the synthesized polymer was studied by the treatment of previously loaded polymer with an excess of extracting reagent. HNO_3 at different concentrations, namely: 2 mol L^{-1}, 3 mol L^{-1}, 5 mol L^{-1}, 7 mol L^{-1}, and 9 mol L^{-1}, was used as an extractant. During regeneration, the mixtures were stirred for one hour, filtered and the polymer washed with deionized water, and dried prior to reuse.

2.5. Application of the developed polymer to wastewater samples

The synthesized polymer was applied for the removal of selenite ions from wastewater samples collected in the vicinity of gold mining activities in the Central Rand goldfield, Johannesburg.

Two samples were used (one pit water and surface water) collected from the Natalspruit, an acid mine drainage-impacted stream (26° 13′07.15″ S and 28° 07′52.74″ E). Sampling was done according to standard water sampling protocols (Hermond and Fechner-Levy 2000). The samples were filtered in the laboratory prior to adsorption experiments. The field measurements were carried out with a portable kit (Multi Line F/Set 3, WTW, Weilheim Germany) equipped with a pH electrode, an integrated temperature probe (Sen Tix 41), a standard conductively cell (Tetra Con 375), and an oxidation-reduction potential probe (Sen Tix ORP). The pH electrode was calibrated according to IUPAC recommendations against two buffer solutions pH 4 and pH 7 and an uncertainty of ±0.1 units. Metal analysis was carried out using ICP-OES. Anion concentrations were determined by ion chromatography (IC) (761 Compact, Metrohm, Switzerland).

In each analytical technique, the limit of detection (LOD) was calculated as 3 × standard deviation of the blank and the method quantitation limit (MQL) was calculated as 10 × standard deviation of the blank. Results are based on three replicates with relative standard deviation (RSD) <10%.

3. Modeling of analytical results

The results from adsorption studies were modeled using kinetic, equilibrium (isotherms), and thermodynamic models.

3.1. Kinetic models

The kinetic models that were used to fit the experimental data are as follows.

The pseudo first-order model was defined by the equation

$$\mathrm{Log}(q_e - q_t) = \log q_e - (k_1/2.303)t.$$

The plot of log $(q_e - q_t)$ vs. t gives a straight line.

The pseudo second-order model was defined by the equation

$$1/q_t = (1/k_2 q_e^2) + (1/q_e)t.$$

The plot of t/q_t vs. t gives a straight line.

The parameters in the above equations are defined as follows: q_e (mg g^{-1}) is the adsorption capacity at equilibrium, q_t (mg g^{-1}) is the adsorption capacity at time t, and k_1 and k_2 (1/min) are the rate constants for the pseudo first-order and pseudo second-order models, respectively. These are obtained from the slope of the plot of log $(q_e - q_t)$ vs. t.

3.2. Isotherm models

Adsorption isotherms describe the nature of the adsorbent–adsorbate interaction as well as the specific relation between the concentration of adsorbate and its degree of accumulation onto the adsorbent surface (Gupta et al. 2003; Li et al. 2008). In order to

understand the adsorption mechanism of Se onto the SCPEI surface, two adsorption isotherm models, Langmuir and Freundlich were used to fit the experimental data (Freundlich 1907). The experimental data for isotherm modeling were obtained by conducting the adsorption experiments using 1 g of SCPEI and 40 mL solutions of different Se concentrations under continuous stirring. At equilibrium, the solutions were filtered and the nonadsorbed Se was determined.

The Langmuir model is given by the following equation:

$$q_e = \frac{q_m b C_e}{1 + bC_e},$$

where q_e (mg g^{-1}) is the amount adsorbed per unit weight of adsorbent at equilibrium, C_e (mg L^{-1}) is the equilibrium concentration of the adsorbate, and q_m (mg g^{-1}) is the maximum adsorption capacity, and b (L mg^{-1}) is the constant related to the free energy of adsorption. The values of maximum capacity (q_m) and Langmuir constant (b) were calculated from the intercept and the slope of the plots.

The Freundlich model is given by the following equation:

$$q_e = K_F C_e^{1/n},$$

where K_F ($mg^{1-(1/n)}$ $L^{1/n}$ g^{-1}) is a constant correlated to the relative adsorption capacity of the adsorbent and n is a constant indicative of the intensity of the adsorption.

3.3. Thermodynamic modeling

The thermodynamic study was done by conducting the adsorption experiments at two different temperatures (15°C and 27°C). The concentrations obtained after adsorption were then used to calculate the activation energy (E_a) according to the Arrhenius equation:

$$E_a = \frac{R \cdot T_1 \cdot T_2 \cdot \ln \frac{K_2}{K_1}}{T_1 - T_2},$$

where E_a is the activation energy; R is the gas constant; T_1 and T_2 are the two different temperatures; k_1 and k_2 are rate constants for the two temperatures.

The constants k_1 and k_2 were calculated using the pseudo second-order equation at each temperature.

The magnitude of the activation energy gives an idea about the type of adsorption, namely physisorption (usually no more than 4.2 kJ mol^{-1}) or chemisorption (Klekamp and Urnbac 1993; Özcan, Öncü, and Özcan 2006).

4. Results and discussion

4.1. Characterization of sulfonated cross-linked polyethylenimine

FTIR spectroscopy was used to characterize the sulfonated derivative of cross-linked polyethylenimine (SCPEI) in order to confirm the introduction of the $–SO_3H$ chelating group. The FTIR spectrum is given in Figure 2.

The absorption bands at 1038.29 cm^{-1}, 1165.42 cm^{-1}, and 589.71 cm^{-1} confirmed the sulfonation reaction, as they refer to the presence of S = O sym, S = O asym, and

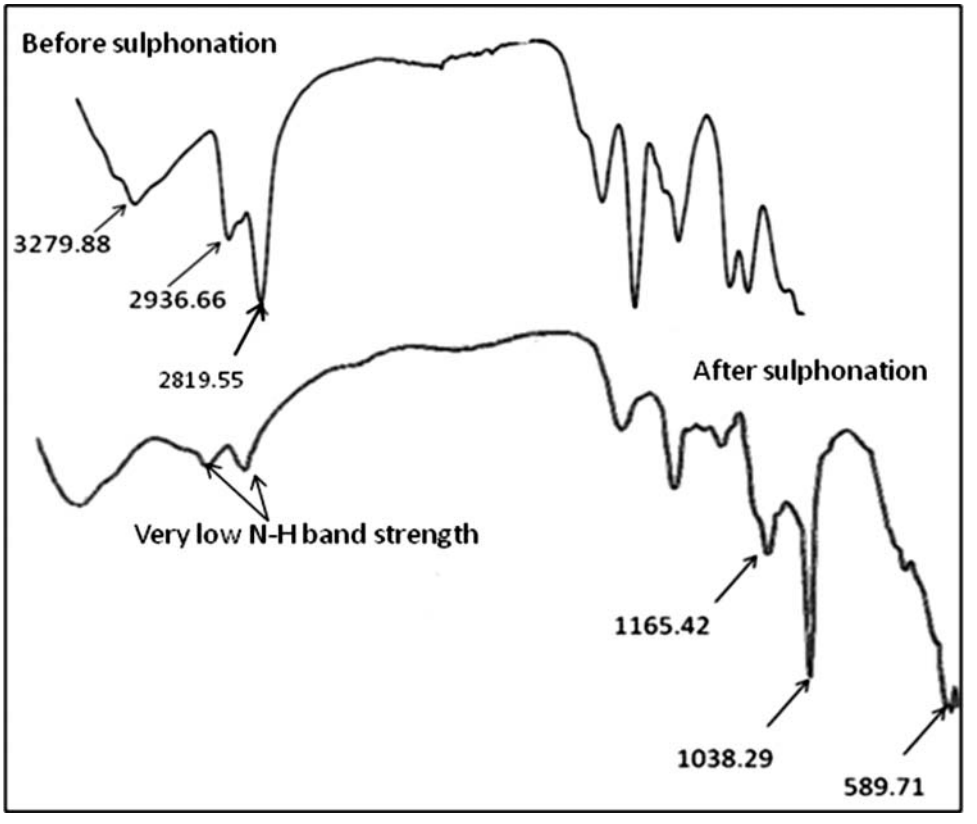

Figure 2. FTIR spectrum of CPEI and SCPEI.

S–O bonds, respectively. The difference in the absorption bands strength for the stretching vibration of N–H could be observed, with the sulfonated polymer yielding lower band strength. This could be attributed to the closure of some secondary amine sites during sulfonation of the polymer. The sulfonated polymer thus contains less secondary amine groups due to the reaction between these groups in CPEI and ($-SO_3H$) groups in chloropropanesulfonyl chloride (Saad, Cukrowska, and Tutu 2012).

4.2. Effect of contact time

The rate of adsorption is one of the most important parameters when designing a batch adsorption experiments. The experimental runs measuring the effect of contact time on the adsorption of Se were conducted at various time intervals (10–120 min) at the conditions: room temperature, pH 8, elemental concentration 40 mg L^{-1}, and adsorbent mass 1 g, in order to obtain the optimal time required for adsorption. The concentration of Se was determined at the end of each time. The obtained adsorption capacities (q_e) were then plotted against the equilibrium time for kinetic modeling.

Figure 3(a) shows the effect of contact time on the adsorption of Se onto SCPEI.

The adsorption increased dramatically with time, showing a gradual increase from 10 to 60 min, with no further increase beyond 60 min. Thus, the minimum required time for adsorption to be completed was 60 min.

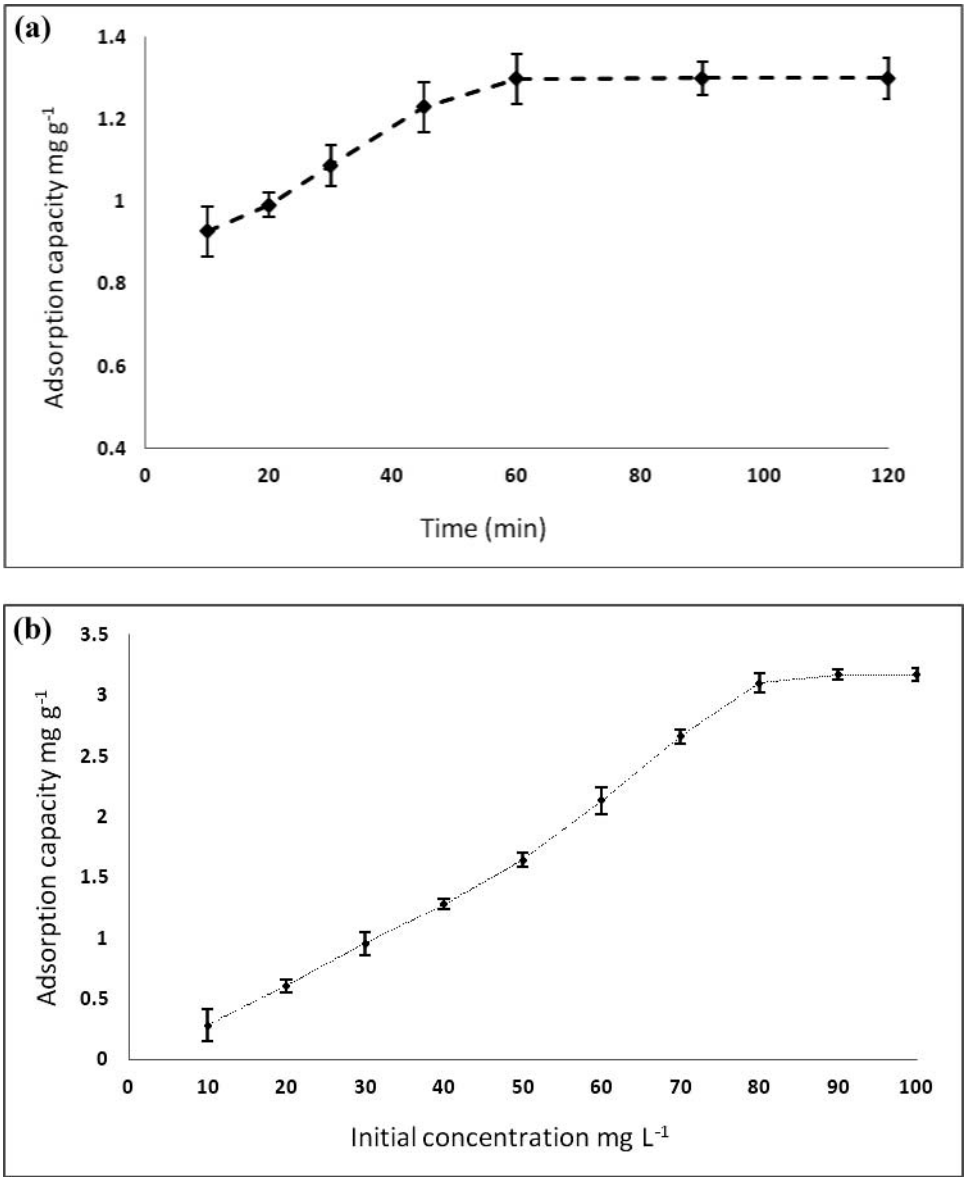

Figure 3. (a) Effect of contact time and (b) initial concentration on the adsorption process.

4.3. Effect of initial concentration

The results for the dependence of adsorption of Se onto SCPEI on initial concentration are given in Figure 3(b).

The adsorption capacity increased with increasing concentration from 0.284 mg g^{-1} at concentration of 10 mg L^{-1} gradually to 3.1 mg g^{-1} at concentration of 80 mg L^{-1}, with no further increase beyond 90 mg L^{-1} (3.17 mg g^{-1}). This could be indicative of maximum adsorption. It should be noted that at each concentration, adsorption increases and reaches a maximum after 60 min as shown in Figure 3.

Table 1. Removal of Se from synthetic solutions by SCPEI.

	C_f (mg L^{-1})	RSD	Adsorption capacity (mg g^{-1})	Adsorption efficiency (%)
pH 3	7.90	0.64	1.28	80%
pH 8	7.60	1.73	1.30	81%

Initial concentration of the ions = 40 mg L^{-1}; C_f: final concentration after adsorption; RSD: relative standard deviation ($n = 3$); LOD: limit of detection in mg L^{-1} = 0.003; MQL: method quantitation limit in mg L^{-1} = 0.01.

4.4. Effect of pH

One of the important factors affecting adsorption of element ions is pH of the solution. Solution pH affects the element binding sites of the adsorbent as well as the element chemistry in aqueous solution. The results for the removal of Se by SCPEI from synthetic solutions at two different pH values are presented in Table 1. The table shows the final concentrations obtained (C_f) after 60 min; in terms of adsorption capacity, percentage, as well as the RSD.

The adsorption percentages showed good removal efficiency at both pH values. As Se exists as a base in solutions, anion replacement could occur. It is in the same group in the periodic table with sulfur (S), thus there is similarity in their chemical behavior. This similarity allows them to replace each other (the Se adsorbed into the polymer surface and S released into the solution).

Furthermore, the adsorption of Se was not affected by the presence of other ions such as Hg, Pb, Zn, etc. However, the removal mechanism is completely different taking into account the fact that Se is a metalloid and exists in the solution as a base (oxoanion) whereas ions like Hg are metals. The mechanism of metals binding onto the polymer is based on the hard-soft Lewis acid-base theory, where the sulfur atom on the chelating group ($–SO_3H$) acts as a Lewis base and donates electrons to metals which are Lewis acids.

On the other hand, the removal of Se could be explained by the possibility of anion replacement between Se (as oxoanion) and $–SO_3H$. To investigate this mechanism, the concentration of S has been measured before and after adsorption. Figure 4(a) shows the concentration of the released sulfur (S) vs. the adsorbed amount of Se.

The results showed that as the amount of adsorbed Se increases, the released amount of S in the solution increases. This suggests the mechanism of Se removal as a substitution of HSO_3^- because of the group similarities between Se and S. They exist in the same group in the periodic table, thus there is similarity in their chemical behavior. This similarity allows them to replace each other (the Se is adsorbed into the polymer surface and the S is released into the solution).

Metals, e.g., Hg are removed via interaction with the sulfate group on the polymer. Thus, the adsorption of Se is by reaction of Se with the polymer backbone while that for Hg is between Hg-HSO_3H. Figure 4(b) demonstrates this mechanism.

