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

by

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DEDICATION

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

Her sacrifices, love and care made my life worthwhile

She always stood by me and told me that no star is out of reach

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

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......... my 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 mother in law for encouraging me to pursue my studies and for supporting me when things have not gone as smoothly as I would have liked, she believed on my capabilities as a strong woman and always reminds me of that

DECLARATION

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

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ABSTRACT

Contamination of water bodies by heavy metals and metalloids 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 insoluble chelating polymers for use as adsorbents to abstract heavy metal ions 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 also modified for selective removal of specifically-targeted heavy metal and metalloid ions.

The binding affinity of the synthesized materials to heavy metal and metalloid ions has been determined as well as their ability to be regenerated for reuse. These processes demonstrated that cross-linked polyethylenimine (CPEI) exhibited good complexation ability with high affinity to Cr and some divalent metal ions such as Fe, Zn, and Ni. 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. The observed order of complexation was: Cr > Zn> Fe >> Ni > Mn > Pb >> As > U > Se.

The phosphonated polyethylenimine (PCPEI) showed high selectivity for As, Mn and uranyl ions. The observed order of removal was: U > Mn> Ni > Zn > As >> Cr > Pb > Fe >> Hg > Se; whereas the suffocated polyethylenimine (SCPEI) exhibited high affinity to Se, and Hg. The observed order of adsorption was: Hg > Se >> U > Zn >Pb > Ni >> As > Cr > Fe.

The adsorption behaviour of these polymeric materials involved more than one mechanism such as complexation, normal surface charge exchange, and anion replacement and all these mechanisms are governed by the functional groups. The nitrogen atom on the chelating group (-NH) in the cross-linked polyethylenimine; the phosphorus atom on the chelating group ($-PO_3H_2$) in phosphonated cross-linked polyethylenimine; and sulphur atom on the chelating group ($-SO_3H$) in suffocated cross-linked polyethylenimine act as Lewis bases and donate electrons to metal cations which are considered Lewis acids.

The existence of the chelating groups in SCPEI and PCPEI facilitate the removal of oxo-anions through anion replacement since they exist as bases in solution and hence cannot be electron acceptors. Thus, the expected mechanism is the normal anion replacement. This mechanism can explain the high removal of Se by SCPEI since Se has similar chemical behaviour as sulphur and are in the same group in the periodic table. As such they can easily replace each other. Sulphur is released from the polymer into the solution by replacing the selenium ions in the polymer. Similar behaviour occurs between phosphorus in PCPEI and arsenic ions as As and P belong to the same group in the periodic table and hence have similarities in their chemical behaviour.

The Langmuir and Freundlich isotherm models were used to interpret the adsorption nature of the metal ions onto synthesized polymers. The Freundlich isotherm was found to best fit and describe the experimental data describing the adsorption process of metal and metalloid ions onto the synthesized polymeric materials

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.

The thermodynamic study of the adsorption of metals and metalloids by the synthesized CPEI, PCPEI and SCPEI resulted in high activation energies > 41 KJ mol^{-1} which confirm chemisorption as a mechanism of interaction between adsorbate and adsorbent.

So far, the developed polymeric materials showed good results and have potential to be applied successfully for remediation of heavy metal-polluted waters, and they have 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.

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Publications and presentations arising from this study

Publications

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Presentations

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Saad D., Development and application of polymeric adsorbent for heavy metal ion recovery from wastewaters, South African Chemical Institute (SACI) international conference 20th of January 2011, oral presentation.

Saad D., Cukrowska E. & Tutu H., Phosphonated cross-linked polyethylenimine for selective removal of uranium ions from Mining wastewater, Water Institute of South Africa, 2nd regional young water professionals, Pretoria 3rd to 5th July 2011, poster presentation.

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Chapter 1

INTRODUCTION

This introductory chapter gives an overview

on the thoughtful project and surrounding the problem statement

and motivations as well as the key questions that have been stated

to pave the study of the project.

1.1. General overview

Environmental pollution has become of global concern and attracts much attention. People are dependent on the natural environment for meeting their needs. This interaction between people and environment can negatively impact the environment and the natural resources. 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).

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).

Heavy metals are natural components of the earth`s crust, and some of them are essential nutrients for healthy life at trace levels. But due to the intensive anthropogenic activities such as industrial operations particularly mining, agricultural processes, and disposal of industrial waste materials; their concentration has increased to dangerous levels. South Africa as a leading country in mining operations faces this crucial environmental problem (Akpor and Muchie, 2010; Gardea-Torresdy *et al.*, 2005; Hussein *et al.*, 2005; Papageorgiou et al., 2009; Saad *et al.*, 2011).

Since heavy metal pollution affects the quality of drinking water and hence human health, there is a considerable urgent need for new, feasible and cost effective methods as the current technologies are inadequate because some of them are expensive, some are time consuming and others are environmentally destructive (Asubiojo and Ajelabi, 2009; Rivas *et al.*, 2006; Shin *et al.*, 2004).

One of the most promising, effective, and dramatically growing methods is using chelating polymers (coordination polymers) as ameliorants and remediation agents for recovery of heavy metal ions from water and wastewater (Bisset *et al.*, 2003; Shentu *et al.*, 2007; Wang et al., 2001).

1.2. Heavy metals distribution and life cycle

The distribution of metals in the environment results from both natural processes and human activities such as industrial, agricultural and mining processes which have increased the levels of heavy metals to levels that are dangerous for plants, animals and humans (Hang *et al.*, 2009; Karnchanawong and Limpiteeprakan, 2009; Velea *et al.*, 2008; Zhuang *et al.*, 2009). Figure 1.1 illustrates the sources of heavy metals and their deposition into ecosystem.

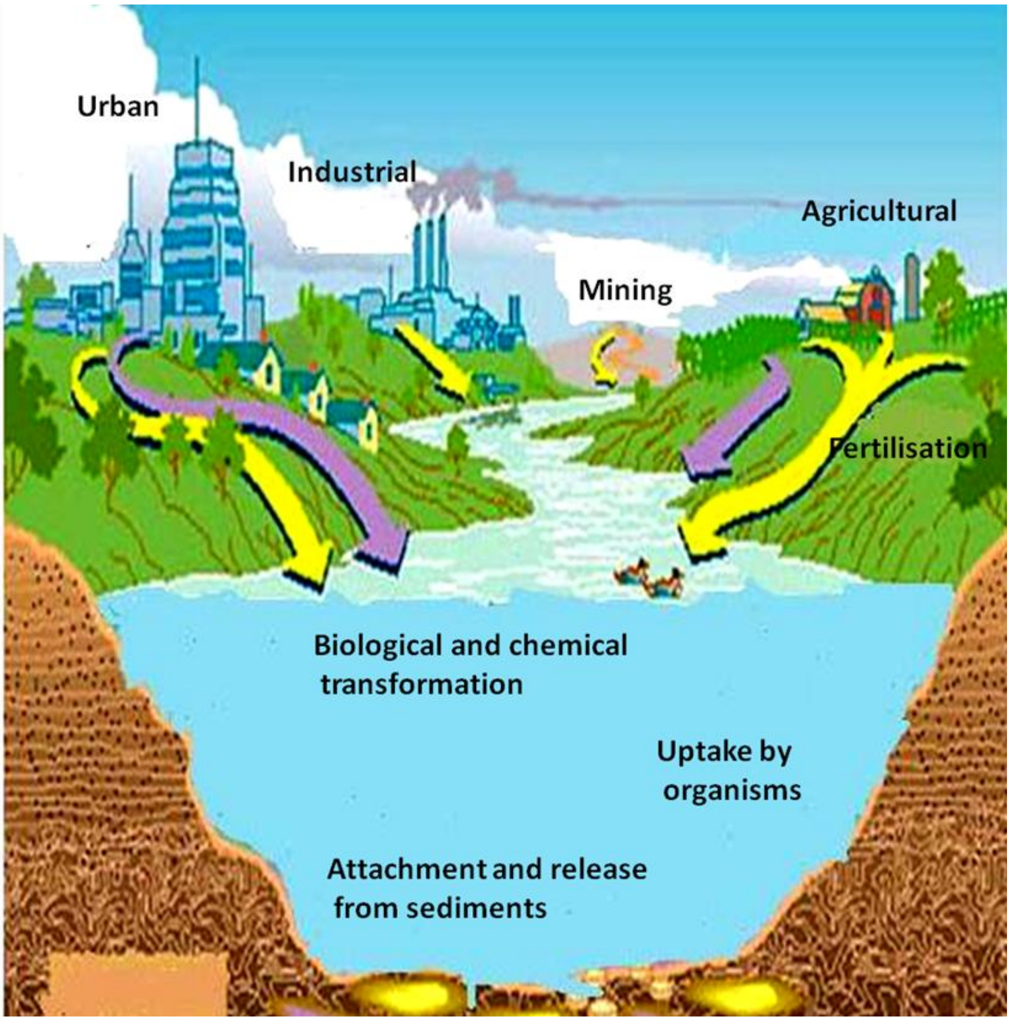


Figure 1.1. Sources and sinks of heavy metals

http://pubs.usgs.gov/circ/circ1133/images/fig21.jpeg

Once heavy metals have been discharged into the air and transported through the atmosphere, then they deposited into ecosystem, including water bodies and soil. In aquatic system the metals exist as free metal ions, inorganic complexes, organic complexes, and associated with colloids. They transport vertically as a particles in the water body and horizontally by water flow. Furthermore, they are adsorbed and retained by soil which has a high capacity for these toxic metals because they can be bound strongly by organic matter in the soil such as humic substances and proteins. They can be transported based on the relative binding ability of the soil, clay content, redox potential, and organic carbon contents (Akpor and Muchie, 2010; Hseu *et al.*, 2010; Molinari *et al.*, 2005).

The distribution of the metals between the different systems depends on the nature of each metal and on different chemical parameters such as pH, redox-condition, concentration of primary cations and anions, and the type and amount of organic and colloidal materials. The natural biogeochemical cycles are disrupted causing increased deposition of heavy metals in terrestrial and aquatic environment. Since heavy metals cannot be rendered harmless by chemical or biological remediation processes, and they are not biodegradable, they tend to accumulate and magnify in food chain resulting in a great threat to both environment and public health (Alluri, H, 2007; Cukrowska *et al.*, 2004).

1.3. Problem statement and Motivation

Heavy metal contamination has become a major concern in the recent years; due to heavy industrial activities particularly mining industry which release toxic heavy metals into water bodies such as (lead, mercury, zinc, nickel, and chromium which have been listed at the top ranking environmental pollutants (Mandoni and Giuseppa, 2005; Navarro *et al.*, 2003).

The seriousness of heavy metals pollution stems from the fact that they are very toxic even at very low concentrations because they tend to persist and accumulate in the environment up to dangerous levels for plants, animals and humans once they enter the food chain, hence the human body cannot metabolize them due to their persistence properties (Alkorta *et al.*, 2004; Rivas *et al.*, 2009; Cavus and Gurdag, 2008, Lai 2010; Volesky, 1999). Figure 1.2 illustrates the degradation of the ecosystem as a result of water pollution.

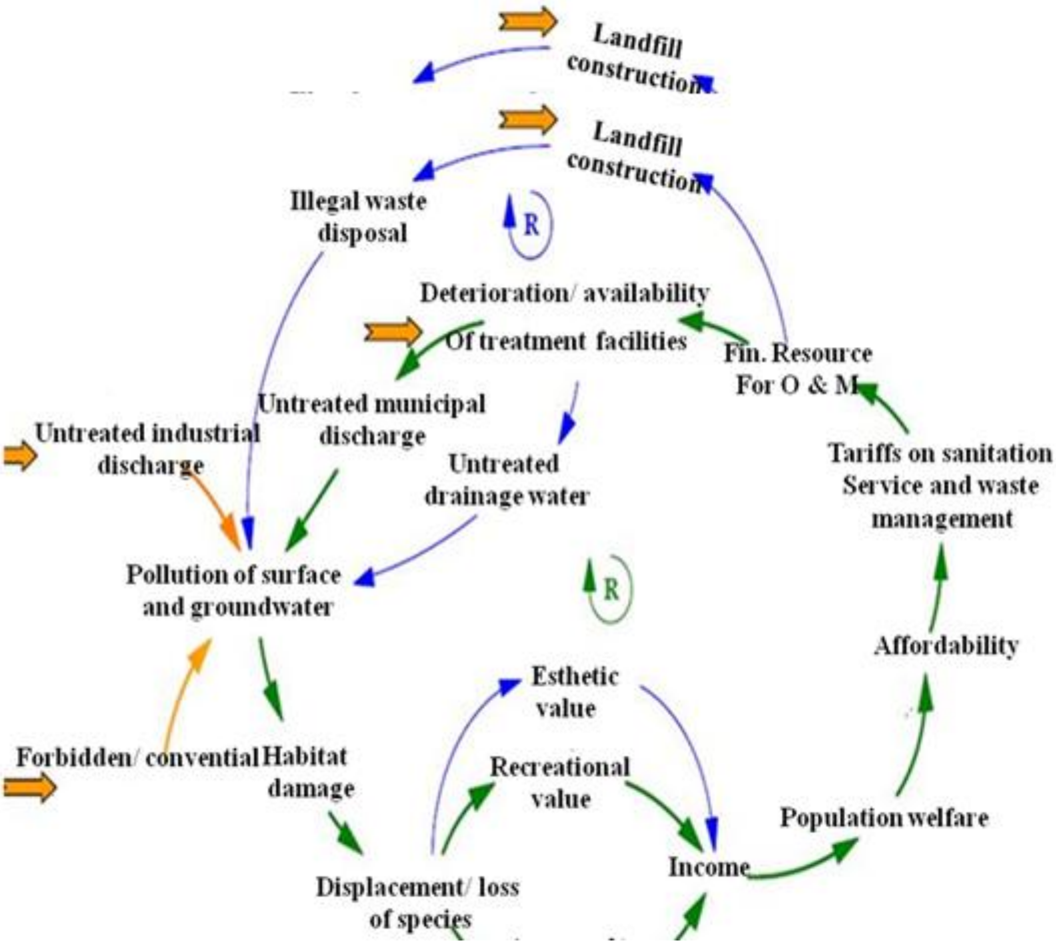


Figure 1.2. Ecosystem degradation due to surface and groundwater pollution

As the contamination of heavy metals has been considered as one of the major causes of water pollution 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 high cost; therefore there is an urgent need for new feasible and cost effective methods (Ahmed *et al.*, 2008; Ghoul *et al.*, 2003).

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 adsorbent is an efficient and widely applied separation process that is 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 water

pollution and wastewater with much more

emphasis on mining pollution and acid mine drainage

as the most important Phenomena relating to

heavy metal contamination as a result of intensive mining industry

as well as a general overview on wastewater

treatment methods with intensive sight on polymeric

adsorbents. Their design and role in pollutant

attention are discussed.

Hegel described water 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).

Water pollution affects drinking water, rivers, lakes and oceans all over the world. This consequently harms human health, natural environment, and even the economy (by killing off fish which are an economic resource in some regions). 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).