4.5. Modeling of the adsorption process

The results for the kinetic modeling of the adsorption were confirmed by correlation coefficient (R^2 values) of the respective plots. A high value ($R^2 = 0.9968$) was obtained for the pseudo second-order compared to that of pseudo first-order model ($R^2 = 0.627$) which

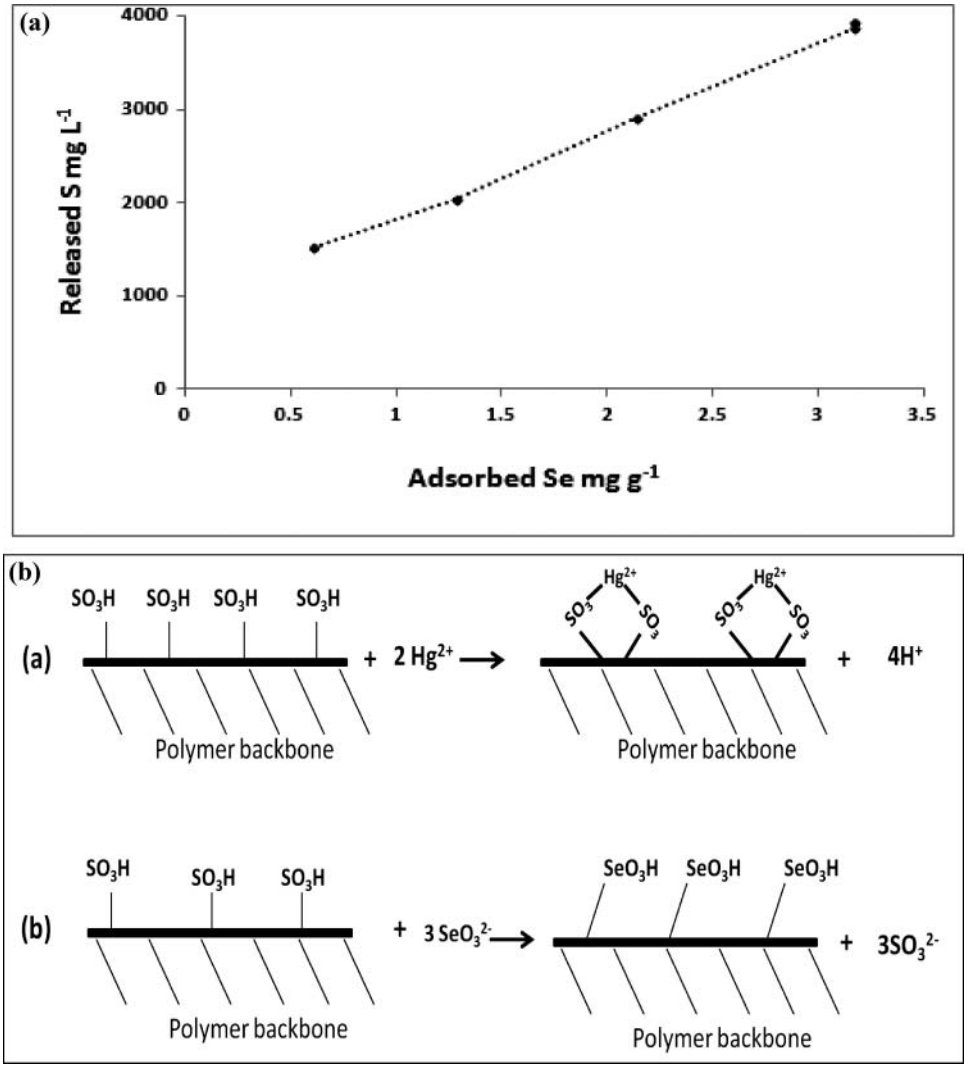

Figure 4. (a) Adsorbed Se vs. released S and (b) removal mechanism of Hg and Se.

demonstrates that pseudo second-order gives the best fit, implying that the adsorption occurs via a chemisorption process (Antures et al. 2003).

The results for the adsorption isotherms are presented in Table 2.

The results suggest that the Freundlich model best fits the data as shown by the correlation coefficient >0.95 whereas that for the Langmuir correlation coefficient is <0.95.

Table 2. Langmuir and Freundlich parameters for the adsorption of Se onto SCPEI.

	b	Langmuir R^2	q_m	K_f	Freundlich R^2	n
Se	1.247	0.536	11.58	4.204	0.963	0.340

This result demonstrates adsorption on a heterogeneous surface. It also assumes that the adsorption capacity of the adsorbent increases with increasing concentration of the adsorbate which is in agreement with the results obtained for the effect of initial concentration on adsorption.

From the thermodynamic study, an activation energy value (E_a) of 58.52 kJ mol^{-1} was obtained.

This elevated value implies that Se is adsorbed onto the SCPEI via a chemisorptions process which is consistent with the results obtained from kinetic modeling.

4.6. Desorption studies

Optimal recovery and regeneration was achieved at a concentration of 5 mol L^{-1} of the regeneration acid solution. Subsequently, regeneration of the used polymer was carried out using 5 mol L^{-1} acid concentration.

The regenerated SCPEI showed 72% removal efficiency and 1.16 mg g^{-1} removal capacity. This is a lower efficiency compared to that for a fresh polymer (dropped by 9%), but was still good.

Serial desorption was conducted in order to assess the amount of intractable Se that would remain bound to the polymer. For example, after a cycle of five desorptions (Figure 5), the adsorbed amount of Se onto SCPEI dropped by 0.8 mg g^{-1} (from 1.3 mg g^{-1} to 0.5 mg g^{-1} after the fifth desorption).

4.7. Application of the developed polymer to wastewater samples

The results for the adsorption of Se and other elements in the collected samples onto fresh SCPEI are given in Table 3.

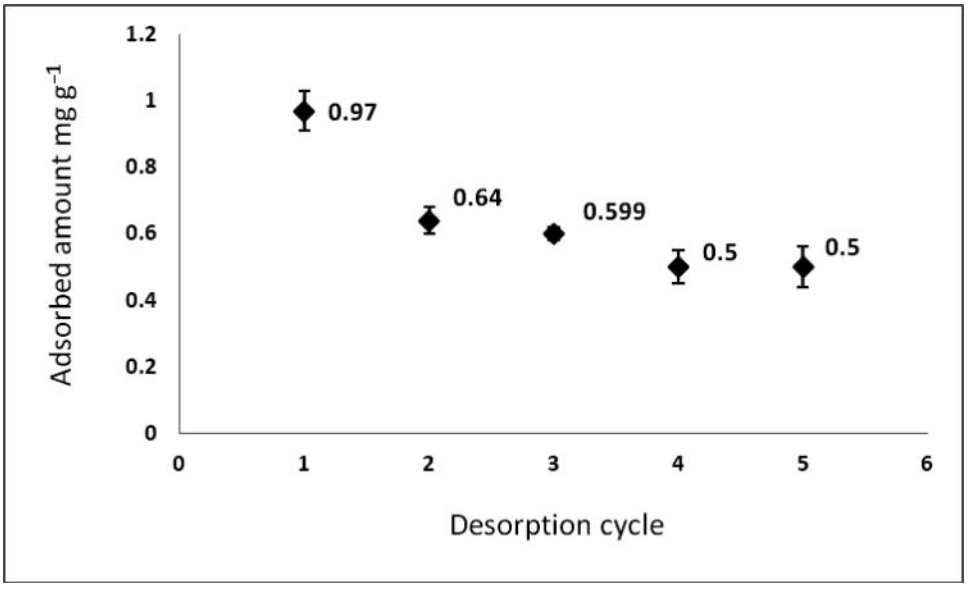

Figure 5. Desorption cycle of Se from SCPEI using 5 mol L^{-1} HNO_3.

Table 3. Removal of Se from mining wastewater samples.

Samples	Elements	C_i (mg L^{-1})	RSD ($n = 3$)	C_f (mg L^{-1})	RSD ($n = 3$)	Ads%
S W, pH (7.2) SO_4^{2-} (19.80 mg L^{-1})	As	0.12	2.59	0.05	1.53	57%
	Ni	1.50	5.28	0.37	2.16	75%
	Se	0.09	1.84	0.02	1.50	82%
Pit water pH $3SO4^{-2}$ (1669 mg L^{-1})	Cr	0.04	7.75	0.02	3.59	42%
	Fe	0.60	3.54	0.36	7.04	41%
	Ni	10.70	0.00	2.20	0.00	79%
	Zn	14.75	8.40	5.55	1.76	62%
	Se	0.05	8.66	0.002	7.56	96%

SW – surface water; C_i – initial concentration before adsorption; C_f – final concentration after adsorption.
LOD (mg L^{-1}): Cr – 0.003; As – 0.014; Fe – 0.002; Ni – 0.007; Zn – 0.008; Se – 0.017; SO_4^{2-} – 0.01 MQL (mg L^{-1}): Cr – 0.010; As – 0.047; Fe – 0.007; Ni – 0.023; Zn – 0.027; Se – 0.057; SO_4^{2-} – 0.03.

Although the concentration of Se detected in the two samples was very low, the adsorption trend was similar to that observed for the synthetic standard solutions. This confirms the high selectivity of SCPEI toward Se even in the presence of high concentrations of coexisting ions such as Ni and Zn in the pit water sample.

Generally, the results obtained from this study showed that the performance of SCPEI is comparable to that of other reported adsorbents of similar nature. Khajeh and coworkers (2007), for example, introduced a polymeric adsorbent (based on 2-vinylpyridine) for selective removal and preconcentration of Se from aqueous solutions. They obtained high efficiency and selectivity as well as good stability and reusability. The developed polymer was found to be very stable and resistant against treatment with acid and base, findings that are quite similar to those of this study.

A study by Suzuki et al. (2000) reported the removal of Se using the Zr(IV)-chelated polymer, where the adsorption of Se onto the polymer has been interpreted by a ligand substitution reaction. However, while they obtained very good results in terms of selectivity and adsorption capacity, this was found to be strongly pH dependent.

Another study by Min and Hering (1999) investigated the applicability of calcium-iron alginate beads for the removal of Se from aqueous solutions. According to their findings, there are some limitations of applying this adsorbent for water treatment, for instance, a kinetic limitation where an equilibrium time up to 120 h was needed to reach saturation. Another limiting factor is the regeneration process which was found to be very slow and reduced the stability of the adsorbent as well. Furthermore, the adsorbent was pH dependent and its efficiency was also dependent on the initial concentration of Se. Poor removal was observed at high initial concentration (less than 1%) with better removal at low concentration (5 mg $L^{-1)}$ but even in such condition the removal process was time consuming (24 h).

Unlike some of these reported adsorbents, the superior performance of SCPEI toward Se could be attributed to three main factors, namely: pH independence which represents an important factor for application to AMD-impacted water in which the pH can be as low as 3; good kinetics (fast removal) which makes it a more efficient and feasible adsorbent; and most importantly an excellent desorption capability, thus making it cost-effective.

5. Conclusions

A water-insoluble resin was synthesized by sulfonation of CPEI using 3-chloropropane-sulfonyl chloride and was successfully employed for the removal of selenite ions from standard solutions and wastewater samples.

The removal mechanism hinges on the existence of the chelating group present in the SCPEI, largely the $–SO_3H$, which facilitates the removal of oxoanions.

SCPEI exhibited commendable potential for reuse through regeneration by 5 mol L^{-1} which is a very significant factor to achieve more feasible and cost-effective removal as it reduces the disposal cost and limits the environmental impacts.

The Freundlich isotherm was found to be the best fit describing the experimental data, suggesting that adsorption occurred on a heterogeneous surface.

The pseudo second-order model was found to explain the adsorption kinetics most effectively. This model and the results of the thermodynamic study showed that Se adsorption occurred via chemisorption.

The study has shown in overall that SCPEI can be used for the abstraction of Se from wastewaters and can perform comparably to other remediation techniques. Moreover, this polymer has potential for use in filter systems for household use in communities that use borehole water impacted by mining and industrial wastewaters. The desorbed metals can be of use to metal processing industries.

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Chapter 8

Paper V

This paper reported

The development of another derivative (by thiolation

of cross-linked polyethylenimine) for the removal of Hg to achieve more

selectivity in which the competition of Se can be overcome.

Appl Water Sci
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ORIGINAL ARTICLE

Selective removal of mercury from aqueous solutions using thiolated cross-linked polyethylenimine

Dalia M. Saad · Ewa M. Cukrowska · Hlanganani Tutu

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Abstract A successful approach to develop an insoluble form of polyethylenimine with a thiol-based functional group for selective removal of Hg(II) from aqueous solutions is reported. The selectivity of the modified polymer for Hg(II) as well as its ability to be regenerated for re-use has been studied. The synthesised polymer exhibited high selectivity for Hg(II) with high removal efficiency of up to 97 %, even in the presence of competing ions. The Freundlich isotherm was found to best fit and describe the experimental data. The pseudo-second-order equation explains the adsorption kinetics most effectively implying chemisorption. The thermodynamic study of the adsorption process revealed high activation energies >41 kJ mol^{-1}, further confirming chemisorption as the mechanism of interaction between mercury ions and the polymer surface. The polymer exhibited good potential for re-use after many cycles of regeneration, giving good removal efficiency up to the fifth cycle.

Keywords Adsorption · Mercury · Thiolation · Selective removal

Introduction

Industrial development has left pronounced effects on the environment generally and on water resources specifically. Many industries generate waste products that contain high concentrations of heavy metals which are discharged directly or indirectly into water systems (Hang et al. 2009; Velea et al. 2008; Zhuang et al. 2009). In South Africa, the mining industry accounts for the largest portion of heavy metal contamination through acid mine drainage (AMD). The removal of these toxic metal ions is an important challenge taking into account that the current methods of remediating contaminated water such as ion-exchange resin, electrolytic or liquid extraction, electrodialysis, chemical precipitation, membrane filtration, and biosorption are sometimes inadequate due to the large quantities of these wastes, resulting in metal-bearing sludges which are difficult to dispose of. Furthermore, most of these traditional methods are expensive. Therefore, there is an urgent need for new feasible and cost effective methods (Ahmed et al. 2008; Ghoul et al. 2003).

There is also a need for such methods to be manipulated for effectiveness in removing certain targeted pollutants. This way, these techniques can be used in tandem with other non-selective methods, thus obtaining efficiency and cost effectiveness.

Among the separation and remediation techniques, polymeric adsorbents are some of the most efficient and widely applied in separation processes (Kwon et al. 2000; Shentu et al. 2007; Wang et al. 2001). They can be of varying configurations, but mainly consist of a polymer backbone and a ligand pendant on the backbone. Metal ions are usually bound to the polymer ligand by a coordinate bond (Kaliyappan and Kannan 2000). The advantage of this chemistry is that a selective removal can be achieved by choosing a suitable polymer ligand to target a specific metal.

It was demonstrated in our previous articles that phosphate and sulphate functional groups substituted in the backbone of polyethylenimine act as strong adsorption sites for removing specific metals in solution (Saad et al. 2012a, b). This study was aimed at developing a polymeric adsorbent based on a

D. M. Saad · E. M. Cukrowska (✉) · H. Tutu
Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, Johannesburg, South Africa
e-mail: ewa.cukrowska@wits.ac.za

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thiol functional group for selective removal of Hg from aqueous systems. Hg exposure can affect kidney functions, the central nervous system, and mental system. As such, its removal from environmental systems has become a research priority (Manohar et al. 2002; Rio and Delebarre 2003; Wahi et al. 2009; Cai and Jia 2010).

Cross-linked polyethylenimine was functionalized with ethylene sulphide (C_2H_4S) for targeted Hg(II) complexation.

This study gives a background to a wider study intended to introduce polymers of this type for use in household filter systems. It has emerged that, due to the scarcity of water, certain households around Johannesburg use mine-polluted groundwater as a source of drinking water. This is common in small plot holdings and farms (Dr. Carl Albrecht, Cancer South Africa, personal communication). Such water has been found to contain Hg and other toxic elements (Lusilao-Makiese et al. 2012). Another configuration would be to pack the polymer into small columns that can be placed in household containers (e.g. water jars) and left to contact with polluted water, allowing mass transfer of the Hg to the adsorbent in the column.

To assess the stability of the thiolated CPEI (TCPEI) for the above-mentioned purposes, the effects of some parameters on adsorption of Hg(II) were studied, namely pH, adsorbent amount, contact time, and the presence of competing ions. Regeneration of the polymer was also done so as to assess its re-usability.

Materials and methods

Materials

All the reagents and solutions were prepared using reagent-grade chemicals from Sigma-Aldrich (South Africa) without further purification.

Cross-linked polyethylenimine (synthesis reported by Saad et al. 2011) and ethylene sulphide were used for the synthesis of TCPEI. The Hg(II) solutions were prepared from $Hg(NO_3)_2$. Competing metal ion solutions were prepared from their nitrate salts, namely $Zn(NO_3)_2$, $Pb(NO_3)_2$, $Co(NO_3)_2$, $Cu(NO_3)_2$, $Fe(NO_3)_3$ H_2O, and $Ni(NO_3)_2$. Adjustments of pH for the adsorption experiments were conducted using 1 mol L^{-1} solutions of HNO_3 and NaOH. Deionised water (Millipore) was used for the preparation of all solutions.

Synthesis of thiolated cross-linked polyethylenimine (TCPEI)

Cross-linked polyethylenimine (CPEI) of 5 g was dissolved in 100 mL of water, and the pH of the solution was adjusted to 7. The solution was purged with nitrogen for 20 min followed by the addition of 1.73 mL of ethylene sulphide. The reaction mixture was then kept overnight under reflux at 90 °C. The collected product was rinsed with abundant deionised water and dried in an oven. The thiolation reaction scheme is shown in Fig. 1.

Fourier Transform Infra Red spectroscopy was used to characterise the thiolated derivative of cross-linked polyethylenimine (TCPEI) to confirm the introduction of thiol group. The content of sulphur in the synthesised polymer was determined using LECO-932 CHNS analyser from LECO Corporation (Michigan, USA).

Batch adsorption studies

Batch adsorption experiments were conducted using a 1,000-mg L^{-1} stock standard solution of $Hg(NO_3)_2$ from which 40 mg L^{-1} working standard solutions were obtained by serial dilution. This concentration was arbitrarily chosen as it represents a "worst-case" scenario of pollution by most toxic elements (e.g. mercury, uranium,

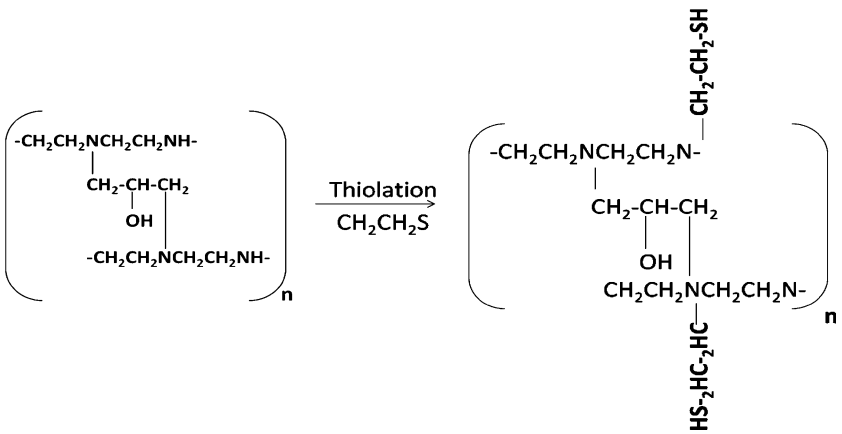

Fig. 1 Thiolation reaction scheme

arsenic and vanadium) in mining-impacted waters in the Witwatersrand Basin goldfields (Tutu et al. 2009).

Adsorption experiments were performed in 50 mL flasks at room temperature. Different amounts of synthetic TCPEI were weighed out into each flask to assess the optimum amount of the adsorbent; 40 mL of 40 mg L^{-1} solution of $Hg(NO_3)_2$ standard was then added to each flask and stirred using magnetic stirrer. Adsorption at different pH values was assessed. At equilibrium, the solutions were filtered and the equilibrium concentrations were determined using an inductively coupled plasma optical emission spectroscopy (ICP-OES) (Genesis Spectro, Germany). The same procedure was followed using the multi-component solution to assess the effect of competing ions. The amount of ions adsorbed per unit mass of adsorbent was calculated on the basis of the mass balance equation:

$$q_e = \frac{(C_i - C_f) \times V}{(1000 \times P)} \quad (1)$$

where q_e (mg metal g^{-1} polymer) is the adsorption capacity, C_i (mg L^{-1}) is the initial concentration of Hg(II) in the solution, C_f (mg L^{-1}) the concentration of Hg(II) in the filtrate, V (mL) the volume of initial solution and P (g) is the amount of polymer used.

Effect of adsorbent amount

The amount of adsorbent was optimised to obtain the optimal removal. Adsorption experiments were conducted using different amounts of TCPEI, namely 0.03, 0.05, 0.1, 0.2, 0.5, and 1.0 g, and synthetic standard mercury solutions of 40 mg L^{-1} at room temperature and fixed time.

Effect of contact time

Adsorption experiments were conducted at room temperature (27 °C) to obtain the optimal time required for adsorption. Adsorption was studied at various time intervals (10–120 min) and fixed concentration (40 mg L^{-1}). The concentration of Hg(II) was determined at the end of each time. The obtained equilibrium capacities (q_e) were then plotted against the equilibrium time for kinetic modelling.

Desorption studies

Desorption of Hg(II) from TCPEI was studied by treating the previously loaded polymer with an excess of extracting reagent. HNO_3 at different concentrations, namely 2, 3, 5, and 7 mol L^{-1}, was used as an extractant. During regeneration, the mixtures were stirred for 1 h, filtered and the polymer washed with deionised water and dried prior to reuse, while the filtrates were analyzed by ICP-OES.

All experiments were repeated three times ($n = 3$), and the limit of detection (LOD) was calculated as 3 × standard deviation of the blank and the method quantitation limit (MQL) was calculated as 10 × standard deviation of the blank.

Modelling of analytical results

The results from adsorption studies were modelled using kinetic (pseudo-first-order and pseudo-second-order

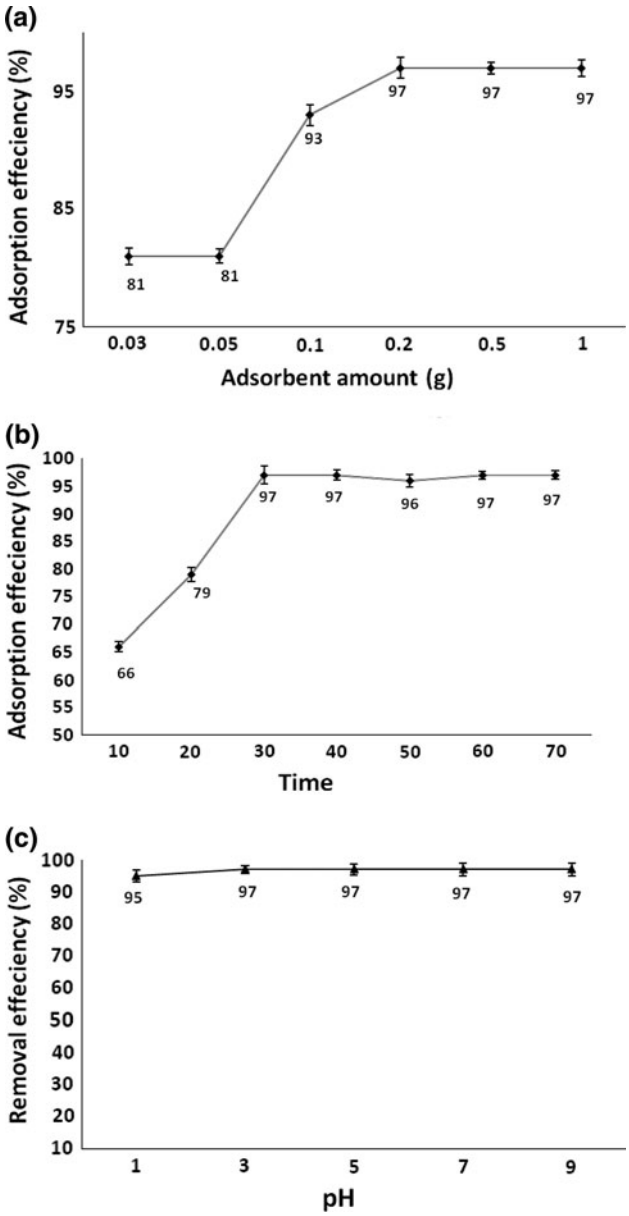

Fig. 2 Effect of adsorbent amount (**a**), contact time (**b**), and pH (**c**) on the adsorption process. Initial concentrations = 40 mg L^{-1}, contact time = 30 min, at pH 3 and room temperature (27 °C). Initial concentrations = 40 mg L^{-1}, adsorbent amount = 0.2 g, at pH 3 and room temperature (27 °C) . Initial concentrations = 40 mg L^{-1}, contact time = 30 min, adsorbent amount = 0.2 g, at room temperature (27 °C)

Table 1 Removal efficiencies of elements in a multi-component solution

	Hg	Co	Cu	Se	Pb	Zn	Ni	Fe
C_f (mg L^{-1})	1.1	4.9	5.1	29.1	7.6	8.3	9.1	21.9
Rsd	0.678	3.33	1.857	1.9	2.76	2.693	2.013	2.002
Capacity (mg g^{-1})	7.78	7.02	6.98	0.436	6.48	6.34	6.18	0.724
Efficiency (%)	97	88	87	28	81	79	77	43
LOD	0.002	0.024	0.003	0.001	0.034	0.090	0.081	0.050
MQL	0.001	0.001	0.026	0.067	0.054	0.022	0.003	0.033

Initial concentration of the ions = 40 mg L^{-1}

C_f Final concentration after adsorption, *RSD* relative standard deviation ($n = 3$), *LOD* limit of detection in mg L^{-1}, *MQL* method quantitation limit in mg L^{-1}

equations), isotherms (Langmuir and Freundlich), and thermodynamic models.

Speciation modelling of the metal ions in solution was conducted using MEDUSA software (KTH Royal Institute of Technology, Sweden).

Kinetic models

The kinetic models that were used to fit the experimental data are as follows.

The pseudo first-order model was defined by the equation

$$\log\,(q_e - q_t) = \log\; q_e - (k_1/2.303)t$$

The plot of log $(q_e - q_t)$ vs. t gives a straight line.

The pseudo-second-order model was defined by the equation

$$1/q_t = (1/k_2 q_e^2) + (1/q_e)t$$

The plot of t/q_t vs. t gives a straight line.

The parameters in the above equations are defined as follows: q_e (mg g^{-1}) is the adsorption capacity at equilibrium, q_t (mg g^{-1}) is the adsorption capacity at time t, and k_1 and k_2 (1/min) are the rate constants for the pseudo-first-order and pseudo-second-order models, respectively. These are obtained from the slope of the plot of log $(q_e - q_t)$ vs. t.

Isotherm models

Adsorption isotherms describe the nature of the adsorbent–adsorbate interaction as well as the specific relation between the concentration of adsorbate and its degree of accumulation onto the adsorbent surface (Gupta et al. 2003; Li et al. 2008). To understand the adsorption mechanism of Hg(II) onto the TCPEI surface, two adsorption isotherm models, Langmuir and Freundlich were used to fit the experimental data (Cozmuta et al. 2012; Freundlich 1926). The experimental data for isotherm modelling were obtained by conducting the adsorption experiments using 1 g of TCPEI and 40 mL solutions of different Hg(II) concentrations under continuous stirring. At equilibrium, the solutions were filtered and the non-adsorbed Hg(II) was determined.

The Langmuir model is given by the following equation:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \tag{2}$$

where q_e (mg g^{-1}) is the amount adsorbed per unit weight of adsorbent at equilibrium, C_e (mg L^{-1}) is the equilibrium concentration of the adsorbate, and q_m (mg g^{-1}) is the maximum adsorption capacity, and b (L mg^{-1}) is the constant related to the free energy of adsorption. The values of maximum capacity (q_m) and Langmuir constant (b) were calculated from the intercept and the slope of the plots.

The Freundlich model given by the following equation:

$$q_e = K_F C_e^{1/n} \tag{3}$$

where K_F ($mg^{1-(1/n)}$ $L^{1/n} g^{-1}$) is a constant correlated to the relative adsorption capacity of the adsorbent and n is a constant indicative of the intensity of the adsorption.

Thermodynamic modelling

The thermodynamic study was done by conducting the adsorption experiments at two different temperatures (15 and 27 °C). The concentrations obtained after adsorption were then used to calculate the activation energy (E_a) according to the Arrhenius equation:

$$E_a = \frac{R \times T_1 T_2 \ln\left(\frac{k_2}{k_1}\right)}{T_1 - T_2} \tag{4}$$

where E_a is the activation energy, R is the gas constant; T_1 and T_2 are the two different temperatures; k_1 and k_2 are rate constants for the two temperatures.

The constants k_1 and k_2 were calculated using the pseudo-second-order equation at each temperature.

The magnitude of the activation energy gives an idea about the type of adsorption, namely physisorption (usually

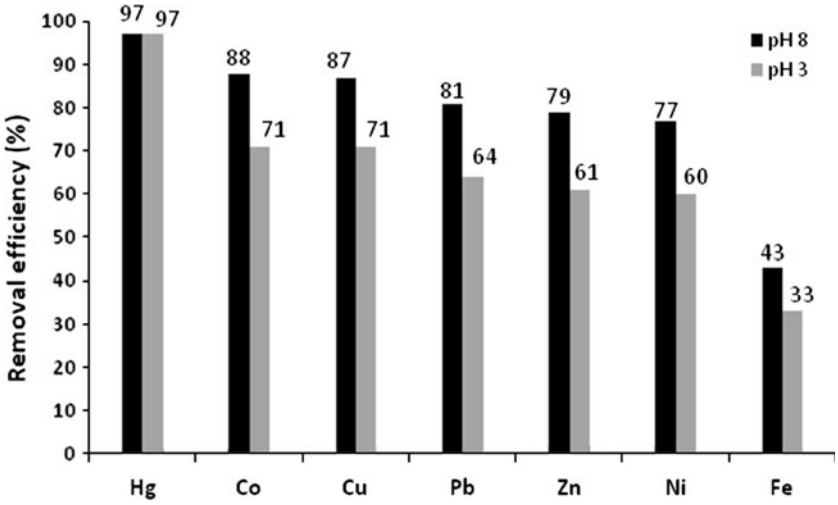

Fig. 3 Comparison between pH dependency of Hg(II) and competing ions removal. Initial concentrations = 40 mg L^{-1}, adsorbent amount = 0.2 g, contact time = 30 min at room temperature (27 °C)

no more than 4.2 kJ mol^{-1}) or chemisorption (Klekamp and Urnbac 1993; Özcan et al. 2006).

Results and discussion

Characterisation of thiolated cross-linked polyethylenimine

Sulphur content could be used as an indicator of the thiolation of the polymer since polyethylenimine only contains C, N, and H. The results from CHNS analysis confirmed the introduction of the thiol group with a sulphur content of 9.1 % being recorded.

IR characterisation confirmed the presence of the thiol group as the sharp peaks observed at 671.47 and 721.80 cm^{-1} which correspond to the stretching vibration of C–S (Coates 2000).

Effect of adsorbent amount

The results for the dependence of adsorption of Hg(II) on the amount of the polymer are shown in Fig. 2a.

The results showed that adsorption increased sharply from 81 % with an adsorbent amount of 0.03 and 0.05 g, 93 % with 0.1 g of adsorbent, and increased and remained constant at 97 % for 0.2–1 g. Thus, 0.2 g was considered as the optimum adsorbent amount required for optimal adsorption.

Effect of contact time

The experimental runs measuring the effect of contact time on the adsorption of Hg(II) were conducted at various time intervals between 10 and 120 min and at room temperature, pH 7, elemental concentration 40 mg L^{-1}, and an

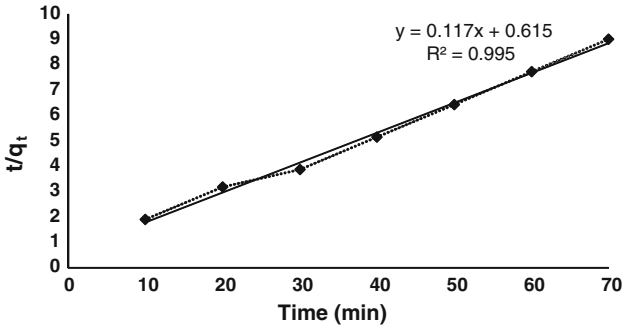

Fig. 4 Pseudo-second-order plot for the adsorption process. Initial concentrations = 40 mg L^{-1}, adsorbent amount = 0.2 g, at pH 3 and room temperature (27 °C)

adsorbent mass of 0.2 g, to obtain the optimal time required for adsorption. The concentration of Hg(II) was determined at the end of each time. The obtained equilibrium capacities (q_e) were then plotted against the equilibrium time for kinetic modelling. Figure 2b shows the effect of contact time on the adsorption of Hg(II).

Adsorption increased rapidly with an increase in contact time from 10 to 30 min. A further increase in time had no effect on the adsorption. A maximum contact time of 30 min was therefore considered as the optimum time for adsorption.

Effect of pH

Synthetic standard solutions of 40 mg L^{-1} with a fixed quantity of adsorbent, fixed time, and fixed temperature were used. The pH of the synthetic solutions was adjusted to five different pH values, namely 1, 3, 5, 7, and 9, using 1 mol L^{-1} sodium hydroxide and 1 mol L^{-1} hydrochloric acid. Figure 2c shows adsorption at different pH values.

The adsorption percentages showed high removal efficiency independent of pH. This independence of the

adsorption of Hg(II) on the pH could hinge on the high affinity of the Hg(II) to thiol group on the polymer surface, as such outperforming the hydrogen ions.