2.1. 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 composition of wastewater varies widely. It partially contains about 95% water which is often added during flushing to carry waste down a drain, pathogenic microorganisms such as bacteria, viruses, and parasitic worms and non pathogenic bacteria, organic particles such as faeces, hairs, food, vomit, plant material, and humus, beside soluble organics such as urea, fruit sugars, soluble proteins, drugs, and pharmaceuticals. It also contains inorganic particles such as sand, grit, and metal particles as well as soluble inorganic materials such as ammonia, road salt, cyanide, hydrogen sulphide, and thiocyanates. In addition, some gases like hydrogen sulphide, carbon dioxide, and methane are present. It can also contain some organisms such as protozoa, insects, arthropods, and small fish. Numerous of toxins could also be found in wastewaters the most commons are pesticides, herbicides, and poisons (Ellis, 2007; Metcalf and Eddy, 1991).

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).

2.2. Sources of water pollution

Water pollution can come from a number of different sources. There are two general major types of pollution namely: point-source pollution which occurs from a single source and nonpoint-source pollution which occurs from multiple sources. Most types of pollution affect the immediate area surrounding the source. Sometimes the pollution may affect the environment hundreds of miles away from the source. This is called transboundary pollution (Centi and Perathoner, 2002; Krantz and Kifferstein, 2010; Rivas *et al.*, 2003).

The most common water pollution types are: sewage pollution, microbiological pollution, industrial pollution, oil pollution, marine dumping, atmospheric deposition, radioactive waste, underground storage leakages, chemical pollution, and mining pollution (Calmano and Förstner, 1983; Mulligan *et al.*, 2001; Pant and Adhoyleya, 2007; Sandhyarani, 2008).

In South Africa the most significant pollution type that has profound effects on water quality is mining pollution. Gold mining for example represents a largest source of wastes pollution in South Africa, as it has been evaluated to be accounted for 22 million tons of waste which is about 47 % of all produced mineral wastes (Bell *et al.*, 2001; DWAF, 2001).

2.3. Mining pollution

Mineral extraction industry is economically profitable but it also brings profound environmental problems as it involves the building of processing sites as well as that of energy and transportation infrastructure linked to the mining sites. Furthermore, with more and more major mineral ores being depleted, extraction creates an increasingly large amount of wastes. There is a growing awareness of the mining environmental impacts all over the world, because mining consumes, diverts and pollutes water sources (Hilson, 2000; Twerefou D., 2009).

The definition of mine water is “Mine water is water in mined ground including waste rock/ tailings depositories and/ or draining into an adjoining body of water including streams, lakes, aquifers, wetlands, and oceans” (Oelofse, 2008).

The most threatening environmental problem relating to mining worldwide, is acid mine drainage (AMD), a problem which normally results from uncontrolled discharge of contaminated water from abandoned mines.

2.3.1 Acid mine drainage

Acid mine drainage (AMD) refers to water with high acidity discharging from mining areas. It causes surface and groundwater pollution as well as the degradation of soil quality, aquatic habitats, and for allowing heavy metals to seep into the environment. Acid mine drainage is the most difficult, uncontrolled environmental problem linked with mining; it is responsible for costly environmental and socio-economic impacts. It threatens the water resources and as a result human health and food security are threatened in mining area; it is also increase the level of heavy metals (Hobbs *et al.*, 2008; Jennings *et al.*, 2008; Oelofse, 2008).

2.3.1.1. Acid mine drainage chemistry

AMD is produced naturally by oxidation of sulphide minerals, chiefly iron pyrite or iron disulfide (FeS_2). This reaction occurs when minerals are exposed to air and water. Acidic drainage is found around the world both as a result of naturally occurring processes and activities associated with land disturbances, such as highway construction and mining where acid-forming minerals are exposed at the surface of the earth. These acidic conditions can cause metals in geologic materials to dissolve, which can lead to impairment of water quality when acidic and used by terrestrial or aquatic organisms (Jennings *et al.*, 2008).

The reaction of pyrite with oxygen and water produces a solution of ferrous sulphate and sulphuric acid as given in equation 1.1.

$$2FeS_2\,(s) + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+ \quad (1.1)$$

This reaction results in hydrogen ion release (acidity), sulphate ions, and soluble metal ions.

Then ferrous iron can further be oxidized to ferric iron producing additional acidity (equations 1.3 and 1.4).

$$2Fe^{2+} + ½\ O_2 + 2H^+ \rightarrow 2Fe^{3+} + H_2O\ (1.2)$$

This reaction occurs when sufficient oxygen is dissolved in water, and catalysed by iron and sulfur oxidizing bacteria at low pH; thereby increasing the rate of reaction by several order of magnitude, otherwise this oxidation process occurs at low rates over geologic time period (Jennings *et al.*, 2008).

The produced ferric ion (Fe^3) can either precipitate as a red-orange precipitate $Fe(OH)_3$ (equation 1.3) or it can react directly with pyrite to produce more ferrous iron and acidity by acting as oxidizing agent (equation 1.4).

$$2Fe^{3+} + 6H_2O \rightarrow 2Fe\ (OH)_3\ (s) + 6H^+\ (1.3)$$

$$14Fe^{+3} + FeS2\ (s) + 8H_2O \rightarrow 2SO_4^{\ -2} + 15Fe^{+2} + 16H^+\ (1.4)$$

Generally the oxidation of pyrite by Fe^{3+} is much faster than the oxidation by dissolved oxygen (Younger *et al.*, 2002).

The rates of all these reactions can be significantly accelerated by bacterial (*Thiobacillus* ferrooxidans) and microbial (*Ferroplasma* Acidarmanus) act (Jennings *et al.*, 2008).

Some other metal sulphides might not necessarily produce acidity when exposed to oxygen; but they can release soluble metal ions to solution according to the following reactions (Younget et al, 2002).

Covellite	$CuS\ (s) + 2O_2\ (aq) \ldots\ldots\ldots\ldots\ldots\ldots Cu^{2+} + So_4^{2-}$
Greenockite	$CdS\ (s) + 2O_2\ (aq) \ldots\ldots\ldots\ldots\ldots\ldots Cd^{2+} + SO_4^{2-}$
Millerite	$NiS\ (s) + 2O_2\ (aq) \ldots\ldots\ldots\ldots\ldots Ni^{2+} + SO_4^{2-}$
Sphalerite	$ZnS\ (s) + 2O_2\ (aq) \ldots\ldots\ldots\ldots\ldots\ldots\ldots Zn^{2+} + SO_4^{2-}$
Galena	$PbS\ (s) + 2O_2\ (aq) \ldots\ldots\ldots\ldots\ldots\ldots\ldots Pb^{2+} + SO_4^{2-}$
Chalcopyrite	$CuFeS_2\ (s) + 4O_2\ (aq) \text{---------} > Cu^{2+} + Fe^{2+} + 2SO_4^{2-}$

Other minerals e.g. calcite ($CaCO_3$) can consume acidity, thereby providing natural buffering system.

2.4. Heavy metals

The classification of heavy metals have been proposed based on different definitions such as atomic weight, specific gravity defining them as those elements with a specific gravity at least four or five times the specific gravity of water. Accordingly they include lanthanides, actinides, some metalloids, and transition metals. Recently, the term heavy metal has been used as a classification or definition for those metals with toxic properties. Generally there are more than 20 heavy metals, all of them have tendency to accumulate in the environment, and the most harmful metals to human health are mercury, cadmium, lead, arsenic, chromium, copper, and zinc (Cavus, 2008; Soghoian and Sinert, 2009).

Some metals are naturally found in the body and they are essential to human biochemical processes. Iron, for example, prevents anaemia because it is one of the components of the haemoglobin; zinc is a cofactor in over 100 enzyme reactions. Magnesium and copper are other familiar metals that, in trace amounts, are necessary for proper metabolism to occur as manganese is essential for strong bones, vitamin B-12 consists of cobalt, and many other metals are important but at minute concentrations. While there are other heavy metals have no known benefit for human physiology. Lead, mercury, and cadmium are prime examples of such toxic metals. Furthermore there are some heavy metals used for therapeutically purposes such as, aluminium, bismuth, gold, gallium, lithium, and silver, but they still have pernicious effects if taken in quantity (Molinari *et al.*, 2004; Soghoian and Sinert, 2009).

Heavy metal exposure can result in significant morbidity and mortality, and it occurs through different ways, from diet, from medications, from the environment, and in the course of work or play. They enter the body via inhalation, ingestion, and skin absorption. Then if they enter and accumulate in body tissues faster than the body's detoxification pathway can dispose of them, a gradual build up of these toxins will occur. High concentration exposure is not necessary to reach the toxic level in the body tissues hence they can accumulate over the time (Life Extension, 2009; Soghoian and Sinert, 2009).

2.4.1. Toxicity 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).

The toxicity of metals also depends a lot on their chemical form, as their distribution, mobility, and bioavailability are governed by the chemical and physical association which they undergo in natural systems. Hexavelent chromium, Cr (VI) for example, is carcinogenic while trivalent chromium Cr (III) is an essential nutrient. Arsenic is toxic in its inorganic form but non-toxic as arsenobetaine, a common arsenic species in fish (Christensen, 1995; Templeton *et al.*, 2000).

Heavy metals can alters the enzymatic activity as they bind to oxygen, nitrogen, and sulfhydryl groups in proteins which are act as ligands. This ligand formation is the basis of the transport of heavy metals through the body. Heavy metals overload in the adrenal glands reduce the production of hormones, resulting in stress, depression, early aging, sexual problems like aggravation of menopausal symptoms, loss of thinking power, causing osteoporosis and hypothyroidism, and they can lead to unresponsiveness of diabetics to their medications. They can also influence behaviour by damaging mental and nervous functions, altering numerous metabolic processes, affect neurotransmitter production and utilization, increase allergic reactions and cause genetic mutations (Life Extension, 2009; Soghoian and Sinert, 2009).

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).

Exposure to some metals, such as mercury and lead, may also cause development of autoimmunity, in which a person's immune system attacks its own cells. This can lead to joint diseases such as rheumatoid arthritis, and diseases of the kidneys, circulatory system, and nervous system. 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. For example, cadmium and zinc can lead to acute gastrointestinal and respiratory damages to brain, heart and kidney damages. Cadmium is reported to be strongly phytotoxic, disturbs enzyme activities and inhibits the DNA-mediated transformation in microorganisms. It is also known to interfere in the symbiosis between microbes and plants, as well as increase plant predisposition to fungal invasion. Toxicity to plants, microorganisms and aquatic organisms has been reported in the presence of nickel and lead (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).

2.5. Water state in South Africa

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 2.1). 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 2.1 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.

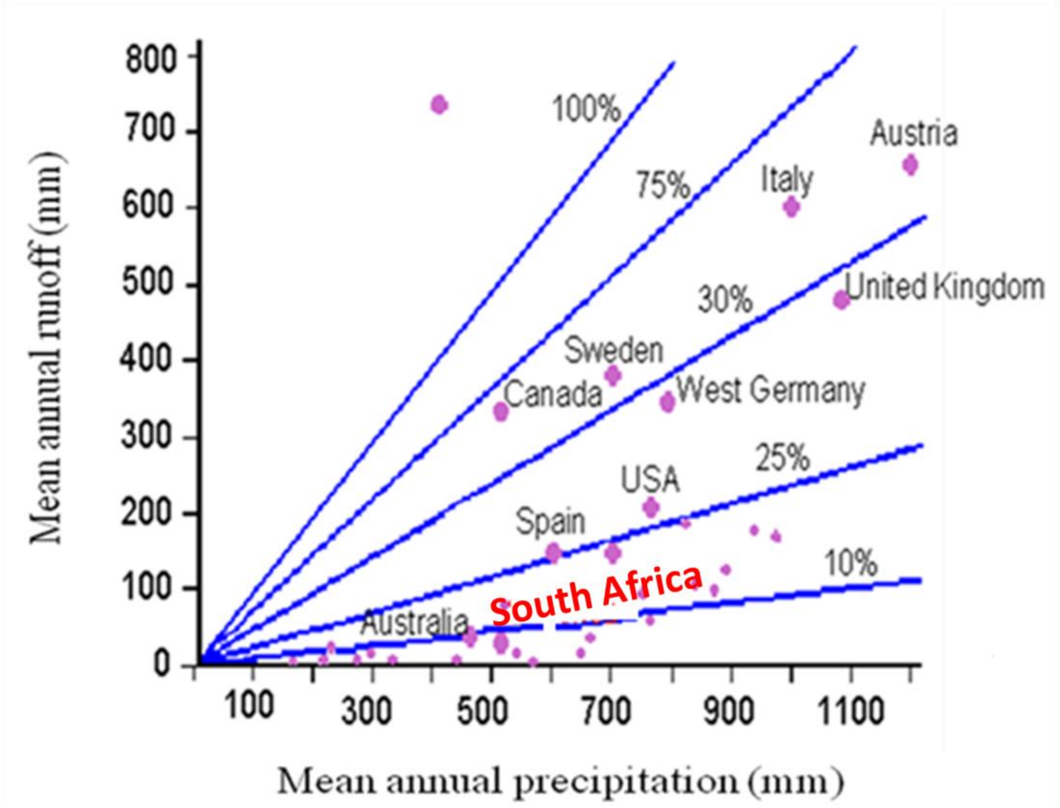


Figure 2.1. Runoff and precipitation state of water in South Africa (Allanson *et al.*, 1990)

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 rapid population growth which leads to greater water demand and increased pollution of available resources. This population growth is accompanied by huge human activities, such as agriculture, industry, and mining which have great negative impacts on the ecosystem generally and on water quality particularly.

Mining industry 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).

For all these above mentioned reasons there is a considerable, urgent need for more treatment technologies since the availability of clean water has universally been classified as a precondition for economic and social development (Rivas *et al.*, 2006; Shin *et al.*, 2004).

2.6. Different techniques for wastewater remediation

Much research is being conducted to develop methods to remove heavy metal ions from wastewater. Conventional and recently applied treatments have been used to remove heavy metals including precipitation, coagulation, solvent extraction, reduction, reverse osmosis, neutralization, electrodialysis, electrochemical separation through membranes, ion exchange, ultrafiltration, adsorption, phytoremediation, electrodeposition, cementation, Activated carbon adsorption and membrane filtration. Most of these techniques are inadequate due to incomplete metal removal, high reagent and energy requirements, and the high quantities of wastes which are difficult to dispose of beside generation of toxic waste products. An example is hydroxide precipitation treatment where the metal hydroxide precipitates may be released to the environment on disposal. As a result, further treatment such as solidification and stabilization to eliminate the contamination from metal hydroxides is needed. Techniques such as membrane separation methods are quite effective but are not feasible solutions for large area remediation due to the high costs associated with these techniques (Ajayi and Osibanjo, 1981; Fu *et al.*, 2006; Gould *et al.*, 1984; Patterson, 1975; Peters *et al.*, 1986; Sauer *et al.*, 2004; Vogel, 1987; Winfield, 1979).

Amongst all these methods, there are some techniques that have been widely applied for heavy metal ions removal with some form of merits and demerits. The most common usable remediation techniques with fewer disadvantages are: chemical remediation including precipitation, reverse osmosis, and ion exchange, phytoremediation including phytoextraction, rhizofiltration, and phytostabilization and microbial remediation.

2.6.1. Physiochemical remediation

2.6.1.1. 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 include: 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).

2.6.1.2. 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).

2.6.1.3. 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.

2.6.2. 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).

2.6.3. Microbial remediation

It is a bioremediation process using microorganisms which are 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).