Effect of competing ions

To investigate the selectivity of TCPEI towards Hg(II), adsorption experiments were performed in the presence of competing ions using multi-component standard solutions containing Co(II), Cu(II), Pb(II), Zn(II), Ni(II), Fe(III), and Hg(II) at pH 7.3 and adsorbent amount of 0.2 g. Table 1 shows the final metal concentrations obtained after adsorption from an initial concentration of 40 mg L^{-1} for all metals. The adsorption capacity, efficiency (%) and the relative standard deviation (RSD) are based on three measurements ($n = 3$).

TCPEI showed good removal efficiency for all metals except Fe. However, the removal of Hg(II) was still the highest. The effect of competing ions was further studied at low pH of 3 to assess the effect of pH on the removal of Hg(II) in the presence of other elements. Figure 3 shows the removal efficiency of elements in a multi-component solution in acidic and basic conditions.

The results show that the removal of Hg(II) by TCPEI was independent of pH, whereas that of other ions was highly dependent. From speciation modelling using MEDUSA, the following species were found to be dominant at pH 3: Hg^{2+}, Co^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+}, Fe^{3+} and $FeOH^{2+}$. At pH 8, the following species were observed to be dominant: $HgOH^{+}$, $Hg(OH)_2$; $CoOH^{+}$, $Co(OH)_2$, $Cu(OH)_2$, $Pb(OH)_2$, $Zn(OH)_2$, $Ni(OH)_2$ and $Fe(OH)_3$. It can be observed that, at pH 3, the metals exist as divalent ions in solution. Thus, any adsorption is influenced by the affinity of the metal to the adsorbent surface. This binding is based on the hard–soft Lewis acid–base theory where the sulphur on the thiolated polymer acts as a Lewis base and binds the metal (Lewis acid) by a coordinate bond (Pearson 1968). Since Hg(II), Co(II) and Cu(II) are soft acids, they tend to preferentially bind to sulphur (a soft base) compared to other metals. However, the affinity of thiol to Hg(II) is superior compared to that for Co(II) and Cu(II), a property that has earned thiol the name mercaptan or mercury capturing (Dujardin et al. 2000). Ni(II), Zn(II) and Pb(II) showed good adsorption as well since they are considered moderate acids (or borderlines acids) and as such they can bind to either soft or hard bases (Pearson 1968). Fe(III), on the other hand, is a hard acid, hence its low removal efficiency. At pH 8, it can be observed that the metals, except partly for Hg and Co, are completely hydrolysed and form precipitates. Their adsorption at this pH is largely due to precipitation, while that for Hg and Co could be due to the combination of both precipitation and interaction of $HgOH^{+}$ and $CoOH^{+}$ with sulphur.

Kinetic modelling of adsorption process

The high correlation obtained by plotting the linearised form of pseudo-second-order model ($R^2 = 0.995$) compared to that for the pseudo-first-order model ($R^2 = 0.758$) demonstrated that the former gives a better fit, implying that the adsorption occurs via a chemisorption process (Antures et al. 2003). A plot of the linearised form of pseudo-second-order model (t/q_t vs. t) is given in Fig. 4.

Adsorption isotherms

The results from isotherm modelling suggest that the Freundlich model fits the data better as shown by the correlation coefficient of 0.963, whereas that for the Langmuir correlation coefficient is 0.536. This result demonstrates adsorption on a heterogeneous surface. It also assumes that the adsorption capacity of the adsorbent increases with increasing concentration of the adsorbate.

Thermodynamic studies

The calculated activation energy value (E_a) for the adsorption of Hg(II) onto TCPEI surface was 55.97 kJ mol^{-1}. This elevated value implies that Hg(II) is adsorbed onto the TCPEI via a chemisorption process which is consistent with the results obtained from kinetic modelling. k_1 and k_2 values are 0.027 and 0.021, respectively.

Desorption studies

Desorption results for TCPEI by different nitric acid concentrations are shown in Fig. 5. The results show the concentrations of Hg(II) desorbed by 2, 3, 5, and 7 mol L^{-1} of HNO_3.

The desorbed amount of Hg(II) increased with increasing HNO_3 concentration from 3.3 mg L^{-1} of 2 mol L^{-1} HNO_3 to 31 mg L^{-1} of 5 mol L^{-1} HNO_3, with no further

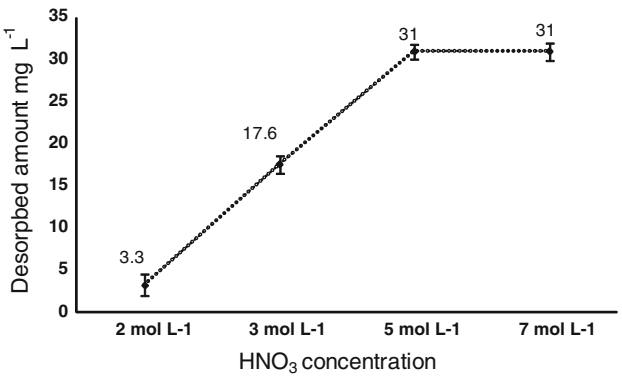

Fig. 5 Desorption of Hg from TCPEI by different HNO_3 concentrations

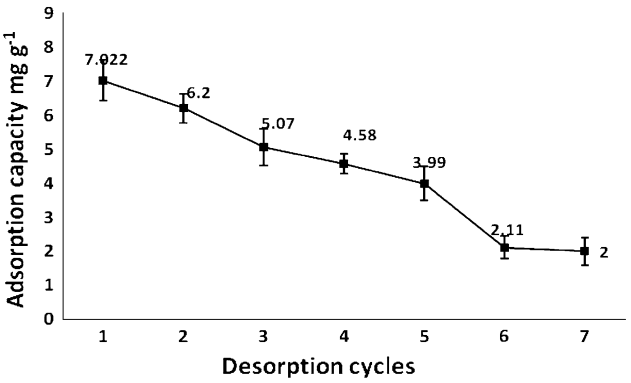

Fig. 6 Adsorption capacity after several subsequent desorptions. Initial concentrations = 40 mg L^{-1}, adsorbent amount = 0.2 g, contact time = 30 min at pH = 3 and room temperature (27 °C)

desorption beyond that. Subsequently, regeneration of TCPEI was carried out using 5 mol L^{-1} acid concentration.

The regenerated TCPEI showed 88 % removal efficiency and 7.022 mg g^{-1} removal capacity after one cycle of desorption. This is a lower efficiency compared to that for a fresh polymer (dropped by 9 %), which was still good.

Serial desorptions were conducted to assess the amount of intractable Hg(II) that would remain bound to the polymer. For example, after seven desorption cycles (Fig. 6), the amount of Hg(II) adsorbed onto TCPEI dropped by 5.48 mg g^{-1} (from 7.78 mg g^{-1} for the fresh polymer to 2.00 mg g^{-1} after the seventh desorption). The decrease of the removal efficiency could be attributed to the fact that, after each desorption process, there will be an amount of Hg(II) that would remain bound to the polymer surface and hence reduce the available sites for adsorption. The removal efficiency decreased in the following percentages: 97 > 88 > 78 > 63 > 57 > 50 > 26 > 25. This suggests that TCPEI could be efficiently re-usable up to five cycles, beyond which the removal efficiency drops below 50 %.

Generally, the results obtained from this study showed that the performance of TCPEI outperforms other reported adsorbents in terms of selectivity and pH dependency. Sreedhar and Anirudhan (1999) studied the removal of Hg using polyacrylamide grafted onto sawdust which had a superior removal capacity, but this was more dependent on the pH (less removal efficiency was observed at pH below 5.5). This limits the use of the adsorbent for Hg recovery from low pH solutions, e.g. AMD-impacted waters in which pH can be lower than 3. Moreover, the removal procedure was time consuming, taking 5 h to reach the optimum removal. Another study by Kesenci et al. (2002) demonstrated very fast adsorption using poly(ethyleneglycol dimenthacrylate-co-acrylamide) beads, where the largest amount of Hg was attached to the adsorbent within the first 10 min with saturation gradually reached within 30 min. Beside the advantage of the fast kinetics, it also showed some demerits such as the high dependency on the pH as well as the poor selectivity towards Hg in the presence of Pb.

Rio and Delebarre (2003) also reported the removal of Hg using silico-aluminous fly ashes and sulfo-calcic fly ashes. They obtained removal efficiencies of 54 and 81 %, respectively. According to their explanation, the difference on the removal efficiency is based on the chemical composition of two fly ashes, in which the one with high removal efficiency contains more sulphur than the other one with poor removal. However, in both cases, the removal process was time consuming, taking 72 h to reach the equilibrium, while in our case, this was achieved in 30 min.

Liu and Guo (2006) reported the removal of Hg using polyacrylamide-grafted attapulgite (PAM-ATP) with removal capacity of 1.12 mg g^{-1}, which is quite similar to the results of this study. On other hand, some differences in terms of efficiency, selectivity, influencing of different conditions such as pH, and time were demonstrated.

In another study by the authors (Saad et al. 2012b), good efficiency of sulphonated cross-linked polyethylenimine was reported with up to 87 % removal of Hg(II), but Se was found to highly compete with Hg(II). In this sense, TCPEI represents a good alternative for Hg(II) removal considering its high selectivity and independence of pH, thus making it an efficient adsorbent for the intended application of this study.

Conclusions

A new, efficient polyethylenimine derivative has been developed by thiolation and successfully employed for the removal of mercury from aqueous solutions under optimal conditions, namely 30 min contact time, 40 mg L^{-1} initial concentration, and 0.2 g adsorbent amount.

The modified polymer showed high efficiency and selectivity towards Hg(II) independent of pH and competing ions, thus outperforming most of the reported adsorbents for Hg capture.

The Freundlich isotherm was found to be the best fit describing the experimental data, suggesting that adsorption occurred on a heterogeneous surface. The pseudo-second-order model was found to explain the adsorption kinetics most effectively. This model and the results of the thermodynamic study showed that Hg(II) adsorption occurred via chemisorption.

The possibility of re-using the developed polymer is also a very significant factor especially with respect to cost effectiveness of the removal process.

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Chapter 9

Paper VI

This paper investigated:

The use of the phosphonated derivative

in fixed-bed mode in order to assess the possibility of designing

an adsorption column for the removal of U. The fixed-bed column study

is to assess the performance of the materials for possible use for

water purification in household filter systems.

Applied Water Science

Column adsorption studies for the removal of U by phosphonated cross-linked polyethylenimine: modelling and optimization

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Corresponding Author:	Hlanganani Tutu SOUTH AFRICA
Corresponding Author Secondary Information:	
Corresponding Author's Institution:	
Corresponding Author's Secondary Institution:	
First Author:	Dalia Saad, MSc
First Author Secondary Information:	
Order of Authors:	Dalia Saad, MSc
	Ewa Cukrowska
	Hlanganani Tutu
Order of Authors Secondary Information:	
Abstract:	A continuous fixed bed adsorption study was carried out by using phosphonated cross-linked polyethylenimine (PCPEI) as an adsorbent for the removal of U from aqueous solutions. The effect of inlet metal ion concentration (40, 70, and 100 mg L-1), feed flow rate (1, 2, and 3 ml min-1), and polymer bed height (2.5, 3.2 and 4.5 cm) on the breakthrough characteristics of the fixed bed adsorption system at pH 2 were studied. The results showed that the breakthrough time appeared to increase with increase of bed height but decreased with increase of both influent U concentration and flow rate. Modelling of the dynamics of the fixed-bed adsorption process was studied and the application of different models to describe the breakthrough curves showed that the model of Adams-Bohart describes only the initial part of the breakthrough curves whereas the Thomas and Yoon-Nelson model gave better results for the operating conditions.
Response to Reviewers:	see attachment

Column adsorption studies for the removal of U by phosphonated cross-linked polyethylenimine: modelling and optimization

Dalia M. Saad, Ewa Cukrowska and Hlanganani Tutu*

School of Chemistry, Molecular Science Institute, University of the Witwatersrand, Johannesburg, South Africa

Corresponding author: Dr. H. Tutu

Tel: (011) 717 6771

E-mail: Hlanganani.tutu@wits.ac.za

Abstract

A continuous fixed bed adsorption study was carried out by using phosphonated cross-linked polyethylenimine (PCPEI) as an adsorbent for the removal of U from aqueous solutions. The effect of inlet metal ion concentration (40, 70, and 100 mg L^{-1}), feed flow rate (1, 2, and 3 ml min^{-1}), and polymer bed height (2.5, 3.2 and 4.5 cm) on the breakthrough characteristics of the fixed bed adsorption system at pH 2 were studied. The results showed that the breakthrough time appeared to increase with increase of bed height but decreased with increase of both influent U concentration and flow rate. Modelling of the dynamics of the fixed-bed adsorption process was studied and the application of different models to describe the breakthrough curves showed that the Thomas and Yoon-Nelson model gave better results for the operating conditions.

Keywords: uranium removal; breakthrough curves; fixed-bed columns.

Introduction

Environmental pollution has become of global concern and attracts much attention. Water bodies are the most common natural resources that have been contaminated as a result of different human activities. One of the most important environmental problems related to water pollution throughout the world is the contamination of water bodies by heavy metal ions because of their toxic effects on the environment and human health (Akpor and Muchie, 2010; Cavus and Gurdag, 2008; Calmano and Förstner, 1983).

Among many toxic metals uranium is known to be one of the most toxic for human health mostly because of its radioactivity and carcinogenicity, thus its maximum level in drinking water recommended by the World Health Organization is 0.015 mg L^{-1}. Uranium is released into the aqueous environment through different sources such as the acid drainage waters from uranium mines. The uranium concentration of acid drainage water from uranium mines was reported in the range of 6-14 mg L^{-1}. Moreover, uranium mining generates around one billion m3 of mill tailings with uranium concentration of nearly 40 mg Kg^{-1}.

Many studies and methods have been developed to eliminate U from aqueous solutions including ion-exchange resins, electrolytic or liquid extraction, electro dialysis, chemical precipitation, membrane filtration, and biosorption (Ahmed et al. 2008). The use of polymeric adsorbents is one of the most common methods. Many studies have reported the successful application of different polymers for the removal of U and these include sulfonated

polyethylenimine, phosphonated polyethylenimine, polyvinylimidazole, polyacrylamide, polyacrylamidoglycolic, and polyacrylamidomethylpropanesulfonic acid (Martinot et al. 1997; Leroy et al. 2003). These polymers have largely been studied in batch sorption mode.

Although batch adsorption experiments provide important information on adsorption equilibrium characteristics and adsorption kinetics, the data obtained is not sufficient to provide accurate scale-up data required in the design of adsorption columns. Therefore, studies of column adsorption systems are needed, in which the most important parameter to be determined is the column breakthrough curves, that is useful for the determination of the operating life span of the fixed adsorbent bed (Bielicka-Daszkiewicz and Voelkel 2009; Naja and Volesky 2006; Chu 2003).

This study, therefore, was aimed at testing the performance of fixed-bed columns packed with PCPEI for the removal of U. Our previous study demonstrated that this polymer offers excellent potential for U removal using batch sorption experiments.

The breakthrough and exhaustion points were determined for fixed-bed columns packed with PCPEI used for the continuous adsorption of U from aqueous solutions. The system variables or parameters such as solution flow rate, inlet concentration and bed height were investigated.

Materials and methods

Materials

All the reagents and solutions were prepared using reagent-grade chemicals from Sigma Aldrich (South Africa) without further purification.

Cross-linked polyethylenimine (synthesis reported by Saad et al. 2011) and Phosphorous acid were used for the synthesis of PCPEI. The U solutions were prepared from $UO_2(NO_3)_2.6\ H_2O$. Adjustments of pH for the adsorption experiments were conducted using 1 mol L^{-1} solutions of HNO_3 and NaOH. Deionized water (Millipore) was used for the preparation of all solutions.

Synthesis of phosphonated cross-liked polyethylenimine (PCPEI)

The synthesis of PCPEI was carried out according to the method reported by Saad et al. (2012). Cross-linked polyethylenimine, 2.5 g, was placed in 80 mL of 6 mol L^{-1} HCl. Phosphorous acid, 19.31 g, was added and the mixture was heated under reflux at 90^{o}C. Formaldehyde, 38 mL, was added drop wise over a period of an hour and the reaction was left over night. A pale powdery

yellow solid was obtained, washed with abundant deionised water before drying in an air oven at 30^{o}C. The solid was then pulverised and sieved (less than 1 mm).

Fixed-bed column studies

Figure 1 represents the schematic diagram of the fixed-bed adsorption system. Continuous flow adsorption studies were conducted in a column made of glass tube having an inner diameter of 1.5 cm and height of 12 cm. The column was packed with PCPEI. A layer of glass wool was placed at the bottom of the column to prevent loss of the adsorbent. A peristaltic pump (MASTERFLEX L/S, Heidolph 5201) was used to pump the standard metal solution (40 mg L^{-1} of U, at pH 2 and room temperature) downward through the column at a constant flow rate of 1 mL min^{-1}. The concentration of 40 mg L^{-1} of U was chosen arbitrarily for the "worst case" scenario of U load in water emanating from gold mining activities around Johannesburg (Tutu et al. 2009). The effluent samples were collected at specified times and measured for the remaining metal concentration using ICP-OES (Spectro, Germany).

Figure 1

Effect of flow rate

The effect of feed flow rate on the adsorption of U onto PCPEI was investigated by varying the feed flow rate (1, 2, and 3 ml min^{-1}) while maintaining a constant bed height of 4.5 cm and inlet concentration of 40 mg L^{-1}.

Effect of inlet concentration

The effect of inlet concentration on the column performance was studied by varying the U concentration of 40, 70, and 100 mg L^{-1} while maintaining a constant adsorbent bed height and feed flow rate.

Effect of bed height

In the first stage, the bed height was changed (2.5, 3.2, and 4.5 cm) with amount of 1, 1.55, and 2 g, respectively. This to assess the height required for optimal removal while the inlet U concentration in the feed and the flow rate were held constants at 40 mg L^{-1} and 1 mL min^{-1},

respectively.

Modelling of analytical results

The dynamic behaviour of the columns was predicted using Adams–Bohart, Thomas, and Yoon–Nelson models. These models are important when designing an efficient fixed-bed adsorption system with the optimum required conditions.

Adams-Bohart model

This model was established by Adams and Bohart to describe the relationship between (C_t/C_0) and time. The Adams-Bohart model basically describes the initial part of the breakthrough curve and focuses on some characteristic parameters such as the maximum adsorption capacity (N_0) and kinetic constant K_{AB} (Aksu and Gonen 2004; Chowdhury et al. 2013). The mathematical equation of the model can be written as:

$$\ln\left(C_t/C_0\right) = K_{AB}\,C_0 t - K_{AB}\,N_0\left(Z/U_0\right) \qquad (1)$$

Where C_0 and C_t are the inlet and outlet adsorbate concentration, respectively (mg L^{-1}), Z is the bed height (cm), U_0 is the superficial velocity (cm min^{-1}), N_0 is the saturation concentration (mg L^{-1}), and K_{AB} is the kinetic constant (L mg^{-1} min^{-1}). The last two values can be calculated from the intercept and slope of the plot of ln (C_t/C_0) against time (t).

Yoon-Nelson model

This model was developed by Yoon-Nelson in 1984 to describe the adsorption breakthrough curves. The Yoon-Nelson model was derived based on the assumption that the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent. It is a simple model that requires no detailed data concerning the type of the adsorbent and the physical properties of the adsorption bed (Aksu and Gonen 2004; Chowdhury et al. 2013). The linearised model for a single component system is expressed as:

$$\ln\left(\frac{C_t}{C_0 - C_t}\right) = K_{YN}\,t - \tau K_{YN} \qquad (2)$$

where K_{YN} is the rate constant (min-1); $\mathcal{T}$ is the time required for 50% adsorbate breakthrough (min) and t is the breakthrough time (min).

The values of K_{YN} and $\mathcal{T}$ can be calculated from a plot of ln $(C_t/C_0 - Ct)$ versus t at different inlet concentrations, flow rates, and bed heights. If the theoretical model accurately characterizes the experimental data, this plot will result in a straight line with a slope of K_{YN} and intercept of $\mathcal{T}K_{YN}$ (Yoon and Nelson 1984).

Thomas model

This model is a general model that is widely used to describe column performance (Thomas 1994). The Thomas model is based on the assumption that the adsorption behaviour follows Langmuir kinetics and assumes that the rate driving forces obey the second order reversible reaction kinetics. The theoretical form of the model is given as:

$$\ln\left(\frac{C_0}{C_t} - 1\right) = \frac{K_{Th}\, C q_0 m}{Q} - \frac{K_{Th}\, C_0}{Q}\left(V_{eff}\right) \qquad (3)$$

where K_{Th} is the Thomas rate constant (ml mg^{-1} min^{-1}), q_0 is the equilibrium adsorbate uptake (mg g^{-1}), m is the adsorbent amount in the column (g), V_{eff} is the volume of the solution (mL), and Q is the feed flow (ml min^{-1}). The values of K_{Th} and q_0 can be calculated from the slope and intercept of the linear graph between ln $(C_t/C_0 - 1)$ versus V_{eff} at different inlet concentrations, flow rates, and bed heights.

Results and discussion

Characterization of phosphonated cross-linked polyethylenimine

Fourier Transform Infra Red spectroscopy was used to characterize the phosphonated derivative of cross-linked polyethylenimine (PCPEI) in order to confirm the introduction of the $–PO_3H_2$ chelating group. The FTIR spectrum is given in Figure 2.

Figure 2

The major peaks of importance on the IR spectrum of PCPEI are: 966.76 cm^{-1} indicating the presence of the P—OH bond; 1060.34 cm^{-1} corresponding to the presence of the P-O bond; and 2803.31 cm^{-1} signifying the presence of the PO—H bond. The difference in the strength of absorption bands for the stretching vibration of N-H before and after the phosphonation could be observed, with the phosphonated polymer yielding lower band strength. This could be attributed to the closure of some secondary amine sites during phosphonation of the polymer. The phosphonated polymer thus contains less secondary amine groups due to the reaction between these groups in CPEI and ($-PO_3H_2$) groups in phosphorous acid.

Effect of inlet concentration

The breakthrough curve is presented in Figure 3 shows the effect of initial concentration on the breakthrough curves using a bed height of 4.5 cm and flow rate of 1 mL min^{-1}. As the figure shows, an earlier breakthrough point was reached at higher concentration (100 mg L^{-1}), where the adsorbent was exhausted faster compared to the lowest concentration (40 mg L^{-1}).

The breakthrough time was found to decrease with increasing adsorbate inlet concentration as the binding sites saturated quicker. A decrease in inlet concentration gave an extended breakthrough curve, indicating that a higher volume of solution could be treated. This could be explained by the fact that a lower concentration gradient caused a slower transport due to a decrease in diffusion coefficient or mass transfer coefficient.

Figure 3

Effect of flow rate

The effect of feed flow rate on the adsorption of U onto PCPEI was investigated by varying the feed flow rate (1, 2, and 3 ml min^{-1}) while keeping a constant bed height of 4.5 cm and inlet concentration of 40 mg L^{-1} as shown in Figure 4. The curve showed that at a higher flow rate the front of the adsorption zone quickly reached the top of the column, that is, the column was saturated early. A lower flow rate resulted in a longer contact time as well as shallow adsorption zone. At a higher flow rate a steeper curve with a relatively early breakthrough and exhaustion time resulted in less adsorption uptake.

Figure 4

Effect of bed height

Figure 5 shows the breakthrough curve obtained for the adsorption of U onto PCPEI for different bed heights of 2.5, 3.2, and 4.5 cm at a constant adsorbate feed flow rate of 1 ml min^{-1} and adsorbate inlet concentration of 40 mg L^{-1}.

Figure 5

As figure 5 shows, the breakthrough time was found to increase with increasing bed height.. Higher uptake was observed at a bigger bed height due to the increase in the amount of the adsorbent which provided more adsorption sites for the adsorption process to proceed. The increase in bed height increases the mass transfer zone. The mass transfer zone in a column moves from the entrance of the bed and proceed towards the exit. Hence for the same influent concentration and fixed bed system, an increase in bed height would create a longer distance for the mass transfer zone to reach the exit, subsequently, resulting in extended breakthrough time. For a bigger bed height, the increase of adsorbent mass would provide a larger surface area leading to an increase in the volume of the treated solution.

Application of Adams-Bohart model

Adams-Bohart model was applied to experimental data to describe the initial part of the breakthrough curves. A linear relationship was obtained between $\ln(C_t/C_0)$ and t by applying equation (1) to the experimental data for varying initial concentrations, flow rates and bed heights. K_{AB} and N_0 values were calculated from the slope and intercept, respectively and listed in Table 1 together with the correlation coefficients (R^2).

Table 1

From the table, it is observed that the kinetic constant (K_{AB}) was influenced by the experimental conditions as it decreased with increasing inlet initial concentration and increased with increase in both flow rate and bed height. The sorption capacity (N_0) increased for increasing initial concentration and bed height while it decreased with flow rate. This showed that the overall

system kinetics was dominated by external mass transfer. However, the relatively poor correlation coefficient for initial concentration and flow rate reflects less applicability of this model.

Application of the Yoon-Nelson model

The column data were fitted to the Yoon-Nelson model to determine the rate constant (K_{YN}) and the time required for 50% adsorbate breakthrough ($\mathcal{T}$). Application to the experimental data with respect to initial concentration, flow rate, and bed height enabled the determination of Yoon-Nelson model parameters (K_{YN} and $\mathcal{T}$) from the slope and intercept of the graph between ln ($C_t/C_0 - Ct$) against t. The calculated values are given in Table 2.

Table 2

As Table 2 shows, both K_{YN} and $\mathcal{T}$ values decreased with increasing initial concentration and flow rate, but increased significantly with increase in bed height. These results are in agreement with some literature findings (Aksu and Gonen 2004; Chowdhury et al. 2013).

The values of K_{YN} relate to the initial concentration, flow rate and bed height as follows:

K_{YN} values are higher at low than at high initial concentration as result of the relationship between the rate, the rate constant and concentration (e.g. Rate = K_{YN} [U]). At low flow rates, there is increased contact time thus K_{YN} is higher compared to at high flow rates. The effect of the bed height is similar to this in that for longer bed heights, there is increased contact time and hence higher values of K_{YN}.

Application of Thomas model

Thomas model was applied to investigate the breakthrough behaviour of U on PCPEI. The values of the Thomas rate constant (K_{Th}) and the equilibrium adsorbate uptake (q_0) were calculated from the slope and intercept of the graph of ln $\left(\frac{C_0}{C_t} - 1\right)$ against $\boldsymbol{V_{eff}}$ at different experimental conditions and listed in Table 3.

Table 3

As can be observed from the table, as the concentration increased, the value of K_{Th} decreased whereas the value of q_0 increased. For both flow rate and bed height K_{Th} values showed a reverse trend, that is increased with increase in flow rate and bed height. The Thomas model is suitable for adsorption processes where the external and internal diffusions will not be the limiting step.

Conclusions

The adsorption of U from aqueous solution onto PCPEI was investigated in a continuous packed fixed-bed column mode. The breakthrough curves for column adsorption of U from solutions to PCPEI have been measured at various inlet U concentrations, flow rates and bed heights.

The results obtained showed that the sorption of U is dependent on the inlet concentration, flow rate, and bed height as the breakthrough time and U removal decreased with increasing flow rate and U concentration and increased with increasing the bed height. The results also indicated that better sorption process could be achieved with lower flow rates and lower concentrations of U solutions as well as long bed heights. This was achieved at flow rate of 1 ml min^{-1}, initial concentration of 40 mg L^{-1}, and bed height of 4.5 cm.

By adjusting the operating characteristics of the packed column, for example the flow rate, inlet U concentration, adsorbent amount (bed height), very rapid and efficient U uptake can be achieved for the system.

The Adams–Bohart, Thomas and Yoon–Nelson models were applied to experimental data to predict the breakthrough curves and to determine the column kinetic parameters. The initial region of the breakthrough curves was defined by the Adams–Bohart model at all inlet concentrations, flow rates and bed height studied while the full description of breakthrough was accomplished by the Thomas and Yoon-Nelson models. The model constants belonging to each model were determined by linear regression and were proposed for use in column design.

The overall performance of the column study demonstrated that PCPEI can be used in fixed-bed columns for removal of U by choosing the optimal running conditions which are (1 ml min^{-1} flow rate, 40 mg L^{-1} initial concentration, and 4.5 cm bed height) according to the findings of this study. Another configuration would be to pack the polymer into columns that can be placed in household containers (e.g. water jars) and left to contact with polluted water, allowing mass transfer of U to the adsorbents in the columns.

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Figure 1

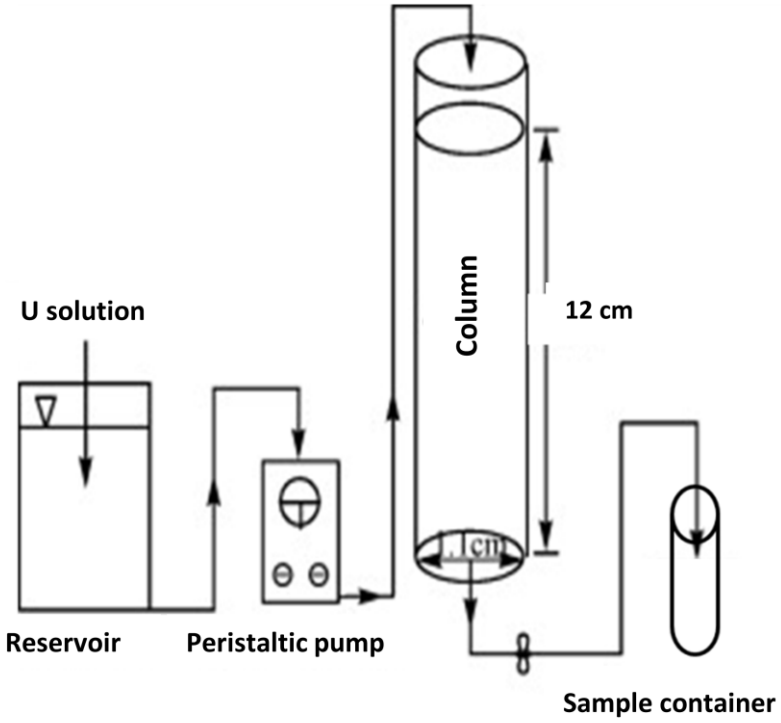

Figure 1. Fixed-bed adsorption system

Figure 2

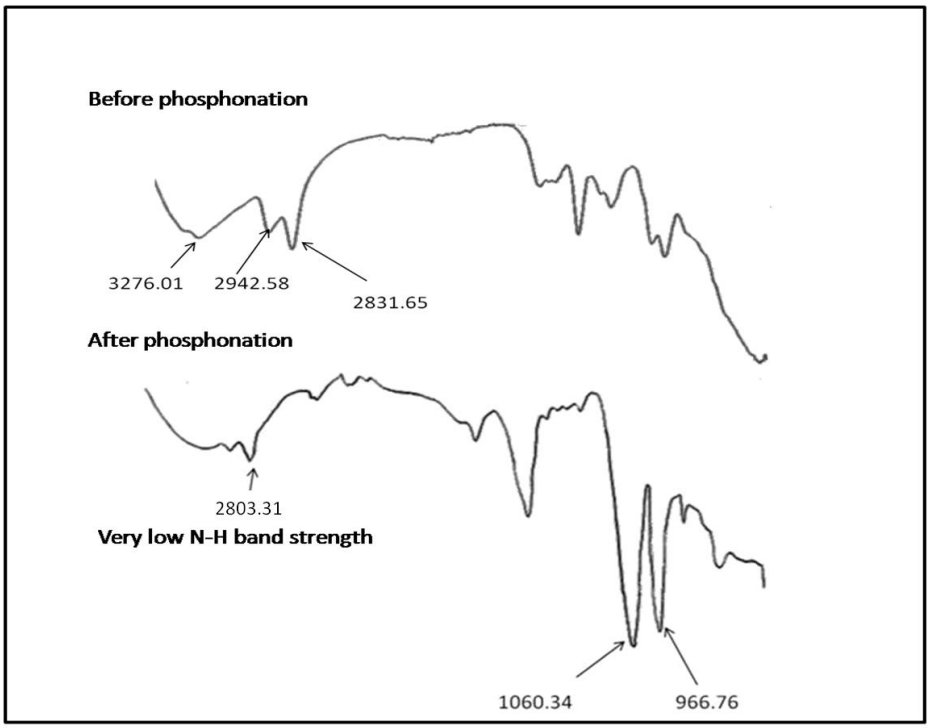

Figure 2. FTIR spectrum of CPEI and PCPEI

Figure 3

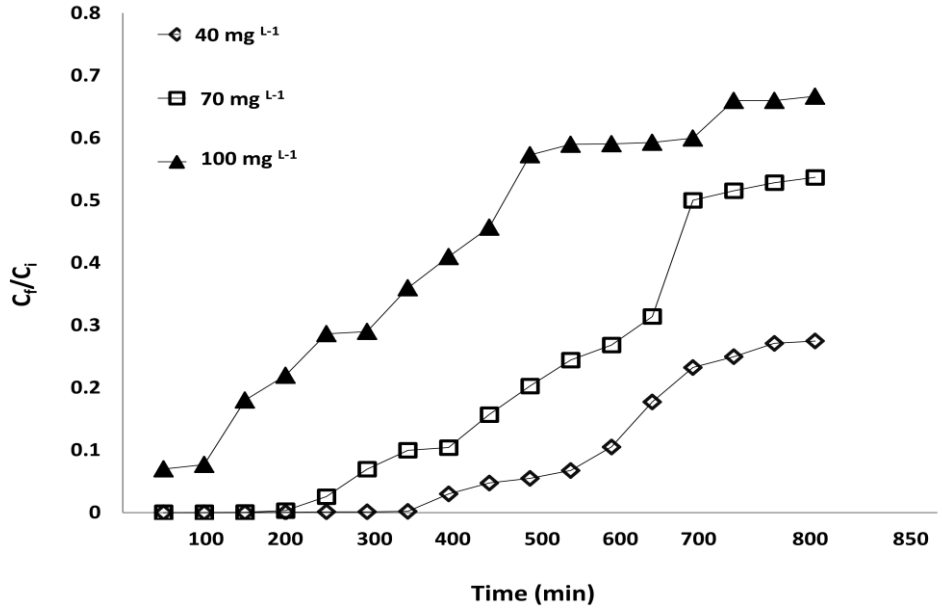

Figure 3. Breakthrough curves for adsorption of U onto PCPEI for different inlet concentration