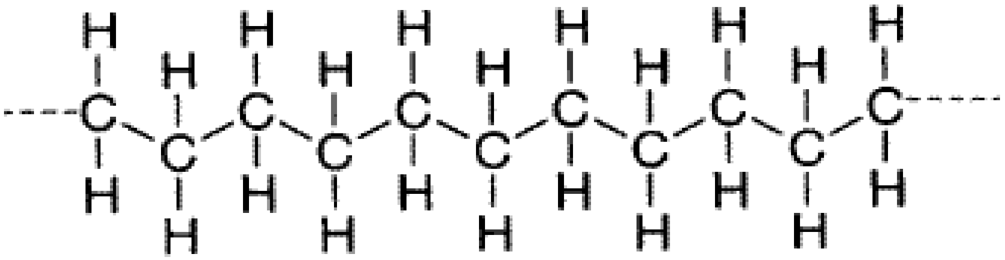
Microbial remediation system has many advantages including the low cost and low-technology techniques, environmental friendly, no wastes to be generated; it is a self-sustaining system and it can also be used alongside other technologies. But just as it is with other technologies it has several disadvantages 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).

2.7. Polymers

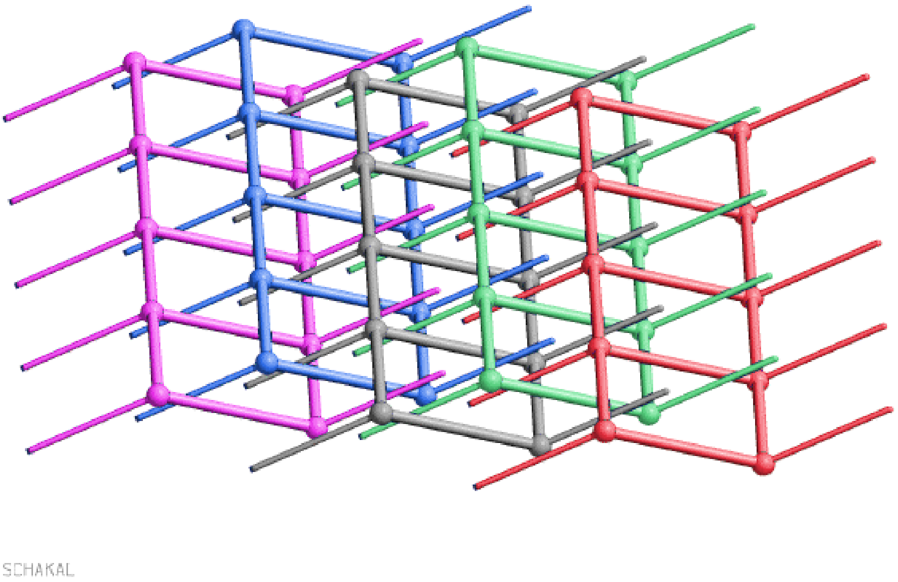
Polymers are natural or synthetic compounds of usually high molecular weight. They are very large molecules (macromolecules) that are comprised or built up of smaller units or monomers (Painter, 1997).

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).

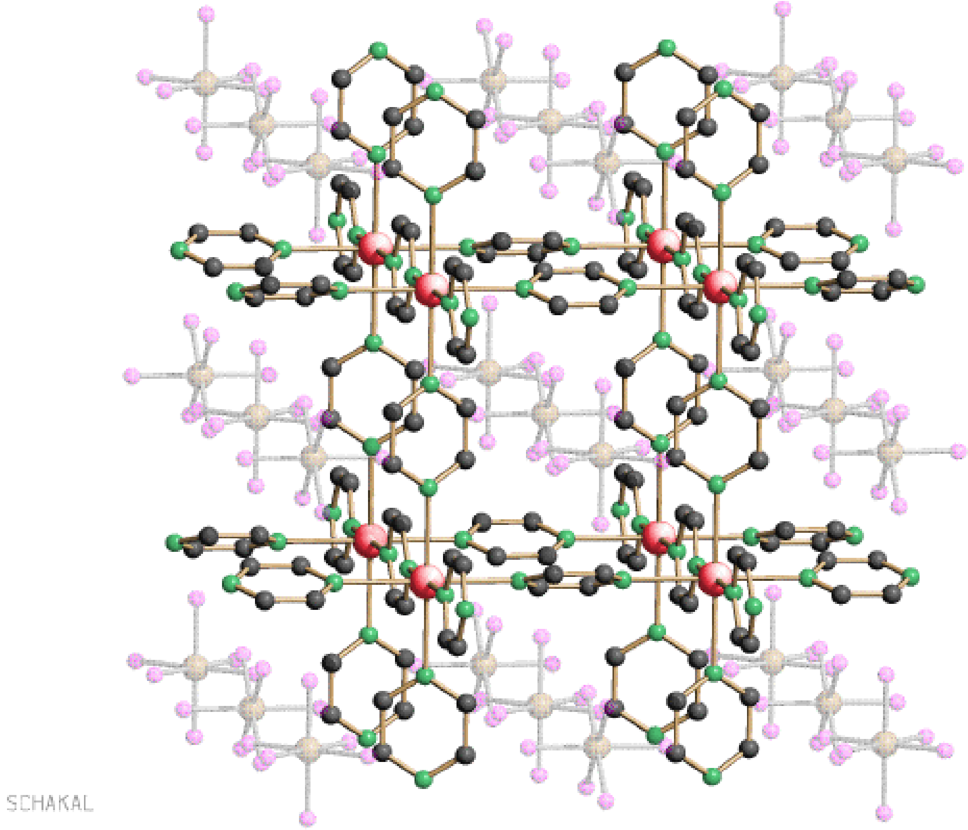
The structure of a polymer is generally described in terms of its structural units. The structural units are groups having two or more available bonding sites and are linked to one another through covalent bonds in a polymer chain (Style, 1962). Figures 2.2 shows some different polymer structures.



(a)



(b)



(c)

Figure 2.2. Polymer structures: (a) linear structure; (b) and (c) branched structures (c)

2.7.1. 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).

2.7.2. Coordination polymers (polymer-metal complex)

A coordination polymer is defined as a polymer that contains a metal which coordinates to Lewis bases–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 2.3 (Abd-El-Aziz, 2005).

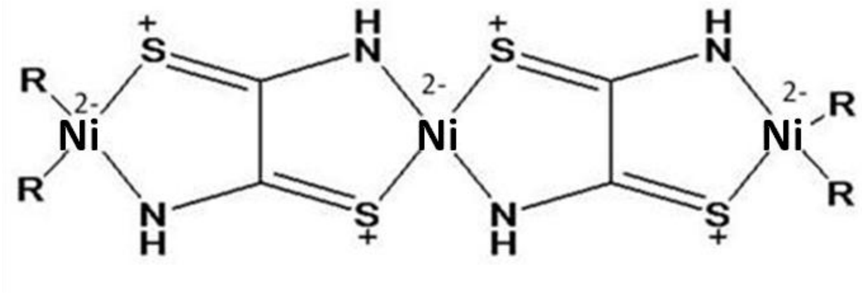


Figure 2.3. **Structure of a polymer containing ligands and metal in the backbone.**

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**

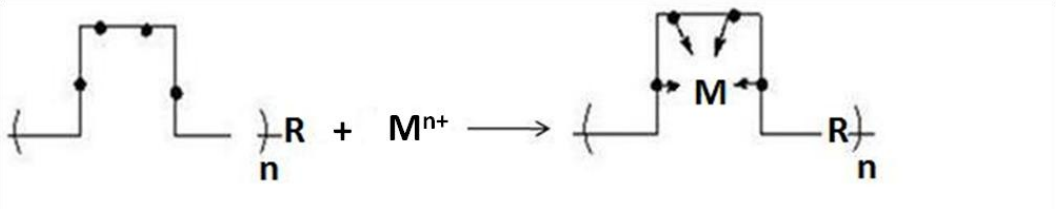


Figure 2.4. All along backbone ligands

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

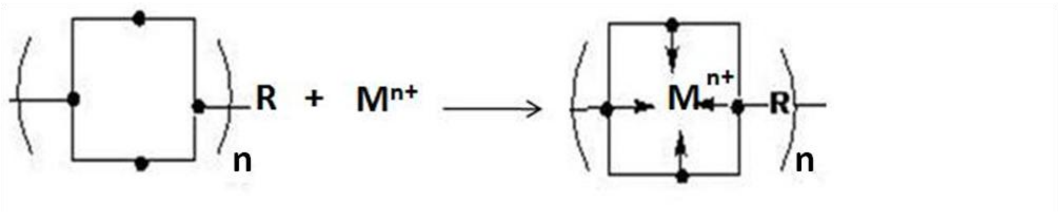


Figure 2.5. Cyclic ligands

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

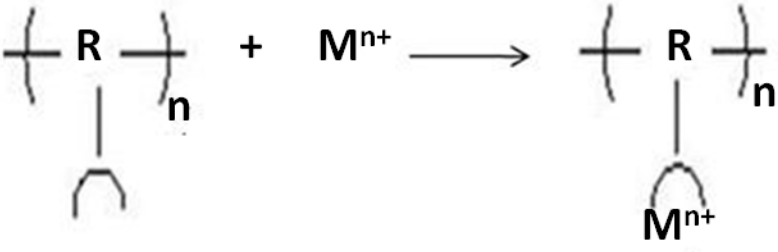


Figure 2.6. Pendent ligands

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 2.7 or 2.8 below.

If two pendent chelating ligands are required, cross-linking can give structure in Figure 2.7 whereas structure which is given in Figure 2.8 is formed if the chelating sites are along the main chains of two polymer molecules.

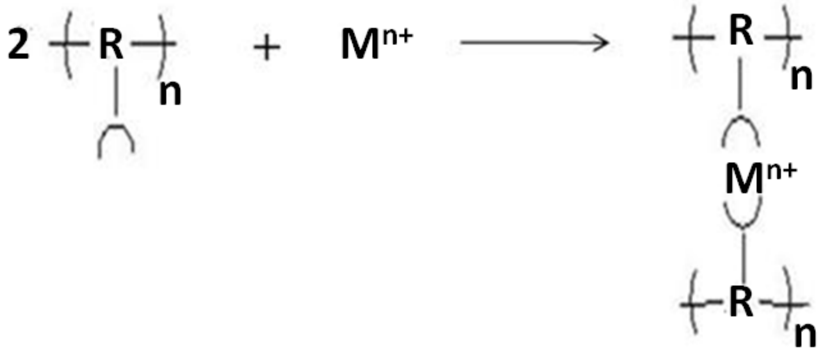


Figure 2.7. Network polymer (pendent ligands)

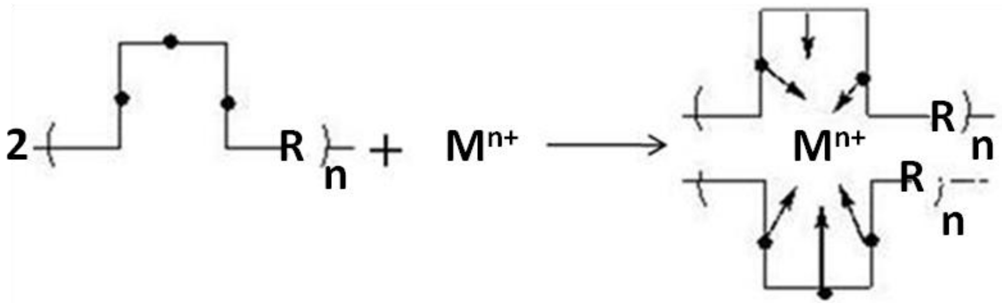


Figure 2.8. Network polymer (attached ligands)

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.

2.7.2.1. Polymer-metal complexes as remediation agents

Synthetic coordination 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 stream. 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 (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).

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 2.9 demonstrate the complexation mechanism.

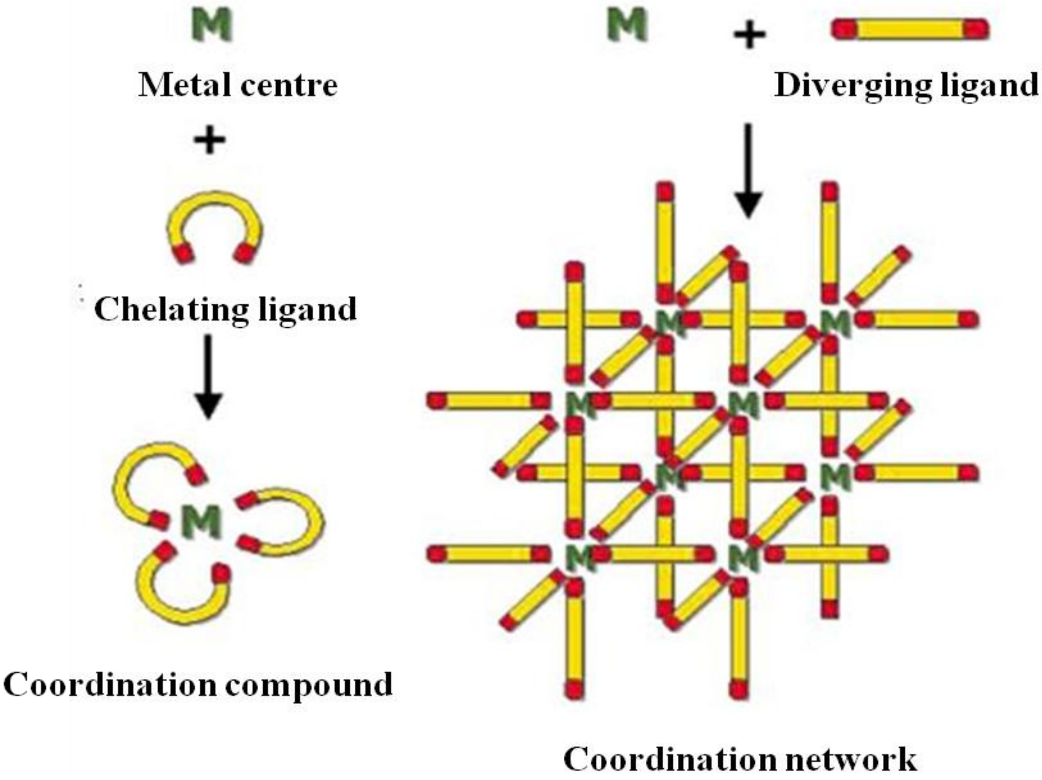


Figure 2.9. Polymer-metal interaction

- ***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 Zn2+ 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 2.10 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).