Figure 4

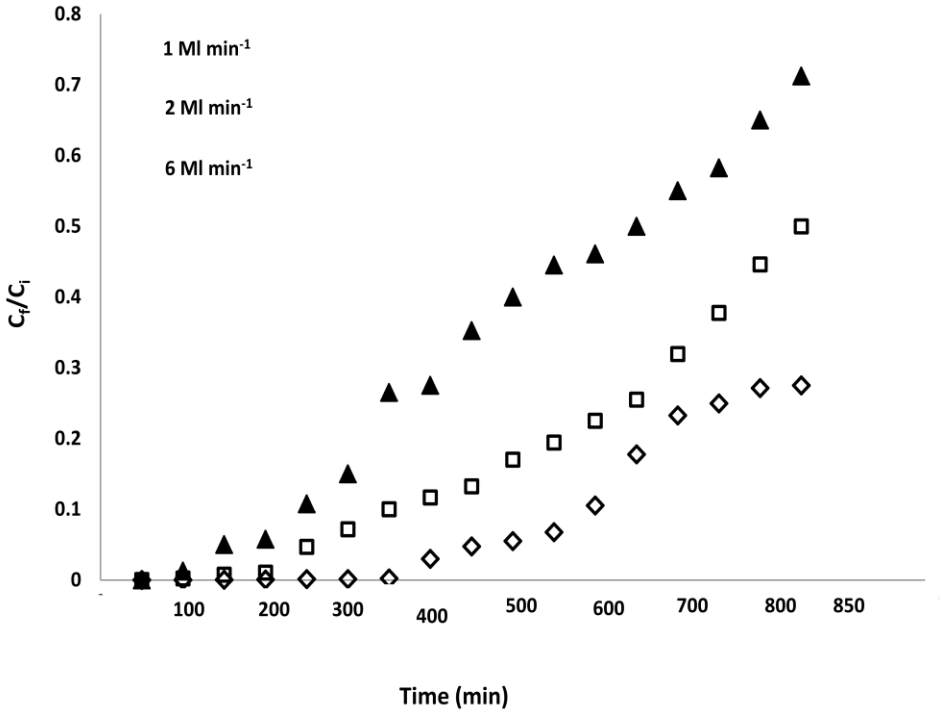

Figure 4. Breakthrough curves for adsorption of U onto PCPEI for different flow rate

Figure 5

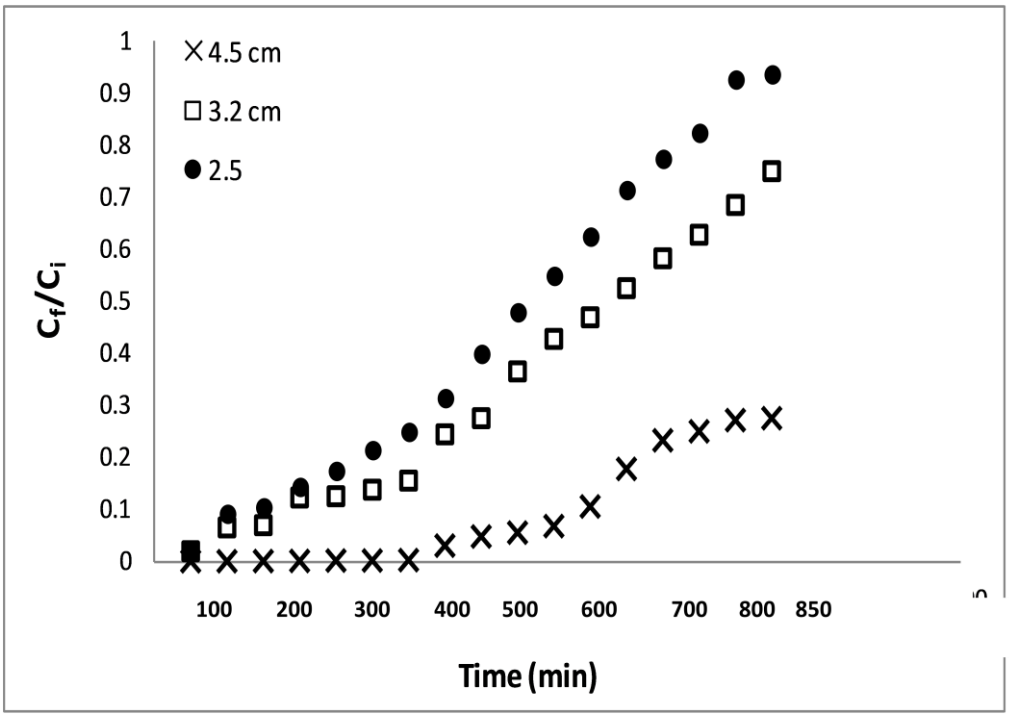

Figure 5. Breakthrough curves for adsorption of U onto PCPEI for different bed height

Table 1

Table 1. Adams-Bohart parameters for U sorption at different conditions.

	Initial concentration (mg L^{-1})			Flow rate (mL min^{-1})			Bed height (cm)		
	40	**70**	**100**	**1**	**2**	**3**	**2.5**	**3.2**	**4.5**
K_{AB}	0.00015	0.00007	0.00002	0.00015	0.00016	0.00018	0.000045	0.00005	0.00015
N_0	678.3	1128.9	1616.9	678.3	326.8	187.3	663.8	718.5	733.3
R^2	0.8968	0.7485	0.8076	0.8968	0.853	0.8633	0.9642	0.9562	0.9638

Table 2. Yoon-Nelson parameters for U sorption at different conditions.

	Initial concentration (mg L^{-1})			Flow rate (mL min^{-1})			Bed height (cm)		
	40	**70**	**100**	**1**	**2**	**3**	**2.5**	**3.2**	**4.5**
K_{YN}	0.0063	0.0058	0.0018	0.0063	0.0034	0.0029	0.0038	0.0041	0.0063
$\mathcal{T}$	1477.3	1270.4	961.78	1477.3	1445.4	1144.0	881.4	1033.5	1477.3
R^2	0.9112	0.8014	0.9247	0.9112	0.9015	0.9398	0.9811	0.9887	0.9112

Table 3. Thomas model parameters for U sorption at different conditions.

	Initial concentration (mg L^{-1})			Flow rate (mL min^{-1})			Bed height (cm)	
	40	**70**	**100**	**1**	**2**	**3**	**2.5**	**4.5**
K_{YN}	0.0058	0.0023	0.00043	0.0058	0.0061	0.0062	0.0019	0.0058
q_0	1.0862	2.1739	4.1860	1.0862	1.0164	0.9193	0.0904	1.0862
R^2	0.9112	0.8014	0.9247	0.9112	0.9015	0.9398	0.9811	0.9112

1. Page 4 row 10: it is specified that the solid was processed by spraying and sieving. The sieve diameter should be mentioned in order to calculated the average diameter of particles. It influenced also the adsorbtion capacity which increases with particle diameter decreasing

This was added under synthesis section.

2. Page 4 rows 26-20: it is mentioned: "the concentration of 40 mg L-1 of U was chosen arbitrarily for the "worst case" scenario of U load in water emanating from gold mining activities around Johannesburg" but for experiments the higher concentrations were selected: 40, 70 and 100 mg U/L respectively. In my opinion it is more useful to work with concentration 40 mg U/L and lower.

These concentrations were used to study the effect of concentration, but for all other experiments 40 mg L^{-1} of U was used.

3. Regarding the models selected for the adsorbtion:

- Adams-Bohart model: N_o should be explained more clearly

  N_0 is already defined under the modeling section as the saturation concentration (mg L^{-1})

- Table 1 should be rearranged thus the values of K_{AB}, N_0 si R^2 should correspond to column entitled "Bed height (cm) of 4.5"

The table is rearranged

- Thomas model: it is mentioned that "K_{Th} and q_0 can be calculated from the slope and intercept of the linear graph between $\ln(C_t/C_0-1)$ versus t" but in the equation 3 did not appear the t parameter.

  The equation is correct as it is; the statement is corrected according to the equation.

- It is specified that q_0 represents "the equilibrium adsorbate uptake (mg g-1)". In table 3 can be observed that parameter q_0 have different values influenced by the initial concentration and flow rate. Normally, the adsorbtion capacity at equilibrium (obtained when the column was filled at maximum) did not depends by the operation condition (concentration of solution that pass the column, flow rate). For every adsorbtion process based on circulation of solutions the most important parameter is the adsorbtion capacity obtaining at the column breakdown (when from the column is eliminated the adsorbed element). Total adsorbtion capacity at equilibrium did not depend by the flowing rate of solution or by their concentrations but is affected by the particles' diameter and pH.

The adsorption capacity does depend on the initial concentration according to the results obtained from this study which agree with reported literature. This is understandable because at higher concentration the adsorbent exhausts faster and that is why the breakthrough time was found to decrease with increasing the inlet concentration as the binding sites became more quickly saturated.

- I recomend a more detailed description of experiments. It should be specified the amount of material used in the column and for each experimental situation the value of adsorbtion capacity at the moment of column breakdown and the total adsorbtion capacities. I suggest to express the adsorbtion capacities at the moment of column breakdown as proportion of total adsorbtion capacity and to correlated the variations obtaining due the increasing of the initial concentration of the solution with the increasing of the flow rate of the solution.

The amount of the material is added for each bed height under the section of bed height

This study focused on the optimization of the operating conditions of the column system, mainly: flow rate, bed height, and initial concentration, the adsorption capacity was not calculated experimentally but it calculated theoretically from the Thomas model.

The present paper studied the influence of the initial concentration and the flow rate of solutions on the U adsorbtion on PCPEI. Experimental date were fitted on 3 column adsorbtion models and the conclusions are logic and accurate**. I propose acceptation for publication after minor revisions**.

Review for the article titled: *Column adsorption studies for the removal of U by phosphonated cross-linked polyethylenimine: modelling and optimization*

The paper focuses on the study of continuous fixed bed adsorption using phosphonated crosslinked polyethylenimine as an adsorbent for the removal of uranium from aqueous solutions. This is certainly a very important subject to many governments and the mineral industry. The approach of the study, which involves experimental and modelling is very good as this is the modern trend. However, before this article can be accepted for publication, some issues need to be attended to.

Comments

1. The title shows that the focus is on modelling and optimization, results show some fitting of experimental data to some literature data and determination of R2. The R2 is a basic concept in statistics and is not sufficient for engineering/science modelling work. What is expected in modelling of a system like this one is the interpretation of the result in line with the fundamental principles (based on the chemistry, physics and mathematics) of the models. For example if the experimental results do not fit well, say, Adam-Bohart model, what does this say about the physical and chemical properties of the mixture? The values of constants calculated should be compared with those in the literature and their implication on the chemistry of the mixture should be explained. These will strengthen the paper. Secondly, if the main focus was indeed optimization, then there is no evidence that this has been achieved. It is not mentioned either in the abstract or in the conclusion what the optimal operating parameters were.

The main focus of the paper is the optimization of the adsorption process in column mode, this includes: flow rate, bed height, and initial concentration. The optimization results are mentioned both in the abstract and conclusions; the exact optimal operating parameters are added in the conclusions as follows:

By adjusting the operating characteristics of the packed column, for example 1 mL min^{-1} flow rate, 40 mg L^{-1} inlet U concentration, and 4.5 cm bed height, very rapid and efficient U uptake was achieved for this system).

More explanation and interpretation is added for each model as follows:

Yoon and Nelson model

Was: As Table 2 shows, both K_{YN} and $\mathcal{T}$ values decreased with increasing initial concentration and flow rate, but increased significantly with increase in bed height. These results are in agreement with some literature findings (Aksu and Gonen 2004; Chowdhury et al. 2013).

Now: As Table 2 shows, both K_{YN} and $\mathcal{T}$ values decreased with increasing initial concentration and flow rate, but increased significantly with increase in bed height. These results are in agreement with some literature findings (Aksu and Gonen 2004; Chowdhury et al. 2013).

The values of K_{YN} relate to the initial concentration, flow rate and bed height as follows:

K_{YN} values are higher at low than at high initial concentration as result of the relationship between the rate, the rate constant and concentration (e.g. Rate = K_{YN} [U]). At low flow rates, there is increased contact time thus K_{YN} is higher compared to at high flow rates. The effect of the bed height is similar to this in that for longer bed heights, there is increased contact time and hence higher values of K_{YN}.

The Thomas model:

Was: As can be observed from the table, as the concentration increased, the value of K_{Th} decreased whereas the value of q_0 increased. For both flow rate and bed height K_{Th} values showed a reverse trend, that is increased with increase in flow rate and bed height.

Now: As can be observed from the table, as the concentration increased, the value of K_{Th} decreased whereas the value of q_0 increased. For both flow rate and bed height K_{Th} values showed a reverse trend, that is increased with increase in flow rate and bed height. The Thomas model is suitable for adsorption processes where the external and internal diffusions will not be the limiting step.

Adam Bohart model

Was: From the table, it is observed that the kinetic constant (K_{AB}) was influenced by the experimental conditions as it decreased with increasing inlet initial concentration and increased with increase in both flow rate and bed height. The sorption capacity (N_0) increased for increasing initial concentration and bed height while it decreased with flow rate. However, the relatively poor correlation coefficient for initial concentration and flow rate reflects less applicability of this model.

Now: From the table, it is observed that the kinetic constant (K_{AB}) was influenced by the experimental conditions as it decreased with increasing inlet initial concentration and increased with increase in both flow rate and bed height. The sorption capacity (N_0) increased for increasing initial concentration and bed height while it decreased with flow rate. This showed that the overall system kinetics was dominated by external mass transfer. However, the relatively poor correlation coefficient for initial concentration and flow rate reflects less applicability of this model.

2. For a good modelling work, there is a need to consider the thermodynamics of the system alongside the reaction kinetics. If thermodynamics was not part of the objectives, that would be fine if more in-depth interpretation of the models considered is given.

The thermodynamics was not part of this study. The thermodynamic and kinetics work was done in a separate paper which dealt with batch experiments (Saad et al., 2012). Already sited in the text. And more interpretation of the models is added for each model.

3. P 5 L20 compare with P2 L21 (Abstract). From P5 it is obvious that the authors knew that the models "describe only the initial part of the breakthrough curve". There is, therefore, no need of presenting that information in the conclusion and abstract.

This part is removed from abstract

4. P9 L 10-19, explanation on the values these parameters need to be given.

The values of the parameters in table 2 are explained as follows:

As Table 2 shows, both K_{YN} and $\mathcal{T}$ values decreased with increasing initial concentration and flow rate, but increased significantly with increase in bed height. This showed that the overall system kinetics was dominated by external mass transfer. These results are in agreement with some literature findings (Aksu and Gonen 2004; Chowdhury et al. 2013).

The values of K_{YN} relate to the initial concentration, flow rate and bed height as follows:

K_{YN} values are higher at low than at high initial concentration as result of the relationship between the rate, the rate constant and concentration (e.g. Rate = K_{YN} [U]). At low flow rates, there is increased contact time thus K_{YN} is higher compared to at high flow rates. The effect of the bed height is similar to this in that for longer bed heights, there is increased contact time and hence higher values of K_{YN}.

5. P 10 L 10-14; What is stated here is obvious. It would be more meaningful to specify values applicable to the system studied.

According to this comment, the following sentence is added to specify the optimal values:

This was achieved at flow rate of 1 ml min^{-1}, initial concentration of 40 mg L^{-1}, and bed height of 4.5 cm.

6. P 10 L 34; the authors mention "optimal operating condition" but they did not specify them in line with the title of the work.

The overall performance of the column study demonstrated that PCPEI can be used in fixed-bed columns for removal of U by choosing the optimal running conditions which are (1 ml min^{-1} flow rate, 40 mg L^{-1} initial concentration, and 4.5 cm bed height) according to the findings of this study.

Minor comments

- References are up to date.
- The quality of figures is not good. For example Fig 1, sample container,
  The quality of all figures is improved.