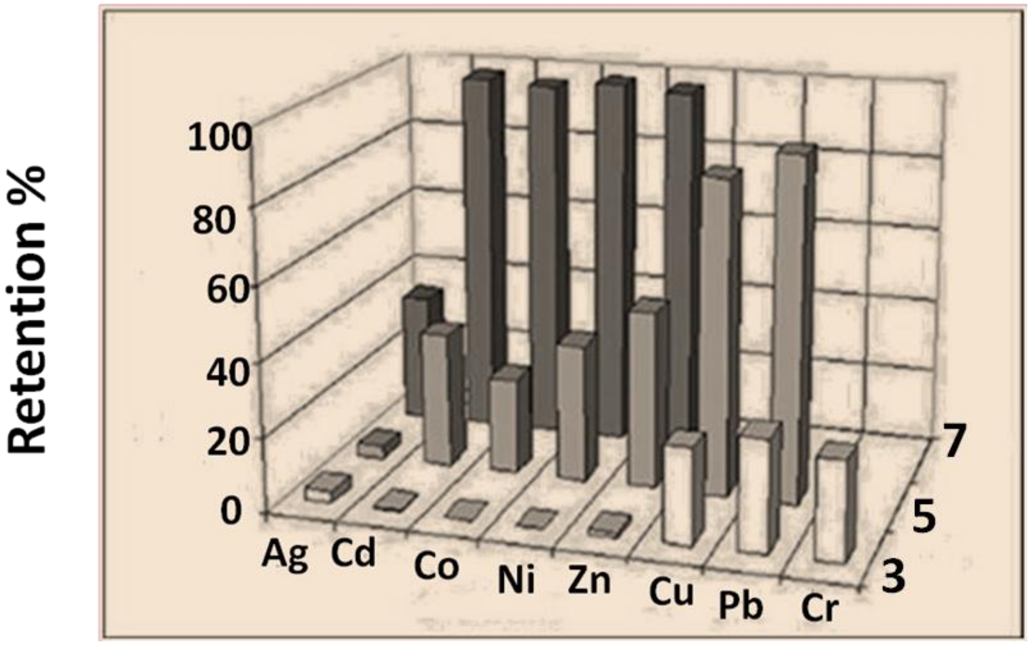


Figure 2.10. Metal ion retention of poly (2-acrylamido glycolic acid) at pH 3, 5, and 7 (Li et al., 2008).

- ***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).

Chapter 3

RESEARCH OBJECTIVES

3.1 Aim of the research

The general aims of the research were the development, modification, characterization, and application of polymeric materials that would be feasibly used as ameliorants and remediation agents for heavy metal-polluted waters, as well as to explore the potential of such materials in recovering metals from industrial and wastewaters

3.2. Specific objectives

- ***Development and modification of polyethylenimine***

The specific objectives addressing the overall aim are as follows:

* Development and modification of in-soluble coordination polymers (chelating polymers) owing immobilized agents by introducing different functional groups as chelating ligands.

* Application of the synthesized materials to investigate their performance in metal ion recovery from wastewaters depending on their triple functions, namely: ion exchange, chelate formation and physical adsorption.

This entailed developing water-insoluble polyethylenimine incorporating a variety of functional groups such as, sulfonic acid, amine, amide, and phosphonic acid for selective removal of heavy metal ions.

- ***Characterisation***

The synthesized materials were characterized by infra red spectroscopy (IR), to assess the produced structure.

- ***Optimization***

The synthesised materials were optimised using synthetic standard solutions in order to outline their main properties as adsorbent agents such as relative binding efficiency, effect of the pH, and selectivity of the synthetic polymers for targeting specific metal ions.

❖ ***Applications***

The applicability of the synthesised materials was investigated, the synthesized polymers were employed on collected wastewater samples and the possibility of applying them in the real environmental samples was assessed.

3.3. Key Questions

The proposed research was based on following fundamental questions.

* How does the subsequent introduction of functional groups or chelating moieties affect either the efficiency or selectivity of the polymers and why?

* How will the selectivity for specific metal ions be achievable in the presence of other metal ions?

* How can the polymers be regenerated for reuse?

* What is the impact of the regeneration on the efficiency of polymers?

* What is the possibility of applying these polymers practically in the real environment?

Chapter 4

MATERIALS AND METHODS

This chapter addresses the research approach used, namely: the synthesis and functionalization of polymers; their characterisation; analysis of the metals and anions; as well as the experimental protocol followed for adsorption and desorption studies. The chapter ends with a quality control section and the various models used to assess the analytical results.

4.1. Synthesis and functionalisation of the polymers

4.1.1. 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.

4.1.2. 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).

In this research branched polyethylenimine (Figure 4.1) 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.

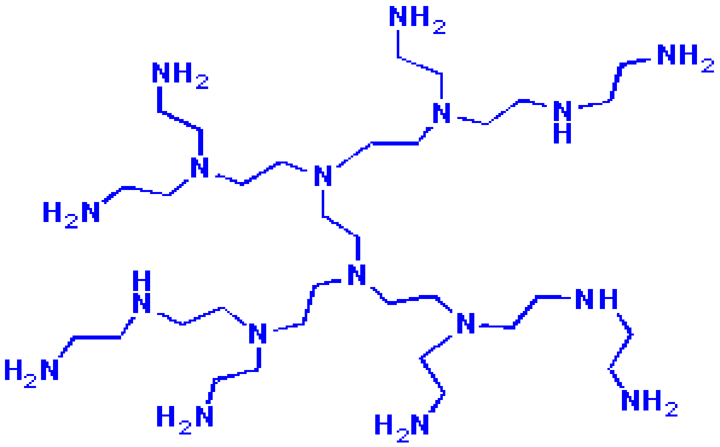


Figure 4.1. Branched polyethylenimine

Polyethylenimine (PEI) is well known for its metal chelating potential owing to the presence of amino groups. It has been widely used for the retention of metal ions, but as a water soluble polymer which requires additional techniques for effective removal such as membrane support or ultrfiltration making it difficult to work with. It has also been used mainly for the removal of single or a few metal ions (Cojocaru *et al.*, 2009; Ghoul *et al.*, 2003; Gohdes *et al.*, 2001; Leroy *et al.*, 2003; Masotti *et al.*, 2010; Molinari *et al.*, 2006; Molinari *et al.*, 2005; Molinari *et al.*, 2004; Ortagi *et al.*, 2008; Taylor *et al.*, 2003).

In this study PEI surface has been modified by introducing different functional groups for selective removal, depending on the difference in the affinity of donor atoms. The functionalization of polyethylenimine produced 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.

So, overall purposes of this phase were 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.

4.2. Analytical techniques

The characterisation of the polymers as well as the metals and anions was conducted using infra-red spectroscopy (IR), inductively coupled plasma optical emission spectroscopy (ICP-OES) and ion chromatography (IC,) respectively.

4.2.1. Fourier Transform Infra-Red spectroscopy (FTIR)

Fourier Transform Infra-Red spectrometer is a subset of spectroscopy that deals with the infrared region of the electromagnetic spectrum. It covers a range of techniques, the most common being a form of absorption spectroscopy. It can be used to identify compounds or investigate sample compositions.

The infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Since each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. Therefore, infrared spectroscopy can result in a positive identification mainly qualitative analysis of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present (quantitative analysis). So, amongst all techniques, infrared is an excellent tool for quantitative and qualitative analysis. It is also been employed to study the changes occurring upon chemical modification, degradation and oxidation of polymers and their fundamental features of vibrational motion (Painter and Coleman, 1997). The basic components of the infrared instrument are shown in Figure 4.2.

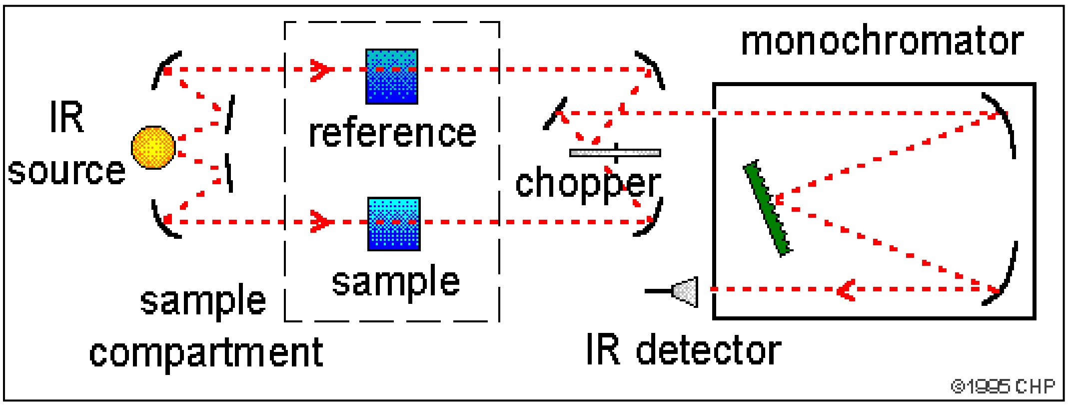


Figure 4.2 Basic components of FTIR

http://www.chemicool.com/definition/fourier_transform_infrared_spectrometer_ftir.htm

The route of FT-IR analysis (Figure 4.3) starts from the source where the infrared energy is emitted from a glowing black-body source and then passes through an aperture which controls the amount of energy presented to the sample which is ultimately to the detector. Then from there, the beam enters the interferometer where the "spectral encoding" takes place. The resulting interferogram signal then exits the interferometer to pass through the sample (analyte) whereby it is transmitted through the surface of the sample. This is where specific frequencies of energy, which are uniquely characteristic of the sample, are absorbed. The beam then passes to the detector for final measurement Finally the measured signal is digitized and sent to the computer where the Fourier transformation takes place and the infrared spectrum is then presented to the user for interpretation (Thermo Nicolet Corporation, 2001).

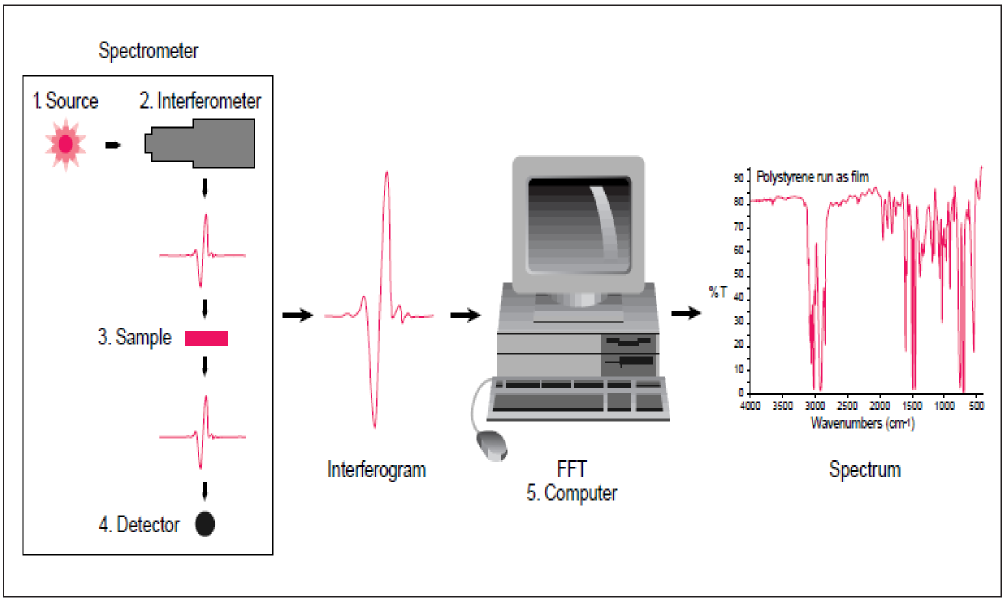


Figure 4.3 Route of FT-IR analysis (Thermo Nicolet Corporation, 2001)

A Fourier Transform Infra-Red spectrometer (Tensor 27, Bruker, Germany) was used in this research to characterize the synthesized polymers.

4.2.2. Inductively coupled plasma-optical emission spectroscopy (ICP-OES)

Inductively coupled plasma-optical emission spectroscopy is an analytical technique used for the detection of trace metals. It is a type of emission spectroscopy that uses the inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element. The intensity of this emission is indicative of the concentration of the element within the sample (Stefansson et al., 2007).

It is based on coupling together an inductively coupled plasma as a method of producing ions (ionization) with a mass spectrometer as a method of separating and detecting the ions.

A typical ICP-OES system is comprised of the following main components (Figure 4.4):

- The sample introduction system which is comprised of a peristaltic pump, nebulizer, spray chamber and drain assembly;
- The plasma, ICP torch and gas supply;
- A source to produce a stable radio frequency;
- Transfer optics and an optical spectrometer;
- Detector and other electronics;
- Computerised instrument control and data collection unit (Botes, 2004).

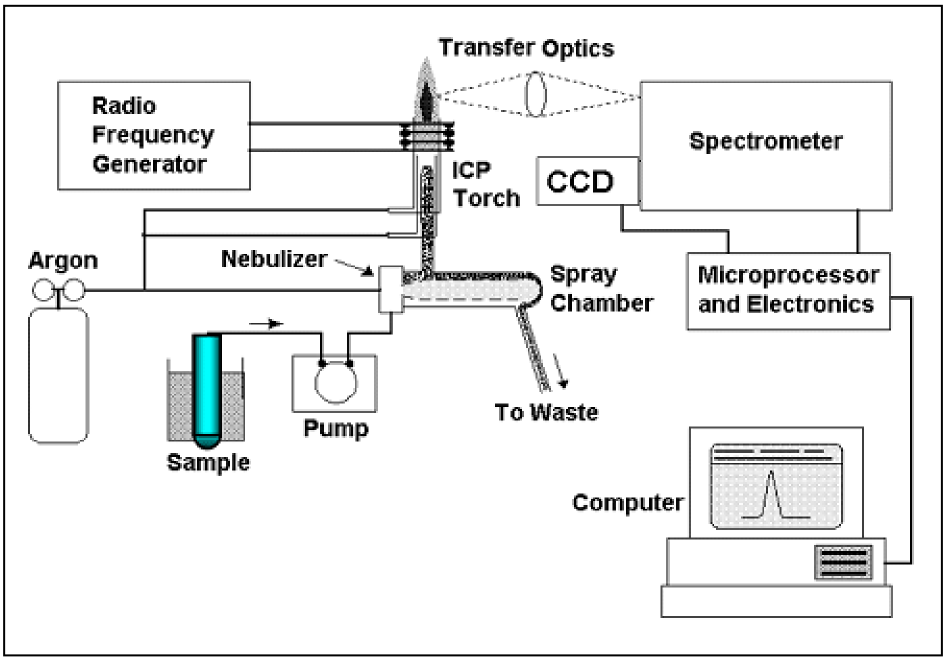


Figure 4.4 Analyte routes in ICP-OES

http://www.aandb.com.tw/Page0001/icp_oes_01_optima_7000_dv.html

The analytical principle used in the ICP-OES system is typically optical emission spectroscopy. The sample (analyte) is nebulised and then vaporised within the argon plasma. The components elements (atoms) contained in the plasma vapour are excited into a state of radiated light (photon) emission. The emitted radiation then passed to the spectrometer optics, where it is dispersed into its spectral components. As every single element has its specific wavelengths, then the most suitable line for the emitted wavelengths is measured by means of charge of couple device (Skoog and Leary, 1992; Smith, 1990).

Generally ICP-OES is a feasible, reliable and high sensitive instrument that can be effectively used for determining the concentrations of every single element in a multi-elements solution simultaneously to very low detection limits (Botes, 2004).

Inductively coupled plasma-optical emission spectroscopy (ICP-OES) (Genesis, Spectro Instruments, Germany) was used to determine the metal ion concentrations in the solutions under these measurement conditions: argon pressure: 800 KPA; pump speed: 2 steps; plasma power: 1400 w; coolant flow: 14 1/min; auxiliary flow: 1.00 1/min; nebulizer flow: 1.00 1/min. Working standards of 0.1, 0.2, o.5, 1 and 2 mg L^{-1} were used for calibrating the instrument. The samples were diluted before analysis in order to fit them in the calibration curve.

4.2.3. Ion Chromatography (IC)

Ion chromatography (Figure 4.5) is a form of liquid chromatography that measures concentrations of ionic species by separating them based on their interaction with a resin depending on their species type and size.

It has been widely used for water analysis to characterise the quality of water by measuring the concentrations of major anions, such as fluoride, chloride, nitrate, nitrite, and sulfate, as well as major cations such as lithium, sodium, ammonium, potassium, calcium, and magnesium in the parts-per-billion (ppb) range. It is the only instrumental technique that may use for rapid, sequential measurements (Weiss and Weiss, 2005).

The analyte in IC passes through a pressurized chromatographic column where ions are absorbed by column constituents through a series of ion exchangers (Figure 4.5). As the eluent (ion extraction liquid) runs through the column, the ions of interest are separated on the column based on the ionic interaction. Then the retention time of different species determines the ionic concentrations in the sample.

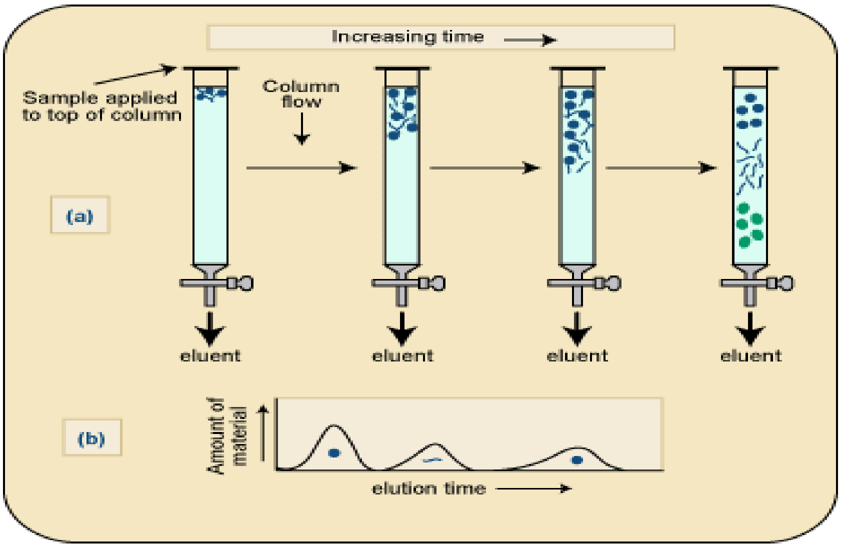


Figure 4.5 Analyte routes in IC

http://serc.carleton.edu/microbelife/research_methods/biogeochemical/ic.html

The stationary phase surface which is being packed in the column displays ionic functional groups (R-X) that interact with analyte ions of opposite charge. This type of chromatography is further subdivided into cation exchange chromatography and anion exchange chromatography. The ionic compound consisting of the cationic species Mn+ and the anionic species Bn- can be retained by the stationary phase (Tutu, 2006; Weiss and Weiss, 2005).

The 761 Compact Ion Chromatograph (Metrohm, Switzerland) with a Metrosep A Supp 5 (6.1006.520) 150 x 4.0 mm analytical column was used to determine anions in water and leachate samples. The eluent was a solution of 1.0 mM $NaHCO_3$ and 3.2 mM Na_2CO_3. The eluent was degassed by filtration through a 0.45 µm filter paper. The working standards of 1, 5 and 10 mgl^{-1} were then prepared from the stock solution and used for calibrating the instrument. The samples were diluted before analysis in order to fit them in the calibration curve and to avoid detector saturation.

4.3. Experimental protocol

The experimental protocol of the research was subdivided in two parts: the synthesis part and the analytical part. The synthesis part involved development and modification of the materials, whereas the analytical part involved characterization, optimization and final application.

4.3.1. Synthesis

This part involved the synthesis of water-insoluble polyethylenimine (PEI) by cross-linking as well as the modification or functionalization of produced insoluble cross-linked polyethylenimine (CPEI) including phosphonation and sulphonation.

❖ ***Chemicals***

All chemicals were obtained from Sigma Aldrich, South Africa without further purification. Branched polyethylenimine (PEI MW 25000) $(C_2H_5N)n$, epichlorohydrin (C_3H_5ClO), sodium hydroxide (NaOH), isopropanol (C_3H_8O), cloropropanesulfonyl chloride ($C_3H_6Cl_2O_2S$), tetrahydrofuran (C_4H_8O), Phosphorous acid (H_3PO_3), formaldehyde 38% (CH_2O), hydrochloric acid 6 mol L^{-1} (HCl) was prepared by dilution from 11.6 mol L^{-1} hydrochloric acid, De-ionized water (H_2O).

4.3.1.1. Cross-linking of polyethylenimine

Polyethylenimine, 10 g, was dissolved in 25 mL de-ionized water. Epichlorohydrin, 1.2 mL, and 2 g NaOH were added and the mixture was heated under reflux at 50°C - 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. The cross-linking reaction scheme is shown in Figure 4.6 (Saad et al., 2011).

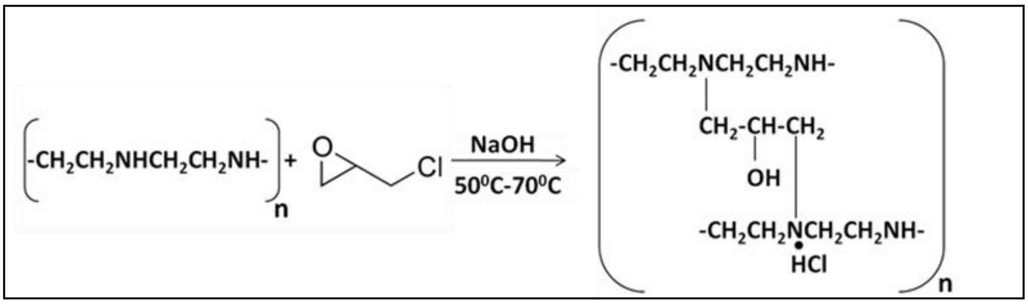


Figure 4.6. Cross-linking reaction scheme

4.3.1.2. Functionalization of polyethylenimine

Polyethylenimine has been modified with different functional groups by replacing the nitrogen atoms as the donor atoms by different donor atoms; once by phosphorus atoms by adding phosphorous acid to produce the phosphonated derivative of cross-linked polyethylenimine (PCPEI) and once again by sulphur atoms by adding 3-chloropropanesulfonyl chloride to produce the sulfonated derivative of cross-linked polyethylenimine (SCPEI).

Phosphonation of cross-linked polyethylenimine

Cross-linked polyethylenimine, 2.5 g, was distributed in 80 mL HCl 6 mol L^{-1}. 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 over night. A pale powdery yellow solid was obtained, washed with abundant water before drying in an air oven at 30°C. The phosphonation reaction scheme is shown in Figure 4.7.

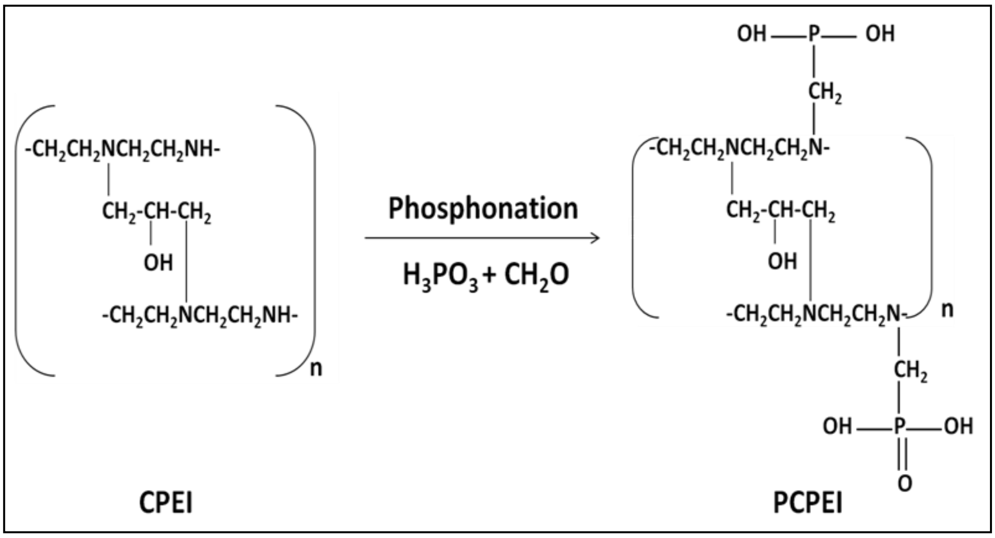


Figure 4.7. Phosphonation reaction scheme

Sulfonation of cross-linked polyethylenimine

Cross-linked polyethylenimine, 2.5 g, was distributed in tetrahydrofuran. 3-chloropropanesulfonyl chloride, 2.4 mL, was added and the mixture was heated under reflux at 70°C over night. A pale rubbery brownish solid was obtained, washed with abundant water three times and dried in an air oven at 30°C. The sulfonation reaction scheme is shown in Figure 4.8.

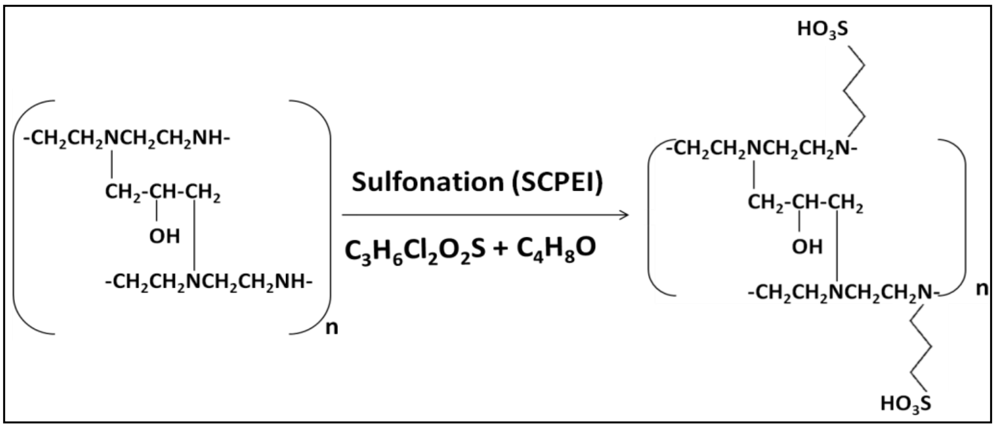


Figure 4.8. Sulphonation reaction scheme

4.3.2. Characterization of synthesized polymers

All obtained materials have been characterized using Fourier Transform Infra-Red Spectroscopy (FTIR), in order to confirm the presence of the introduced functional groups.

4.3.3. Optimization of synthesized polymers

The synthesised materials were optimised in order to outline their main properties as adsorbent agents and to determine their efficiency with regard to the following:

1. The relative binding efficiency of the synthetic polymers.
2. The effect of the pH.

The pH effect is an important physicochemical variable in the complexation governed adsorption processes as it plays a definitive role in controlling chelating properties, by which surface charges may be changed or modified (Zander, 2009).

3. The effect of concentration and adsorption isotherms

Adsorption isotherms are quantified to describe the interaction between the adsorbent (polymer) and the adsorbate (metal ions) which is very critical for optimization and the design of adsorption process. The

Langmuir and Freundlich are the most common and frequently used models (Atkins, 2006; Gupta *et al.*, 2003).

1. The effect of contact time and kinetic models

Kinetics of metal ion adsorption governs the rate which determines the residence time, which is one of the most significant factors defining the efficiency of the adsorbent. The adsorption of metal ions onto in-soluble chelating adsorbent is generally considered as a liquid-solid phase reactions. Kinetics of adsorption is influenced by the diffusion of adsorbate particles. This includes the diffusion of the adsorbate (metal ions) through the solution to the surface of the adsorbent (polymer) and the diffusion of ions within the adsorbent (Krishnan and Anirudhan, 2003; Streat, 1984).

The adsorption kinetics is governed by the slowest step, if the ions diffusion from the solution to the adsorbent surface is the slowest step, the adsorption kinetics is liquid-film diffusion controlled, whereas the adsorption kinetics is particle diffusion controlled if the ionic diffusion inside the solid adsorbent is the lowest step (Krishnan and Anirudhan, 2003; Streat, 1984).

Among several existing kinetics models, the most commonly used kinetics models are pseudo-first-order model and pseudo-second-order model.

1. The selectivity of the synthesized polymers for the metal ions
2. Proper regeneration and reusability.

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 (Zander 2009).

Since polyethylenimine and its derivatives: phosphonated derivative and sulfonated derivative are classified as an acidic basic polymers, it can be regenerated by protolysis by changing the pH of the solution in order to cleave the polymer-metal bond.

This has been done by applying the developed polymers on synthetic standard solutions in laboratory.

4.3.3.1. Sorption studies

- **Batch adsorption studies**

The developed materials were applied for metal ion removal from synthetic standard solutions in order to study their chelating properties prior to apply them in real environmental samples for optimum removal conditions.

Chemicals

All metal solutions were prepared from their respective nitrate salts, namely: $Zn(NO_3)_2$, $Pb(NO_3)_2$, $Cr(NO_3)_3$, $Hg(NO_3)_2$, $Mn(NO_3)_2$, $Fe(NO_3)_3.H_2O$, while the oxo-anions Se and As were prepared from Na_2SeO_3 and $NaAsO_2$, respectively. pH adjustments for the adsorption experiments were conducted using 1 mol L^{-1} solutions of HNO_3 and NaOH. De-ionized water was used for the preparation of all solutions.

Preparation of solutions

All metal solutions were prepared from their respective nitrate salts by weighing out the appropriate amount of salts and dissolving in de-ionized water. A 1000 mg L^{-1} stock solution containing each metal was prepared by weighing out the required mass of appropriate metal salt, from which the 40 mg L^{-1} multi-component working standard solution was obtained by serial dilution.

The titrant solutions of NaOH and HNO_3 were prepared by weighing out the required amount of NaOH and HNO_3 respectively and dissolving with de-ionized water.

Adsorption procedure

Adsorption experiments were performed in 50 mL flasks at room temperature. 1 g of synthetic cross-linked polyethylenimine, phosphonated cross-linked polyethylenimine, and sulfonated cross-linked polyethylenimine 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 amount of metal ions adsorbed per unit mass of adsorbent at equilibrium was calculated on the basis of the mass balance equation 4.1.

$$\text{Capacity (mg metal g}^{-1}\text{ polymer)} = \frac{(C_i - C_f) \times V}{1000 \times P} \quad (4.1)$$

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

- ***Effect of pH***

The effect of pH was determined by conducting the adsorption experiments following the above mentioned procedure at two different pH values; to assess the effect of pH on the adsorption of metal ions from synthetic solutions of 40 mg L^{-1} with a fixed quantity of adsorbent, fixed time, and fixed temperature. The pH of the synthetic solutions was adjusted to pH 3 and pH 8 using 1 mol L^{-1} sodium hydroxide and 1 mol L^{-1} hydrochloric acid.

- ***Effect of initial concentration and adsorption isotherms***

Adsorption isotherms were carried out in a series of 50 mL flasks at room temperature. Each flask was filled with 40 mL of different initial concentration solution of multi-component standard, varying from 10 to 60 mg L^{-1} while maintaining the adsorbent mass and pH at constant level. At equilibrium the solutions were filtered and the equilibrium concentrations determined using (ICP-OES). Each of the data sets was used to calculate the adsorption capacity based on the mass balance equation 4.1. The obtained equilibrium capacities (q_e) were then plotted against the equilibrium concentrations (C_e).