- It would be easier to read the units in Fig. 4 if presented in days rather than minutes
  There was a mistake in the units, after correction no need to present them in days as it less than a day (around half day).
- The axes for the figures are very faint
  This is improved as well.
- Figures do not need to be in an outer box
  All outer boxes are removed

Chapter 10

CONCLUSIONS

This chapter summarizes the outputs of the study on the abstraction capacity of the synthesized materials based on their functionality. It compares their potential, efficiency, affinity, selectivity and removal mechanism as well as a brief introduction to the possible application.

New efficient adsorbents were developed based on polymeric materials, namely: phosphonated cross-linked polyethylenimine (PCPEI), sulphonated cross-linked polyethylenimine (SCPEI), and thiolated cross-linked polyethylenimine (TCPEI). The synthesized materials exhibited excellent adsorption capability toward specific elements (U, Hg, As, and Se) even at very low pH values. The good performance at low pH values presents these materials as ideal adsorbents for metal abstraction from contaminated water impacted by acid mine drainage. The modified polymeric adsorbents were found to have an easy and cheap route of synthesis; stability; fast kinetics and rapid equilibration with metal-containing solutions and most importantly high capacity and selectivity.

Chemical modification (functionalization) of cross-linked polyethylenimine by different functional groups was found to be very efficient in enhancing the selectivity of the desired or targeted elements. This process can be a good alternative for low cost materials for the treatment of mine-impacted waters as well as for the recovery of precious metals.

The synthesized polymers exhibited commendable potential for re-use through regeneration which is a very significant factor especially with respect to cost effectiveness of the removal process (the cost of the removal process as well as waste disposal). The regeneration step can also be conducted selectively through the use of different desorbing solutions, thus creating the possibility of collecting the desorbed metals for use in other metal processing industries. The high selectivity for Hg by TCPEI could mean that this polymer can be applied for the recovery of gold and silver from gold mining waste streams since these two elements exhibit similar chemistry to Hg. This possibility has been left for future work. Its success will make it possible to recover low levels of these precious metals, making water remediation a self-financing process.

The variation in selectivity and affinity of the developed materials presents them as potential selective adsorbents for the removal

of heavy metals from wastewaters. This variation on the performance of each adsorbent highlights the role of the functionality of the polymer on the adsorption process.

The good performance of PCPEI in fixed-bed mode (column experiments) gave an insight on the potential performance of this material in water purification such as household filter systems.

This study therefore, gave a background to a wider application to introduce polymers of this type for use in household filter systems. Another configuration would be to pack the polymer into small columns that can be placed in household containers (e.g. water jars) and left to contact with polluted water, allowing mass transfer of the toxic elements to the adsorbent in the column.

Chapter 11

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Appendix

Published conference proceeding arising from this study

1. **D. Saad**, E. Cukrowska, and Hlanganani Tutu, High efficiency functionalised solid chelating polymers for selective removal and pre-concentration of metals and metalloids from impacted waters, 17th Euroanalysis conference (the European Conference on Analytical Chemistry), Warsaw, Poland, 25-29 August, **Keynote lecture.**

2. **D. Saad,** E. Cukrowska, and Hlanganani Tutu, Selective removal of mercury from aqueous solutions using thiolated cross-linked polyethylenimine, 44th World Chemistry Congress (IUPAC), Istanbul, Turkey, 9-16 August, **Poster presentation**.

3. **D. Saad**, Ewa M. Cukrowska, and H. Tutu, Engineered materials for selective removal of toxic elements from acid mine drainage impacted waters, 12th International Chemistry Conference Africa (ICCA 2013), Pretoria, South Africa 9-12 July 2013, Technical lecture.

4. **D. Saad**, Ewa M. Cukrowska, and H. Tutu, Engineered materials for selective removal of toxic elements from acid mine drainage impacted waters, Water and Sanitation – Early career scientists working in Africa workshop/conference, Polokwane, South Africa 26-29 May 2013, **Oral presentation**.

5. **D. Saad**, Ewa M. Cukrowska, and H. Tutu, Modification of viable and cost-effective materials for the removal of trace elements from mining wastewaters, SACI young chemist symposium, Pretoria, South Africa 9th November 2012, **Oral presentation**

6. **D. Saad**, Ewa M. Cukrowska, and H. Tutu, Feasible and cost-effective materials for removal of heavy metals from wastewaters, Wits Cross-faculty symposium, University of the Witwatersrand, Johannesburg, South Africa 18-22 October 2012, **Oral presentation**.

7. **D. Saad**, E. Cukrowska, and H. Tutu, Feasible and cost-effective polymeric adsorbents for removal of trace elements from industrial wastewaters as a proactive step for healthy water, 17th Annual Conference of the International Association for Impact Assessment (Integrated Environmental management in Urban Evolution: Creating Tomorrow`s Cities Today) Resource planning and management sub theme**,** Cape Town, South Africa 27-29 August 2012, **Oral presentation**.

8. **D. Saad,** E Cukrowska, and H. Tutu, Cross-linking of polyethylenimine for efficient removal of trace elements from mining wastewater, Water Research Showcase 2012**,** Johannesburg, South Africa 22 June 2012**,** **Oral presentation**.

9. **D. Saad,** E. Cukrowska, and H. Tutu, Feasible and cost-effective removal of trace elements from mining and industrial wastewaters, TWAS/BioVisionAlexandria.NXT (Scientific Innovation in the Developing World: from Theory to Practice), Alexandria, Egypt, 21-22 2012.

10. H. Tutu, E.N. Bakatula, **D. Saad**, E. Cukrowska, I.M. Weiersbye and E.Rosenberg, Engineered materials for the containment of radionuclides and toxic elements in mine leachates and wastewaters, Environmin 2012, Loskop Dam, Limpopo, South Africa, 11 – 15 March 2012. **Keynote lecture**.
11. **D. Saad,** E. Cukrowska, and H. Tutu**,** Phosphonated cross-linked polyethylenimine for selective removal of uranium ions from Mining wastewater, 2nd regional young water professionals conference, Water Institute of South Africa, Pretoria, South Africa 3- 5 July 2011, **poster presentation**.

12. **D. Saad,** E. Cukrowska, and H. Tutu Development and application of

polymeric adsorbent for heavy metals recovery from wastewaters, South African Chemical Institute (SACI) international conference, Johannesburg, South Africa 16- 20 January 2011, **oral presentation**.

13. **D. Saad,** E. Cukrowska, and H. Tutu**,** Development and application of cross-linked polyethylenimine and its functionalized derivatives for heavy metal ion recovery from aqueous solutions, South African Chemical Institute (SACI) international conference, Johannesburg, South Africa , 16- 20 January 2011, **poster presentation**.

Awards

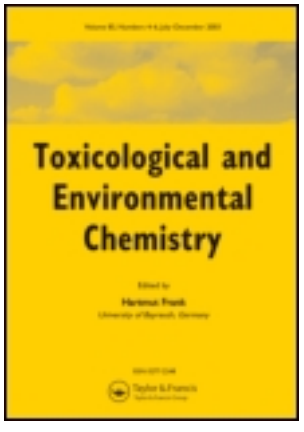
- Student best poster presentation award (3rd place) at Wits cross-faculty symposium, Johannesburg, South Africa 2nd August 2013.

- Full cost award (travel and accommodation) to participate in early career scientists at the SNOWS Water and Sanitation conference in South Africa, 27-30 May 2013.

- Student best oral presentation award (3rd place) at South African Chemical Institute and Royal Society of Chemistry Young Chemist Symposium, Pretoria, South Africa 9th November 2012.

- Full cost award (travel and accommodation) to participate in TWAS/BioVisionAlexandria.NXT 2012, (amongst the top 100 young promising scientists in the developing countries 2012 selected to participate in this event).

- Awarded, Membership of Golden Key International Honour Society as one of top 15% Wits Academic achievers 2012. (Membership by invitation only).



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Development and application of cross-linked polyethylenimine for trace metal and metalloid removal from mining and industrial wastewaters

Dalia M. Saad [a], Ewa M. Cukrowska [a] & Hlanganani Tutu [a]

[a] School of Chemistry, University of the Witwatersrand, Johannesburg, South Africa

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Development and application of cross-linked polyethylenimine for trace metal and metalloid removal from mining and industrial wastewaters

Dalia M. Saad, Ewa M. Cukrowska and Hlanganani Tutu*

School of Chemistry, University of the Witwatersrand, Johannesburg, South Africa

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Pollution of water bodies by trace metals is an established problem and several studies have been conducted to deal with it. South Africa is amongst those countries whose water systems are most affected as a result of intensive mining activities. This research was dedicated to the development of an insoluble chelating polymer for use as an adsorbent for abstraction of metal ions from mining and industrial wastewaters. Polyethylenimine (PEI), well known for its metal chelating potential, was cross-linked by epichlorohydrin (ECH) in order to convert it into a water-insoluble form for direct use as an adsorbent. The binding affinity of the cross-linked polyethylenimine (CPEI) to heavy metal ions was assessed as well as its ability to be regenerated for re-use. CPEI exhibited good complexation ability to metal ions with high affinity to Cr and most divalent metal ions. The observed order of complexation was: $Cr > Zn > Fe > Ni > Mn > Pb$. On the other hand, it showed very poor ability to bind oxo-anions such as SeO_3^{2-} and AsO_2^{-} which has been attributed to the unavailability of suitable functional groups to interact with these ions.

Keywords: polyethylenimine; cross-linking; adsorption; trace metals

1. Introduction

Contamination of the environment by trace metal ions has become a major concern in the recent years (Madoni and Giuseppa 2005; Bhattacharya, Mandal, and Das 2007) due to heavy industrial activities. Mining industry in particular releases toxic metals such as lead, mercury, nickel, and chromium into water bodies, as some of the most significant environmental pollutants (Navarro, Wada, and Tatsumi 2003; Tutu, McCarthy, and Cukrowska 2008; Tutu et al. 2009).

Metal ions may be hazardous to the environment and human health above particular threshold concentrations; they tend to persist and accumulate in the environment and cannot be rendered harmless (Forstner 1983; Cavus and Gurdag 2008).

Removal of toxic metal ions is an important challenge. Current remediation technologies of contaminated water such as ion-exchange resins, electrolytic or liquid extraction, electro dialysis, chemical precipitation, membrane filtration, and biosorption (Ahmed et al. 2008) are inadequate due to the high quantities of aqueous wastes, which might lead to nested problems such as metal-bearing sludge which is difficult to dispose of. Furthermore, most of these traditional methods are quite costly. Therefore, there is an urgent need for feasible and cost effective methods (Ghoul, Bacquet, and Morcellet 2002).

*Corresponding author. Email: Hlanganani.tutu@wits.ac.za

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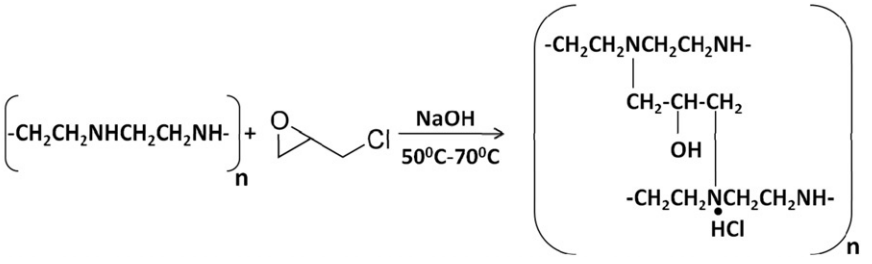

Figure 1. Cross-linking reaction scheme.

Using chelating polymers as ameliorants or remediation agents for polluted water is one of the most effective methods (Zander 2009).

Coordination polymers have a good potential for metal ions recovery as they have chelating ligands or anchoring sites with functional groups containing donor atoms like nitrogen, oxygen, or sulfur that can donate electrons to the metal ions, thus forming a coordination polymer–metal complex (Kaliyappan and Kannan 2000).

Polyethylenimine (PEI) is well known for its metal chelating potential (Leroy et al. 2003) owing to the presence of amino groups. It has been widely used for the retention of metal ions, but as a water soluble polymer (Gohdes et al. 2001; Taylor et al. 2003; Masotti, Giuliano, and Ortagi 2010) which requires additional techniques for effective removal such as membrane support or ultrafiltration (Molinari, Gallo, and Poerio 2004; Molinari, Poerio, and Argurio 2005; Molinari, Argurio, and Poerio 2006; Cojocaru, Zakrzewska, and Jaworska 2009; Masotti, Giuliano, and Ortagi 2010) making it difficult to work with. It has also been used mainly for the removal of single or a few metal ions (Leroy et al. 2003; Molinari, Argurio, and Poerio 2004).

This study was aimed at developing a water-insoluble cross-linked polyethylenimine (CPEI) for the removal of metal ions and metalloids (Se and As). The water-insoluble polymer gives the advantage of being used *in situ* and a possibility of regeneration and re-use, making it a more feasible and cost-effective method.

The insoluble property of the polymer was achieved by cross-linking using epichlorohydrin (ECH). The reaction scheme is shown in Figure 1.

2. Experimental protocol

2.1. *Materials*

All chemicals were obtained from Sigma–Aldrich, South Africa, and used without further purification.

For the polymer synthesis, PEI (PEI MW 25000), ECH, NaOH, and isopropanol were used. Metal solutions were prepared from their respective nitrate salts, namely: $Zn(NO_3)_2$, $Pb(NO_3)_2$, $Cr(NO_3)_3$, $Hg(NO_3)_2$, $Mn(NO_3)_2$, $Fe(NO_3)_3 \cdot H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $UO_2(NO_3)_2 \cdot 6H_2O$ while the oxo-anions Se and As were prepared from Na_2SeO_3 and $NaAsO_2$, respectively. Adjustments of pH for the adsorption experiments were conducted using $1\,mol\,L^{-1}$ solution of HNO_3 and NaOH. De-ionized water was used for the preparation of all solutions.

2.2. *Synthesis of CPEI*

PEI, 10 g, was dissolved in 25 mL de-ionized water. ECH, 1.2 mL and 2 g NaOH were added and the mixture was heated under reflux at 50–70°C. A gel-like solid was formed after few minutes, washed with abundant water and then with isopropanol before drying in an air oven at 30°C. A rubbery solid product was obtained which was pulverized to particles <2 mm.

2.3. *Adsorption procedure*

The batch metal adsorption experiments were conducted using multi-component standard metal nitrate salts and salts of oxo-anions Se and As as mentioned above.

A 1000 mg L^{-1} stock solution containing each metal was prepared from which the 40 mg L^{-1} multi-component working standard solution was obtained by serial dilution.

Adsorption experiments were performed in 50 mL flasks at room temperature. About 1 g of synthetic CPEI was weighed out into each flask. 40 mL of 40 mg L^{-1} solution of multi-component standard were then added to each flask and stirring done by means of magnetic stirrer. Adsorption at pH 3 and pH 8 was assessed. At equilibrium, the solutions were filtered and the equilibrium concentrations determined using inductively coupled plasma–optical emission spectroscopy (ICP–OES). The metal-binding capacity of the polymer (the amount of metal ions absorbed per unit mass of adsorbent) was calculated on the basis of the mass balance equation:

$$\text{Capacity (mg metal g}^{-1}\text{ polymer)} = (C_i - C_f) \times V(1)1000 \times P$$

where: C_i (mg L^{-1}) is the initial concentration of metal ions in the solution; C_f (mg L^{-1}) the concentration of metal ions in the filtrate; V (mL) the volume of initial solution; P (g) the amount of polymer used.

2.4. *Regeneration of PEI*

The possibility to regenerate the synthesized polymer for re-use is one of the most important factors to be considered to achieve much more feasibility and cost effectiveness. On the other hand, the regeneration in the ion recycling process limits waste disposal costs and reduces the environmental impacts (Zander 2009).

Since PEI is classified as an acidic–basic polymer, it can be regenerated by protolysis by changing the pH of the solution in order to cleave the polymer–metal bond. This was carried out by the treatment of previously loaded polymer with an excess of extracting reagent. HNO_3 at different concentrations, namely: 2, 3, 5, and 7 mol L^{-1} was used as an extractant. During the regeneration, the mixture was stirred for about 1 h, filtered and the polymer washed with de-ionized water and dried prior to re-use. The overall steps of the experimental protocol are presented in Figure 2.