- ***Effect of contact time and adsorption kinetics***

Contact time adsorption experiments were conducted at room temperature at pH 6.4 to determine the time needed for the adsorption to reach equilibrium. The adsorption was studied at various time intervals (10 – 120 min) at the concentration of 40 mg L^{-1} following same procedure described in section 4.3.3.1. The mixture was left for the different time intervals and the concentration of ions was determined at the end of each time.

4.3.3.2. Desorption studies

The regeneration of the synthesized materials was carried out by the treatment of previously loaded polymers 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 the regeneration, the mixtures were stirred for about one hour, filtered and the polymers washed with de-ionized water and dried prior to re-use.

4.3.4. Application of the developed materials on wastewater samples

The synthesized polymers were applied for the removal of heavy metal ions from wastewater samples collected in the vicinity of gold mining activities in the Central Rand goldfield, Johannesburg. The map of the sampling site is given in Figure 4.9.

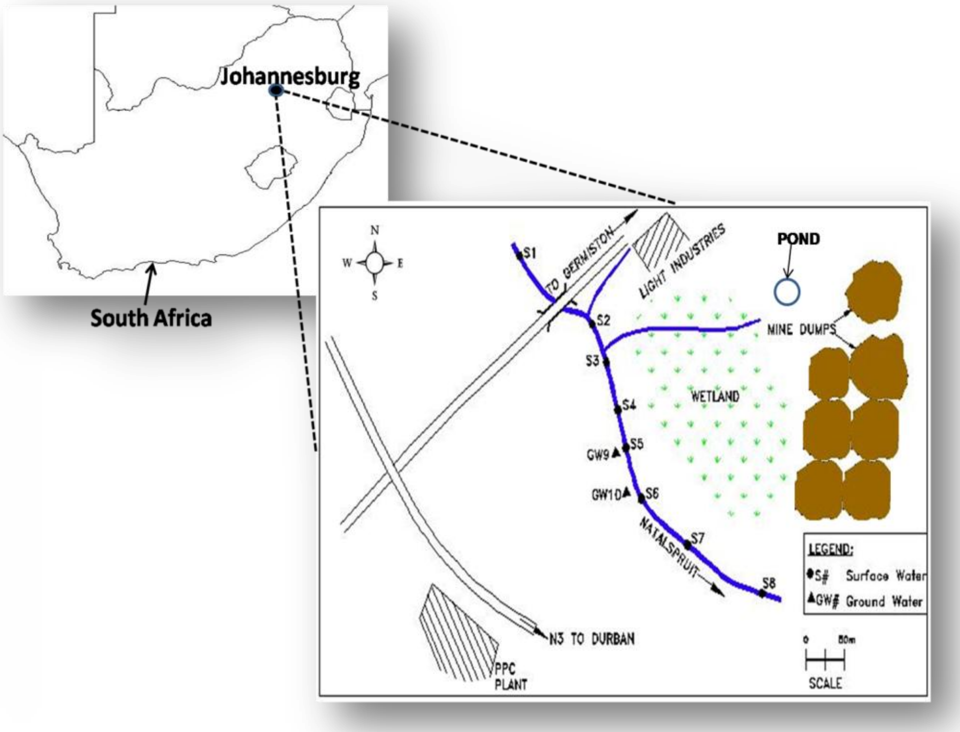


Figure 4.9. Sampling site map

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. Redox potentials were obtained from

Pt electrodes versus Ag/ AgCl. The electrodes were checked using a standard buffer solution and all reported potentials were corrected relative to the standard hydrogen electrode (SHE).

Five samples were used (one pit water and four surface water samples). The samples were collected at a site to the east of the city of Johannesburg. Surface water samples were collected on the banks of 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 (Hermond and Fechner-Levy 2000; Mugo *et al.*, 1983) 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).

The removal of metal ions from wastewater samples were done following the same above mentioned adsorption procedure.

4.3.5. Modelling of analytical results

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

4.3.5.1. Kinetics

- *Pseudo-first-order model*

The pseudo-first-order is a kinetic model described by Lagergern equation 4.2 (Babarinde *et al.*, 2009).

$$\log (q_e - q_t) = \log q_e - (k/2.303)\, t \qquad (4.2)$$

Where q_e (mg g^{-1}) is adsorption capacity at equilibrium, q_t (mg g^{-1}) is the adsorption capacity at time t, and K (1/min) is the rate constant of pseudo-first-order. The value of k can be obtained from the slope by plotting Log ($q_e - q_t$) vs. t.

- *Pseudo-second-order model*

Pseudo-second-order mode is applied when the applicability of the first-order kinetics becomes untenable. The equation of pseudo-second-order is given in equation 4.3.

$$1/q_t = (1/k_2q_e) + (1/q_e)\, t \qquad \textbf{(4.3)}$$

This equation is applied with a view to obtain k_2, the second order rate from the plots of t/q_e vs. t.

Contact time adsorption experiments were conducted at room temperature at pH 6.4 to determine the time needed for the adsorption to reach equilibrium. The adsorption was studied at various time intervals (10 – 120 min) at the concentration of 40 mg L^{-1} following same procedure described in section 4.3.3.1. The mixture was left for the different time intervals and the concentration of ions was determined at the end of each time.

4.3.5.2. Isotherms

- *Lagmuir model*

The Lagmuir 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; they only adsorbed on the free surface of the adsorbent. Hence it assumes uniform surface (all adsorbent sites are equivalent), the adsorbed molecules do not interact and they all adsorbed through same mechanism (Hamdaoui and Naffrechoux, 2007). The Langmuir model is given by the equation 4.4.

$$q_e = \frac{q_m bC_e}{1 + bC_e} \qquad (4.4)$$

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 qm (mg g^{-1}) is the maximum adsorption capacity, and b (L mg^{-1}) is the constant related to the free energy of adsorption.

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

Plotting of 1/ C_e vs. 1/ q_e was obtained from the linearized form of the Langmuir equation ($1/C_e = bq_m\ 1/q_e - b$). The values of monolayer capacity (q_m) and Langmuir constant (b) have been calculated from the intercept and the slope of the plots.

The adsorption capacity can be correlated to the surface area of the adsorbent. The highest the adsorption capacity; the highest surface area and pore size.

- *Frendlich model*

The Frendlich model is an empirical formula for heterogeneous adsorption given by the equation 4.5.

$$q_e = K_F C_e^{1/n} \qquad (4.5)$$

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.

Since the Frendlich model is an exponential equation, it assumes that the adsorption capacity of the adsorbent increases with the increasing of the concentration of the adsorbate.

Plotting of ln q_e vs ln C_e was obtained from the linearized form of the Frendlich equation ($\ln q_e = \ln K_F + 1/n \ln C_e$). This would give the value of 1/n as slope and K_F as an intercept; these values can be correlated to the adsorption capacity and intensity (Frendlich, 1926).

Adsorption isotherms were carried out in a series of 50 mL flasks at room temperature. Each flask was filled with 40 mL of different initial concentration solution of multi-component standard, varying from 10 to 60 mg L^{-1} while maintaining the adsorbent mass and pH at constant level.

At equilibrium the solutions were filtered and the equilibrium concentrations determined using (ICP-OES). Each of the data sets was used to calculate the adsorption capacity based on the mass balance equation 4.1. The obtained equilibrium capacities (q_e) were then plotted against the equilibrium concentrations (C_e).

4.3.5.3. Effect of temperature on adsorption

The thermodynamic study was done by conducting the adsorption experiments at two different temperatures in order to investigate the mechanism of the adsorption of the metal and metalloid ions onto the materials surface by calculating the activation energy (Ea). Activation energy is an important parameter in a thermodynamic study as it determines the temperature dependence of the adsorption. Hence it represents the energy that must be overcome in order for an adsorbate-adsorbent to interact.

The magnitude of activation energy gives an idea about the type of adsorption. There are two main types of adsorption: chemisorption and physisorption. The 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 in physisorption are weak. On the other hand, chemisorption involves forces much stronger than in physisorption. Therefore, the activation energy for chemisorption is high 83.7 kJ mol^{-1} (Aksakal and Ucun, 2010; Klekamp and Urnbac, 1993; Özcan *et al.*, 2006).

The thermodynamic studies were carried out following the previously mentioned procedure (4.3.3.1) at two different temperatures namely 15^{o}C and 27^{o} C with a fixed quantity of adsorbent and fixed initial concentration.

The concentrations obtained after the adsorption were then used to calculate the activation energy Ea according to the Arrhenius equation 4.6:

$$Ea = \frac{R.\ T_1.\ T_2}{T_1.\ T_2}\ .\ \ln K_1/ K_2 \qquad (4.6)$$

where: Ea 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 T_1 and T_2.

The constants K_1 and K_2 could be calculated as follows:

$$K = \frac{C_i - C_e / M}{C_e} \qquad (4.7)$$

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.

CHAPTER 5

RESULT AND DISCUSSION

This chapter presents the results for the experimental work conducted. The results relate to: the characterization of the synthesized polymers; adsorption studies on synthetic solutions and environmental samples (including important kinetic, equilibrium and thermodynamic modelling of the adsorption process); desorption studies.

5.1. Cross-linked polyethylenimine

5.1.1. Physiochemical characterization of cross-linked polyethylenimine

The synthesis of CPEI has been discussed in chapter four, section 4.3.1.1.

The synthesized cross-linked polyethylenimine was characterized by Fourier transform Infra-red spectroscopy. The commercial branched polyethylenimine (before cross-linking) was also characterized for comparative study.

The FTIR spectrum of branched soluble polyethylenimine (PEI) and cross-linked insoluble polyethylenimine (CPEI) are given in Figure 5.1 and Figure 5.2 respectively.

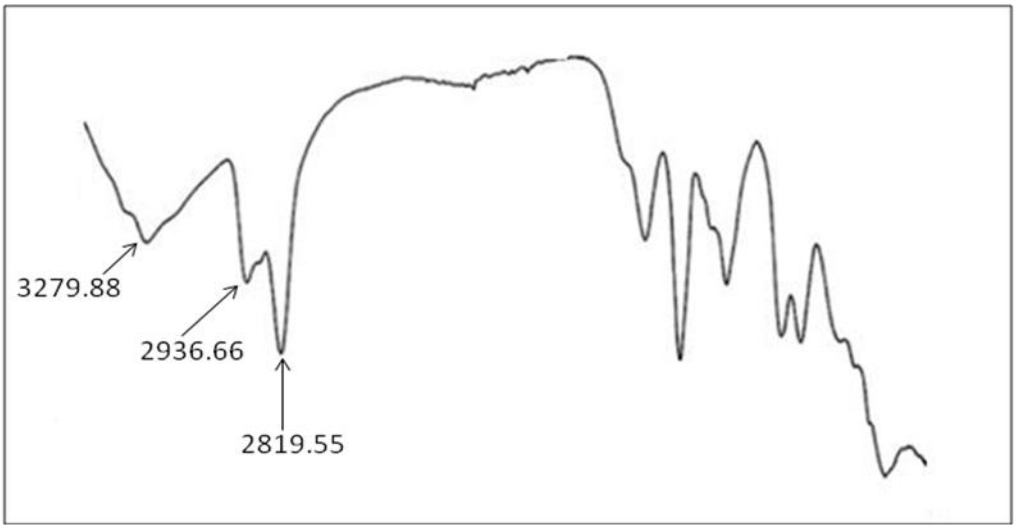


Figure 5.1. IR spectrum of PEI

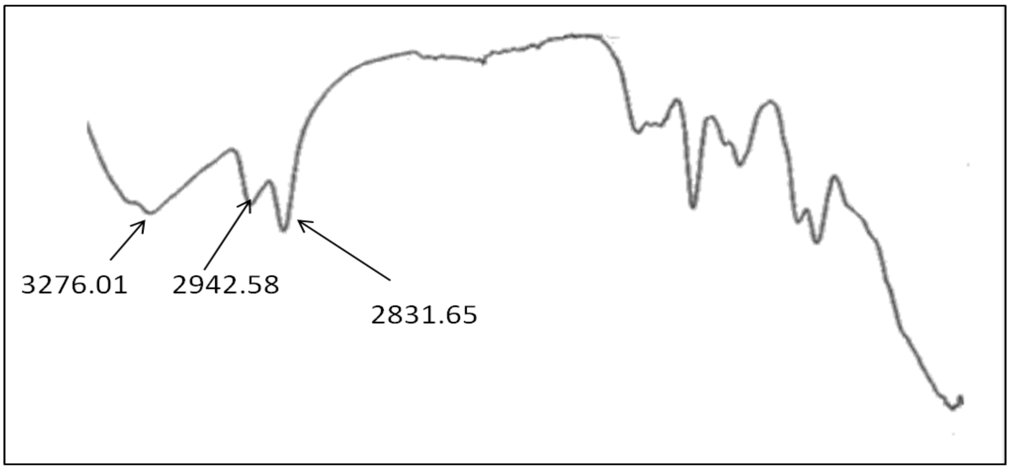


Figure 5.2. IR spectrum of CPEI

The broad absorption bands at 3279.88 cm^{-1} (Figure 5.1) and 3276.01 cm^{-1} (Figure 5.2) are corresponding to the stretching vibration of N – H. Whereas the sharp peaks at 2819.55 cm^{-1} and 2936.66 cm^{-1} in Figure 5.1 and 2831.65 cm^{-1} and 2942.58 cm^{-1} in Figure 5.2 are corresponding to the stretching vibration of C- H.

The difference in the absorption bands strength for the stretching vibration of N- H could be observed, with the cross-linked polymer (Figure 5.2) yielding lower band strength. This could be attributed to the closure of some secondary amine sites during cross-linking of the polymer (Zhu *et al.*, 2006). The cross-linked polymer thus contains less secondary amine groups due to the reaction between these groups in PEI and chloromethyl groups in epichlorohidrin.

5.1.2. Removal of metal and metalloid ions from synthetic solutions by CPEI

The results for the adsorption of metal and metalloid ions in synthetic solutions by CPEI are presented in Table 5.1. The table shows the final metal concentrations (C_f) obtained 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) were based on three measurements (n = 3).

Table 5.1. Removal of metal and metalloid ions from synthetic solutions by CPEI

pH		Cr	As	Fe	Hg	Ni	Zn	Mn	U	Pb	Se
3	C_f (mg L^{-1})	4.220	18.60	4.650	18.50	12.36	4.090	11.60	19.20	14.72	34.00
	RSD (n = 3)	0.971	0.967	0.798	3.807	1.603	2.102	0.701	4.797	0.304	1.610
	Ads. Capacity (mg g^{-1})	1.431	0.856	1.414	0.860	1.106	1.436	1.136	0.832	1.011	0.240
	Ads percentage	89%	54%	88%	54%	69%	89%	71%	52%	63%	15%
8	$\mathrm{C_f}$ (mg L^{-1})	0.580	17.30	1.370	18.00	7.200	0.670	8.440	19.50	13.54	34.50
	RSD (n = 3)	1.8	0.5	2.2	6.5	0.9	0.6	0.9	6.7	0.6	1.9
	Ads. Capacity (mg g^{-1})	1.577	0.908	1.545	0.880	1.312	1.573	1.262	0.820	1.058	0.220
	Ads 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	0.050	0.017	0.040	0.077	0.007	0.057	0.010	0.082

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 standard deviation (n=3).

The trend shows a decrease in percentage adsorption for both pH regimes as follows: Cr > Fe > Zn > Ni > Mn > Pb >> As > Hg > U >> Se.

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 oxyanions Se and As showed poor adsorption since they exist mainly as bases in solution (Saad *et al.*, 2001).

The results obtained showed that the performance of the insoluble cross-linked polyethylenimine (CPEI) is comparable to that of the soluble uncross-linked polyethylenimine (PEI). Masotti *et al.* (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 work, under similar conditions, adsorption percentages of: Cr 97%, Ni 82%, Mn 79%, Pb 63%, and Zn 96%, were obtained (Table 5.1).

5.1.3. pH effect on the adsorption process by CPEI

The adsorption percentages of metal ions by CPEI at pH 3 and pH 8 presented in Figure 5.3 below were carried out according to the procedure described in section 4.3.3.1, in order to investigate the efficiency of the CPEI at both acidic and basic conditions.

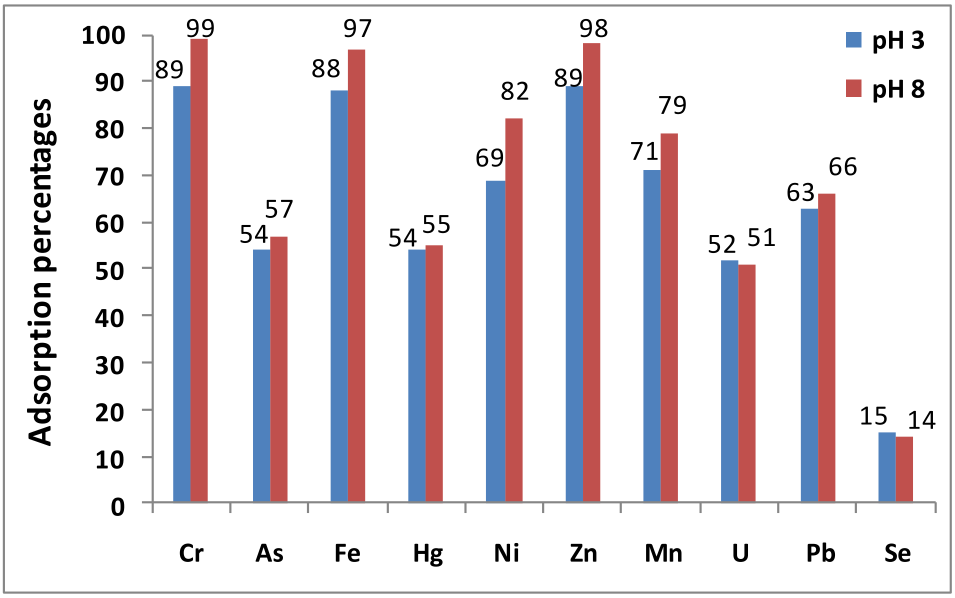


Figure 5.3. The pH effect on the adsorption process by CPEI

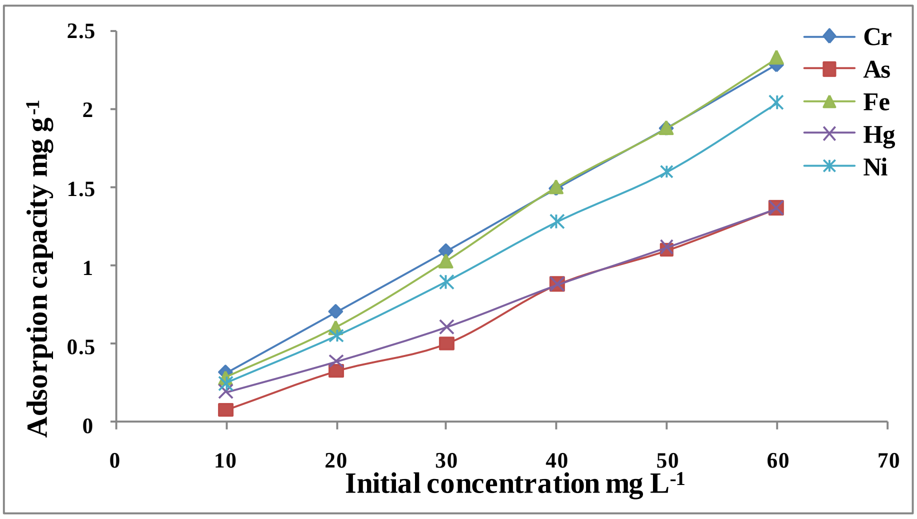
The variation of the adsorption percentages with the pH is clearly noticeable as they are a bit lower in acidic medium (pH 3) whereas at basic condition (pH 8) the uptake of all metal ions increases, For example, increases of: 89% to 99% for Cr; 89% to 98% for Zn; 71% to 79% for Mn and 69 to 82 for Ni were observed.

This result indicates that the pH plays an influential role in the adsorption of metal ions. This may be due to the fact that the higher concentration and mobility of H^+ ions at low pH favour the preferential adsorption of hydrogen ions compared to other metal ions. H^+ ions act as competitors due to the protonation of the polymer resulting in a decrease of the reactivity and, ultimately, the complexation between the adsorbent and the desired metal ions (Ajmal *et al.*, 2000; Rivas and Maureira, 2007).

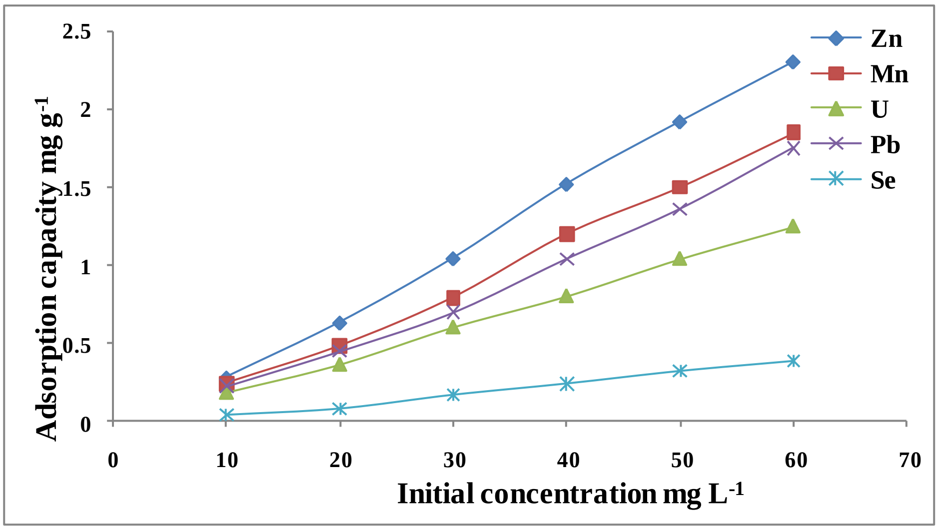
It should be noted, however, that there could be a combination of precipitation and adsorption at pH 8. The solubility of many metals is amphoteric in the sense that the metals tend to dissolve and form cations at low pH and anions at high pH, with minimal solubility at intermediate pH (Smith, 2007).

5.1.4. Effect of initial concentration on the adsorption process by CPEI

The results for the dependence of adsorption on metal ion concentrations are shown in Figure 5.4.



(a)



(b)

Figure 5.4. Effect of initial concentration on the adsorption of (a) Cr, As, Fe, Hg, Ni (b)Zn, Mn, U, Pb, Se by CPEI

All metals showed similar trend as the amount of metal ions adsorbed increased with increasing concentration. Cr, Fe, and Zn showed high adsorption capacity even at very low concentrations and the removal efficiency increased slightly whereas other elements with lower affinity to CPEI such as Se, U, Hg, and As started with very low removal which increased significantly at high concentrations.

5.1.5. Adsorption isotherms for CPEI

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 mechanisms of metal ions onto the CPEI surface, two adsorption isotherm models, Langmuir and Freundlich, were used to fit the experimental data obtained from the adsorption equilibrium experiments described in section 4.3.3.1.

The Langmuir model assumes that the uptake of metal ions occurs on homogenous surface by monolayer adsorption without any interaction between adsorbed ions meaning that the adsorption takes place at specific homogenous sites within the adsorbent. So, once a metal ion occupies a reaction site, then no further adsorption occurs at that location (Langmuir, 1918).

The adsorption data for metal ions onto CPEI were analyzed firstly using the linearized expression of the Langmuir isotherm model which is given in section 4.3.5 (equation 4.1) to estimate the Langmuir constants (b and q_m) from the plots. Values of the Langmuir constants and correlation coefficient (R^2) obtained are tabulated in Table 5.2.

Table 5.2. Parameters of the Langmuir model for the adsorption by CPEI

	Cr	As	Fe	Hg	Ni	Zn	Mn	U	Pb	Se
b	0.243	1.433	0.578	2.466	0.622	0.439	0.944	2.707	1.198	0.378
R^2	0.853	0.790	0.274	0.906	0.885	0.308	0.742	0.834	0.753	0.816
q_m	13.63	27.53	1.202	28.98	20.43	2.556	22.06	32.63	25.33	246.9

The low coefficient of correlation values for the Langmuir linear expression, suggest that this model does not describe perfectly the adsorption mechanism based on multi-component solutions.

The adsorption data were further analyzed using the linearized form of the Freundlich equation using the same set of experimental data, by plotting ln qe versus ln Ce. The calculated Freundlich constants (n and K_f) and coefficient of correlation (R^2) values are shown in Table 5.3.

Table 5.3. Parameters of the Freundlich model for the adsorption by CPEI

	Cr	As	Fe	Hg	Ni	Zn	Mn	U	Pb	Se
n	0.230	0.242	0.215	0.822	0.483	0.243	0.602	0.837	0.682	0.729
R^2	0.961	0.953	0.970	0.992	0.955	0.960	0.918	0.995	0.928	0.988
K_f	4.085	7.227	4.707	3.679	4.172	4.089	3.863	3.791	3.809	6.307

The high coefficients of correlation values (R^2 > 0.95) for most of the studied metals except Mn and Pb showed a good linearity;

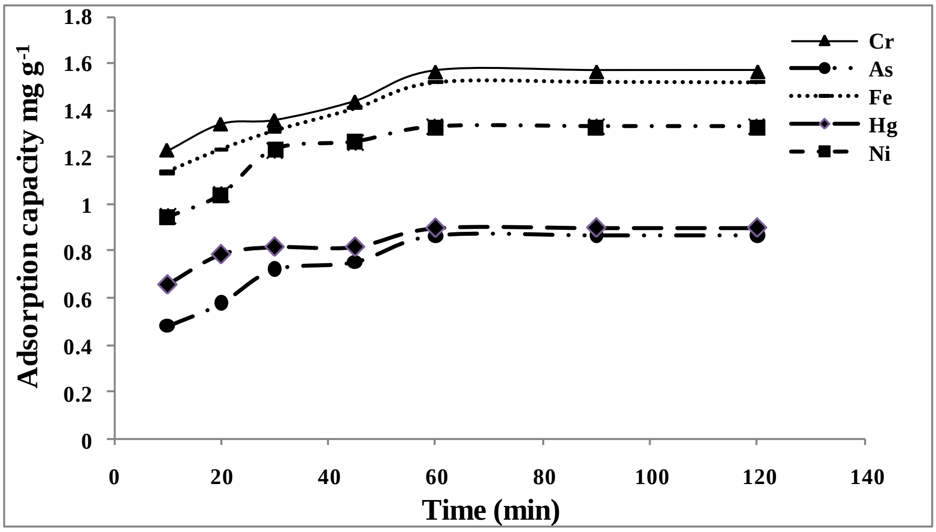
suggesting that the Freundlich isotherm provides a good model of the adsorption process for these metals.

Mn and Pb adsorption were best described by the Freundlich model as can be seen from their R^2 values of 0.918 and 0.928, respectively compared to those for the Langmuir model (0.742 and 0.753 respectively).

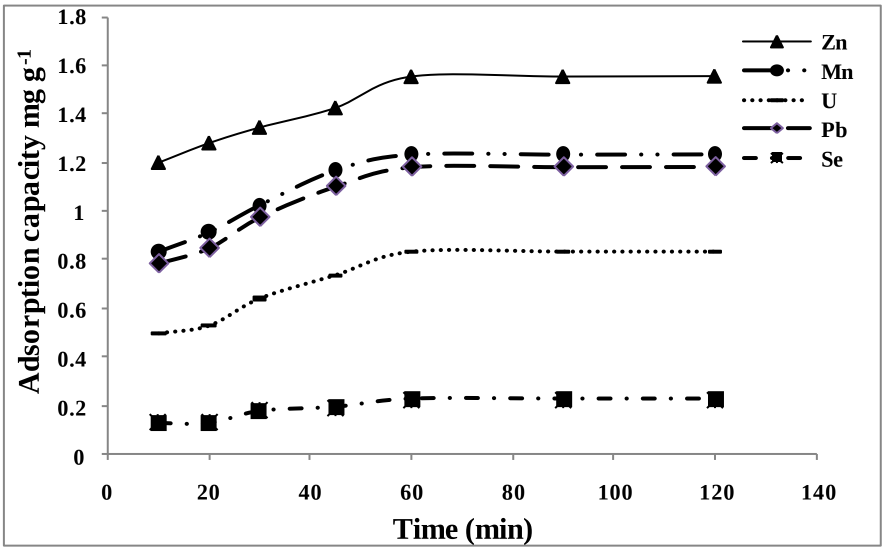
5.1.6. Effect of contact time on the adsorption process by CPEI

Effect of contact time on the adsorption process by CPEI was the minimum exposure time to reach adsorption equilibrium considered in all sorption experiments. It was assessed using a synthetic multi-component solution containing 40 mg L^{-1} metal ion concentration. The required contact time for adsorption to be completed is very important to design the adsorption process since it provides the minimum time required for metal ions uptake.

Figures 5.5 illustrates the adsorption of metal ions onto CPEI as a function of time (adsorption capacity versus time).



(a)



(b)

Figure 5.5. Effect of contact time on the adsorption of (a) Cr, As, Fe, Hg, Ni (b)Zn, Mn, U, Pb, Se by CPEI

The adsorption increased rapidly with an increase in contact time from 10 to 45 minutes, with equilibrium reached within 45 - 60 minutes. A further increase in time had no effect on the adsorption of the metal ions. The maximum contact time of 60 minutes was therefore considered as the optimum time.