2.5. *Application of CPEI for wastewater samples*

The synthesized CPEI was applied for the removal of metal ions from wastewater samples collected in the vicinity of gold mining activities in the Central Rand goldfield, Johannesburg. The above-mentioned adsorption procedure was followed. Five samples were used (one pit water and four surface water samples). The samples were collected at

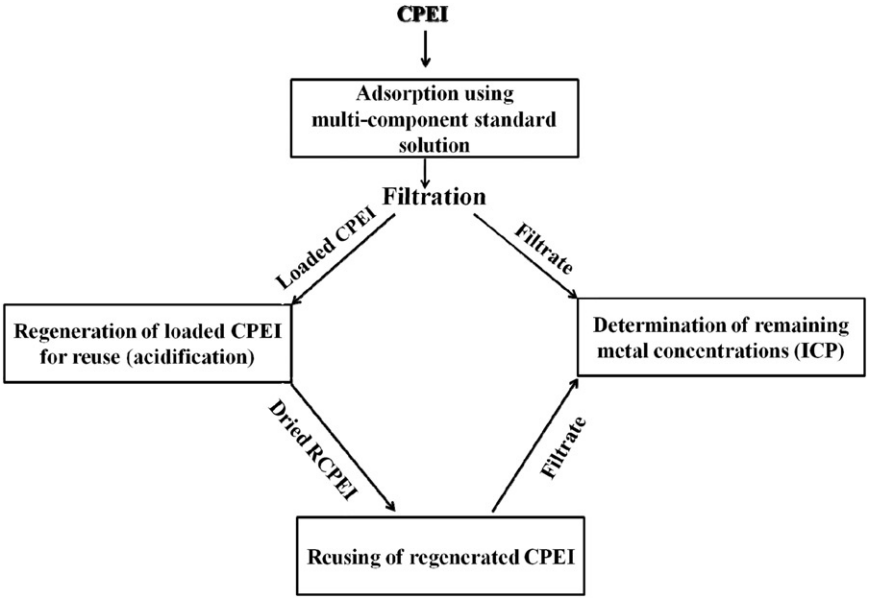

Figure 2. Experimental protocol diagram.

a site to the east of the city of Johannesburg. The samples were collected from the Natalspruit, an acid mine drainage-impacted stream and the pit water sample was collected at a pit on a footprint of a re-worked gold tailings dump adjacent to the stream. The water samples were collected according to standard water sampling protocols (Mugo and Orians 1983; Hermond and Fechner-Levy 2000) and geochemical parameters (pH, redox potential, and electrical conductivity) recorded in the field using field meters. The samples were filtered in the laboratory prior to application in the adsorption experiments. Metal analysis was carried out using ICP–OES. Anion concentrations were determined by ion chromatography (IC).

In each analytical technique, the limit of detection (LOD) was calculated as $3 \times$ standard deviation (SD) of the blank and the method quantitation limit (MQL) was calculated as $10 \times$ SD of the blank.

A Fourier transform infra-red spectrometer (Tensor 27, Bruker, Germany) was used to characterize the synthesized polymer. The field measurements were carried out with a portable kit Multi Line F/Set 3 of the Wissenschaftlich-Technische Werkstatten, Weilheim (WTW, Germany) equipped with a pH electrode, an integrated temperature probe (Sen Tix 41), a standard conductively cell (Tetra Con 375) and an oxidation–reduction potential probe (Sen Tix ORP). The pH electrode was calibrated according to IUPAC recommendations against two buffer solutions pH 4 and pH 7 and an uncertainty of ± 0.1 units.

ICP–OES (Genesis, Spectro Instruments, Germany) was used to determine the metal ion concentrations in the filtrate.

An ion chromatograph (761 Compact, Metrohm, Switzerland) with a Metrosep A Supp 5 analytical column was used to determine anions.

3. Results and discussion

The results for the adsorption of metals in synthetic solutions are presented in Table 1.

Table 1. Removal of metal ions from synthetic solutions by CPEI.

pH		Cr	As	Fe	Hg	Ni	Zn	Mn	U	Pb	Se
3	C_f (mg L^{-1})	4.2	18.6	4.7	18.5	12.4	4.1	11.6	19.2	14.7	34.0
	RSD ($n=3$)	1.0	1.0	0.8	3.8	1.6	2.1	0.7	4.8	0.3	1.6
	Adsorption capacity (mg g^{-1})	1.43	0.86	1.41	0.86	1.10	1.43	1.14	0.83	1.01	0.24
	Adsorption percentage	89%	54%	88%	54%	69%	89%	71%	52%	63%	15%
8	C_f (mg L^{-1})	0.6	17.3	1.4	18.0	7.2	0.7	8.4	19.5	13.5	34.5
	RSD ($n=3$)	1.8	0.5	2.2	6.5	0.9	0.6	0.9	6.7	0.6	1.9
	Adsorption capacity (mg g^{-1})	1.58	0.91	1.54	0.88	1.31	1.57	1.26	0.82	1.06	0.22
	Adsorption percentage	99%	57%	97%	55%	82%	98%	79%	51%	66%	14%
	LOD	0.027	0.001	0.151	0.005	0.012	0.023	0.002	0.017	0.003	0.024
	MQL	0.090	0.003	0.0503	0.017	0.040	0.077	0.007	0.057	0.010	0.080

Notes: Initial concentration of the ions = 40 mg L^{-1}; LOD: limit of detection in mg L^{-1}; MQL: method quantitation limit in mg L^{-1}; RSD: relative SD; C_i, initial concentration before adsorption; C_f, final concentration after adsorption.

The table shows the final metal concentrations obtained (C_f) after adsorption from an initial multi-metal solution of concentration 40 mg L^{-1}. The adsorption capacity, percentage as well as the relative standard deviation (RSD) are based on three measurements ($n = 3$).

The trend shows a decrease in percentage adsorption for both pH regimes as follows: Cr > Zn Fe > Ni > Mn > Pb > > As > Hg > U > > Se. The adsorption percentages showed high removal efficiency for most metal ions even at low pH. It is known that in such conditions the ability of ligands to donate electrons and form complexes with metal ions decreases due to the protonation of the polymers (Rivas and Maureira 2007). The results agreed with this theoretical concept where the adsorption capacity is a little higher at pH 8 than pH 3. It should be noted, however, that there could be a combination of precipitation and adsorption at pH 8. The solubility of many metals is amphoteric in the sense that the metals tend to dissolve and form cations at low pH and anions at high pH, with minimal solubility at intermediate pH (Smith 2007).

The mechanism of metal binding onto the polymer is based on the hard–soft Lewis acid–base theory, where the nitrogen atom on the chelating group (–NH) acts as a Lewis base and donates electrons to metal cations which are considered Lewis acids. This explains the high selectivity of CPEI to Cr, Mn, and Fe, which are hard acids since the nitrogen atom is a hard base. Ni, Zn, and Pb showed good adsorption as well. They are considered moderate acids and as such can bind to either soft or hard bases (Pearson 1968). Hg is a soft acid, hence its low adsorption capacity. The oxo-anions Se and As showed poor adsorption since they exist mainly as bases in solution.

The results obtained showed that the performance of the insoluble CPEI is comparable to that of the soluble uncross-linked PEI. Masotti, Giuliano, and Ortagi (2010) studied the performance of PEI for metal ions removal and obtained adsorption percentages of: Cr 99%, Ni 86%, Mn 77%, Pb 66%, and Zn 77%. In this study, under similar conditions, adsorption percentages of: Cr 97%, Ni 82%, Mn 79%, Pb 63%, and Zn 96%, were obtained (Table 1).

Desorption results for CPEI are shown in Figure 3. The results show the concentrations of metals desorbed by 2, 3, 5, and 7 mol L^{-1} of HNO_3.

For most metal ions, the most effective HNO_3 acid concentrations were 3 mol L^{-1} and 5 mol L^{-1}, with the latter giving optimal recoveries. Subsequently, regeneration of the used polymer was carried out using 5 mol L^{-1} acid concentration. The desorption percentages are shown in Figure 4.

The adsorption percentages for the recovered polymer (regenerated CPEI) on the same synthetic solutions are given in Table 2.

The percentages, though lower, still portrayed good recoveries. For instance the adsorption at pH 3 of Cr dropped by 16%; Fe dropped by 19%; Ni dropped by 4%, and U dropped by 6%, just to mention a few. At pH 8, the trend was also similar: Cr dropped by 24%; Fe dropped by 27%; Ni dropped by 17%, and U dropped by 6%. Generally, the results confirm that CPEI can be regenerated for re-use. It can be stated here that the regeneration of the polymer can further be exploited by use of serial desorptions which will depict the actual unrecoverable residual metal adsorbed on the polymer.

The wastewater samples showed a variation in their water chemistry. The pit water flows into the Natalspruit and mixes with water from a channel draining some waste water (not analyzed in this study) from small industries. The point SW1 is the first point downstream of the mixing zone of these two water systems. The original water upstream of the Natalspruit was not analyzed. Thus the effect of enhancement, dilution, and/or precipitation cannot be conclusively attributed to in this case. Further, the contribution of

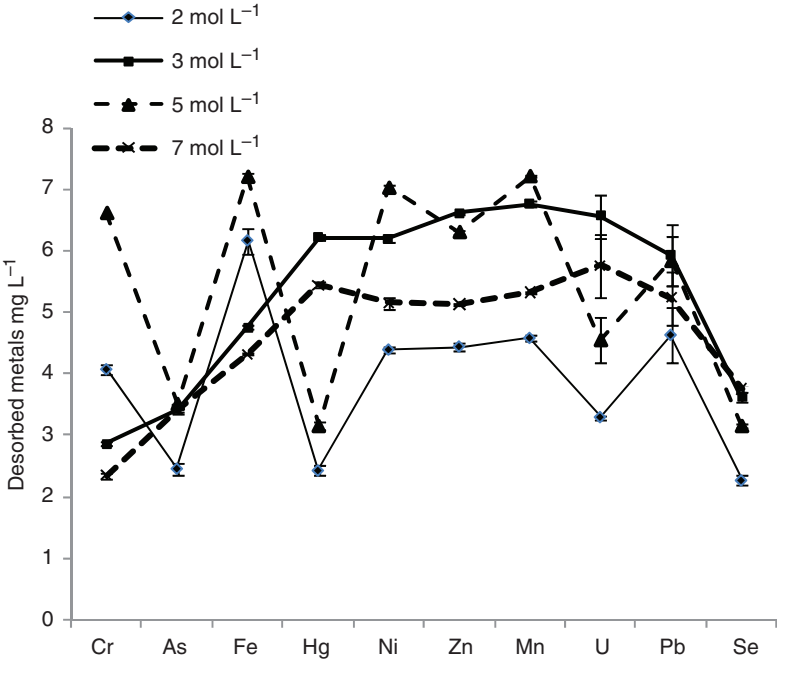

Figure 3. Desorption of CPEI by different HNO_3 concentrations.

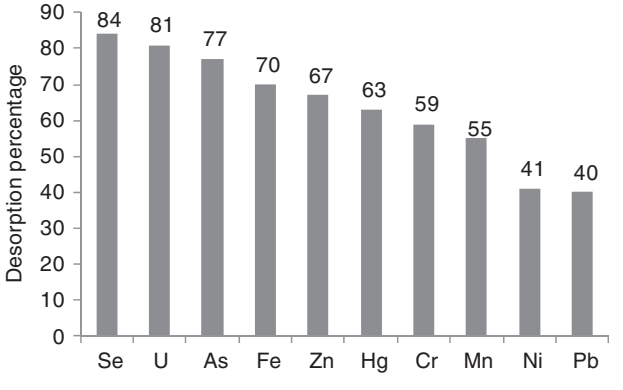

Figure 4. Desorption percentage of CPEI by 5 mol L^{-1} HNO_3.

groundwater (both polluted and unpolluted) cannot be ascertained without the analytical results. The study was not intending to do so, but rather to simply apply the polymer to the remediation of such waters.

The results of adsorption of metal ions from these waters by CPEI are given in Table 3.

The adsorption trends were similar to those observed for the standard multi-element solutions. Adsorption percentages for most elements were significantly high while those for U and Se were low. As and Hg adsorption percentages were fairly comparable although they were still low to compare with other elements. This means that the CPEI has

Table 2. Removal of metal ions from synthetic solution by regenerated CPEI.

pH		Cr	As	Fe	Hg	Ni	Zn	Mn	U	Pb	Se
3	C_f (mg L^{-1})	10.7	22.0	12.4	20.6	14.2	11.8	13.8	21.5	18.9	37.0
	RSD ($n=3$)	0.6	3.2	1.6	9.4	0.8	0.4	0.7	10.4	1.7	1.6
	Adsorption capacity (mg g^{-1})	1.17	0.72	1.10	0.78	1.03	1.13	1.05	0.74	0.84	0.12
	Adsorption percentage	73%	45%	69%	49%	65%	71%	66%	46%	53%	8%
8	C_f (mg L^{-1})	10.2	22.5	12.0	18.0	14.2	11.0	13.8	21.9	18.1	37.0
	RSD ($n=3$)	5.6	2.2	4.6	8.4	4.3	4.0	0.6	13.6	4.5	5.7
	Adsorption capacity (mg g^{-1})	1.19	0.71	1.12	0.88	1.03	1.16	1.05	0.72	0.88	0.12
	Adsorption percentages	75%	44%	70%	55%	65%	73%	66%	45%	55%	8%
	LOD	0.019	0.048	0.024	0.039	0.041	0.032	0.038	0.060	0.051	0.040
	MQL	0.063	0.160	0.080	0.130	0.137	0.017	0.127	0.200	0.170	0.133

Notes: Initial concentration of the ions = 40 mg L^{-1}; LOD: limit of detection in mg L^{-1}; MQL: method quantitation limit in mg L^{-1}; RSD: relative SD; C_i, initial concentration before adsorption; C_f, final concentration after adsorption.

Table 3. Removal of metal ions from mining wastewater samples.

Samples	Metals	C_i (mg L^{-1})	RSD ($n=3$)	C_f (mg L^{-1})	RSD ($n=3$)	Adsorption %
SW 1	Fe	6.1	0.1	0.2	8.1	97%
pH (3.8)	Ni	6.0	7.0	2.1	6.6	65%
SO_4^{-2} (383.2 mg L^{-1})	Zn	4.3	9.9	0.1	1.5	97%
	Mn	111.7	3.8	17.3	5.6	85%
SW 2	As	0.1	2.59	0.05	5.9	58%
pH (7.2)	Se	0.09	5.8	0.08	1.5	14%
SO_4^{-2} (19.80 mg L^{-1})	Ni	1.6	5.3	0.4	5.9	75%
SW 3	Cr	0.3	6.9	<0.003	5.2	$>99\%$
pH (4)	As	0.3	2.1	0.1	5.6	55%
SO_4^{-2} (819.4 mg L^{-1})	Fe	4.5	6.5	0.2	2.6	96%
	Ni	1.8	1.7	0.8	4.7	56%
	Zn	1.6	5.0	0.4	5.2	75%
	Mn	22.0	8.8	4.7	9.3	79%
SW 4	Fe	5.8	8.9	0.2	9.6	97%
pH (5.6)	Ni	4.7	3.5	1.0	6.7	79%
SO_4^{-2} (653.6 mg L^{-1})	Zn	7.7	7.1	0.8	7.7	90%
	Mn	179.2	2.7	20.4	1.9	89%
Pit water	Cr	0.04	7.8	<0.003	2.4	$>95\%$
pH (3)	Fe	0.6	3.5	0.03	3.7	95%
SO_4^{-2} (1669 mg L^{-1})	Hg	0.3	1.8	0.1	1.8	56%
	Ni	10.7	7.9	2.4	1.9	78%
	Zn	14.8	8.4	0.03	5.2	99%
	Mn	136.4	8.0	34.3	4.7	86%
	U	0.2	6.7	0.1	5.1	44%
	Se	0.1	8.7	0.04	1.3	6%

Notes: LOD (mg L^{-1}): Cr, 0.003; As, 0.014; Fe, 0.002; Hg, 0.001; Ni, 0.007; Zn, 0.008; Mn, 0.002; U, 0.035; Pb, 0.065; Se, 0.017; SO_4^{2-}, 0.01 (by IC).
MQL (mg L^{-1}): Cr, 0.010; As, 0.047; Fe, 0.007; Hg, 0.003; Ni, 0.023; Zn, 0.027; Mn, 0.007; U, 0.117; Pb, 0.217; Se, 0.057; SO_4^{2-}, 0.03 (by IC).
SW, surface water; C_i, initial concentration before adsorption; C_f, final concentration after adsorption.

to be used in tandem with another material that can extract these elements better should these elements be encountered in polluted waters.

This polymer has potential for use in filter systems for household use in communities that use borehole water impacted by mining and industrial waste waters. The desorbed metals can be of use to metal processing industries.

4. Conclusion

A water-insoluble resin was synthesized by cross-linking of PEI using ECH as a cross-linker and was successfully employed in the removal of metals and metalloids from standard solutions and wastewater samples. While the removal of metalloids was poor, that of metals was superior.

The ions removed as well as the mechanism of removal of the contaminants hinges on the functional groups present in the CPEI, largely the amine groups.

CPEI exhibited commendable potential for re-use through regeneration by 5 mol L^{-1} HNO_3. The study has shown in overall that CPEI can be used for the abstraction of metal

and metalloid contaminants from waste waters and can perform comparably to PEI which has commonly been used.

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