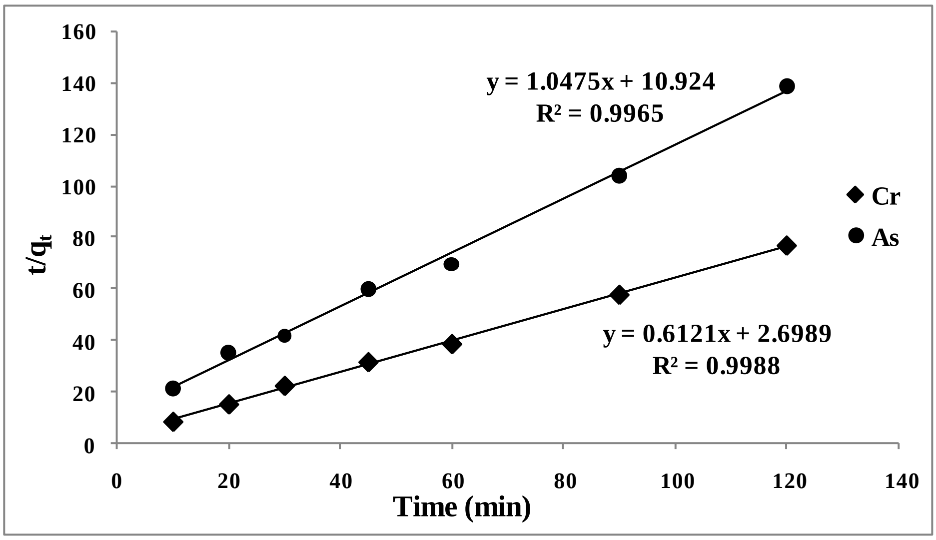
5.1.7. Kinetic modelling of adsorption process by CPEI

Two different types of kinetic models (pseudo first-order and pseudo second-order) were used to investigate the kinetics of adsorption of metal ions onto CPEI, in order to gain insight into the mechanism and rate controlling steps affecting the kinetics of adsorption.

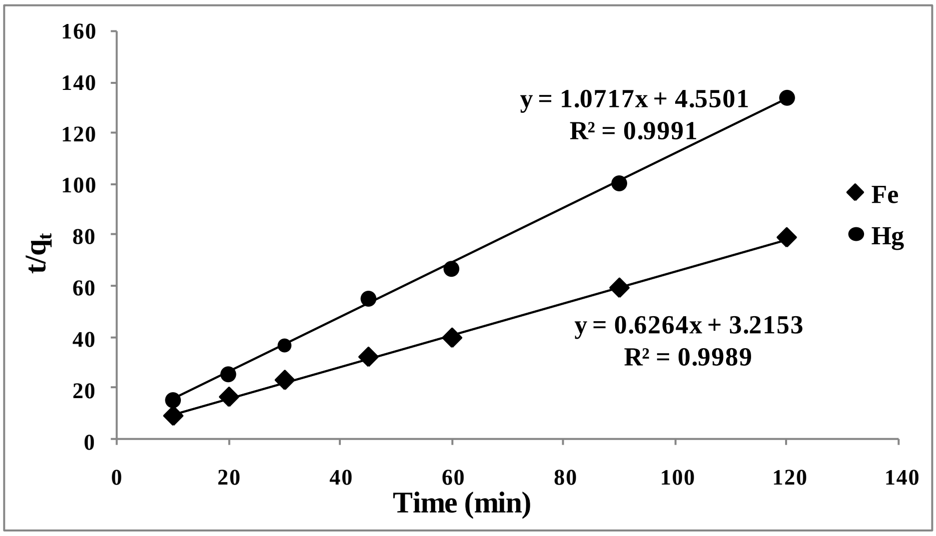
The experimental kinetic data showed better correlation with the pseudo-second-order model because of the high values of correlation coefficients based on the linear regression $R^2 > 0.95$. The pseudo second-order rate constants (K_2) of the adsorption of metals were calculated from the slopes of the plots.

The calculated rate constants (K_2) and the correlation coefficients (R^2) of pseudo second-order equation for the metals are presented in Figure 5.8.

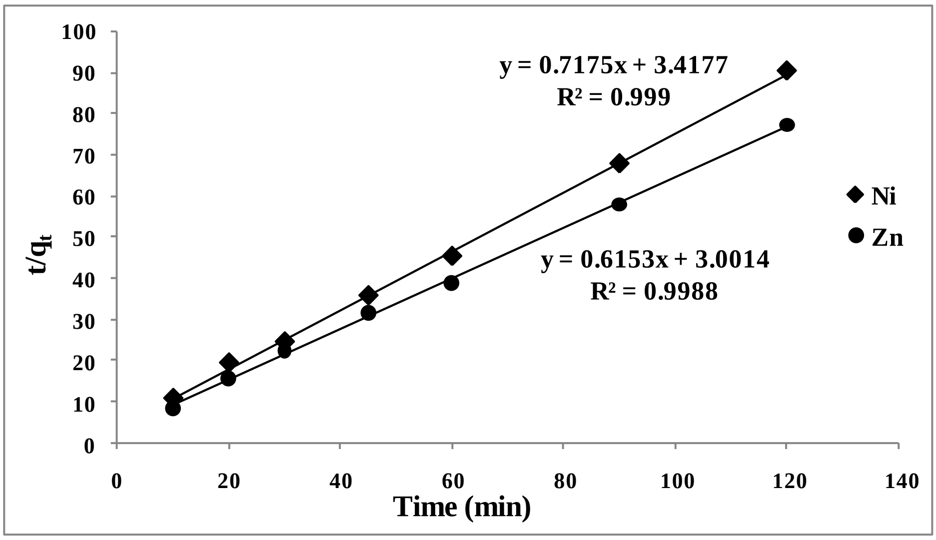
The plots of the linearized form of pseudo second-order model (t/q_t vs. t) for the adsorption of metals by CPEI are given in Figures 5.6.



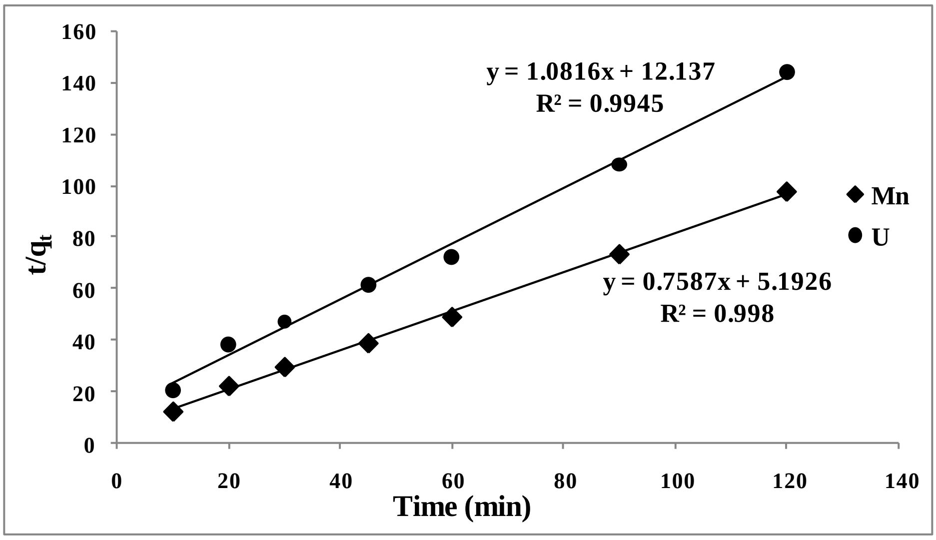
(a)



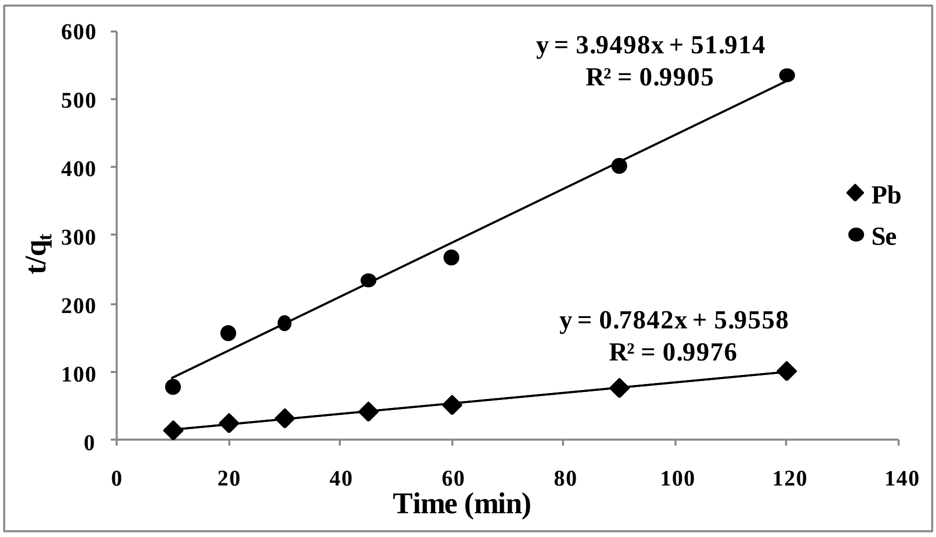
(b)


y = 0.7175x + 3.4177
R² = 0.999
y = 0.6153x + 3.0014
R² = 0.9988
Ni
Zn
t/q_t
Time (min)
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140

(c)


y = 1.0816x + 12.137
R² = 0.9945
y = 0.7587x + 5.1926
R² = 0.998
Mn
U
t/q_t
Time (min)
0
20
40
60
80
100
120
140
160
0
20
40
60
80
100
120
140

(d)



(e)

Figure 5.6. Pseudo second-order plots for the adsorption of (a) As and Cr (b) Fe and Hg (c) Ni and Zn (d) Mn and U (e) Pb and Se by CPEI

Overall, the pseudo second-order was found to give the best fit and therefore, it could be used to predict the kinetics of adsorption of metal ions onto CPEI. This confirms chemisorption, since the rate limiting step is a chemical sorption (Antures *et al.*, 2003).

5.1.8. Thermodynamic modelling of adsorption process by CPEI

The results for the thermodynamic study of the adsorption of metal and metalloid ions onto CPEI surface are tabulated in Table 5.4.

The table shows the calculated activation energies (Ea values) as well as the calculated constants K_1 and K_2 from the Arrhenius equation.

Table 5.4. Activation energy values of the adsorption of metal and metalloid ions by CPEI

Metals	K_1	K_2	Ea J mol^{-1}	Ea K J mol^{-1}
Cr	0.019	0.015	56491	56.49
As	0.008	0.003	49753	49.75
Fe	0.017	0.013	56163	56.16
Hg	0.003	0.001	50340	50.34
Ni	0.014	0.01	55487	55.49
Zn	0.015	0.011	55744	55.74
Mn	0.014	0.011	56659	56.66
U	0.002	0.001	53854	53.85
Pb	0.003	0.002	55955	55.96
Se	0.002	0.0001	41466	41.47

The high values of activation energies imply chemisorptions. This is completely consistent with the results obtained from the kinetic modelling where the pseudo second-order model best fitted the experimental data, confirming chemisorption as the rate limiting step.

5.1.9. Regeneration of CPEI

Desorption results for CPEI by nitric acid solutions of different concentrations are shown in Figure 5.7.

The results show the concentrations of metals desorbed by 2 mol L^{-1}, 3 mol L^{-1}, 5 mol L^{-1}, and 7 mol L^{-1} of HNO_3. The coloured parts of the columns show the desorbed concentrations of metal ions.

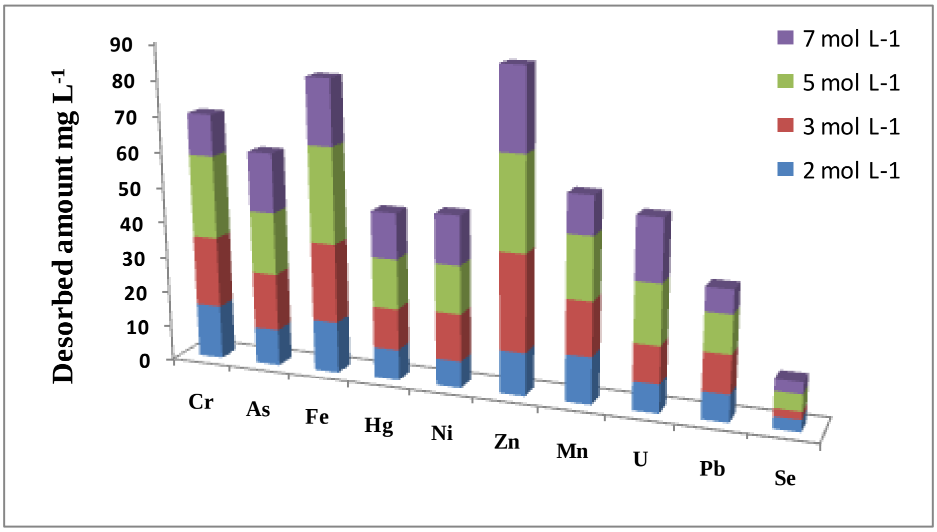


Figure 5.7. Desorption of metal and metalloid ions from CPEI by different HNO_3 concentrations

For most 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 5.8

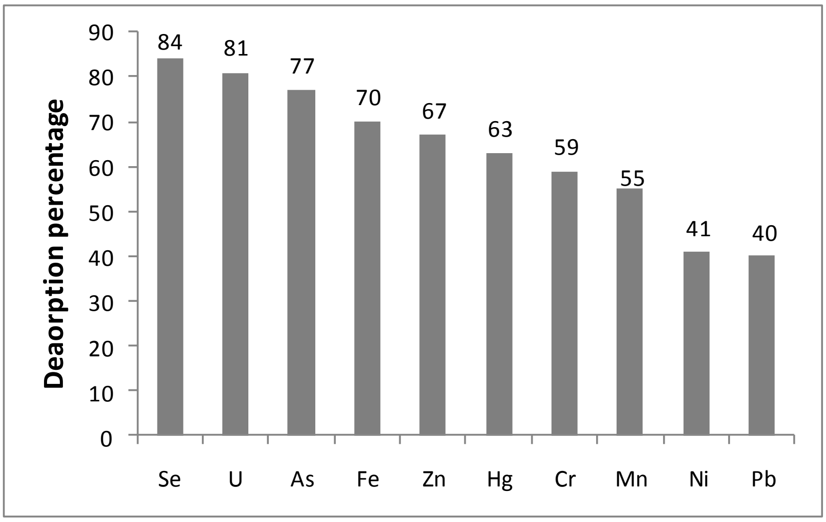


Figure 5.8. Desorption percentages of metal and metalloid ions from CPEI by 5 mol L^{-1} HNO_3

The adsorption percentages for the recovered polymer (regenerated CPEI) on the same synthetic solutions are given in Table 5.5.

Table 5.5. Removal of metal and metalloid ions from synthetic solutions by regenerated CPEI

pH		Cr	As	Fe	Hg	Ni	Zn	Mn	U	Pb	Se
3	C_f (mg L^{-1})	10.70	22.00	12.40	20.60	14.20	11.80	13.80	21.50	18.90	37.00
	RSD (n = 3)	0.616	3.165	1.620	9.401	0.846	0.413	0.680	10.46	1.721	1.566
	Ads Capacity (mg g^{-1})	1.172	0.720	1.104	0.776	1.032	1.128	1.048	0.740	0.844	0.120
	Ads percentage	73%	45%	69%	49%	65%	71%	66%	46%	53%	8%
8	C_f (mg L^{-1})	10.20	22.50	12.00	18.00	14.20	11.00	13.80	21.90	18.10	37.00
	RSD (n = 3)	5.606	2.181	4.612	8.380	4.274	4.042	0.580	13.63	4.490	5.650
	Ads Capacity (mg g^{-1})	1.192	0.700	1.120	0.880	1.032	1.160	1.048	0.724	0.876	0.120
	Ads 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	0.133
	MQL	0.063	0.161	0.080	0.130	0.137	0.017	0.127	0.200	0.170	0.133

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 standard deviation.

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 reuse. The regeneration of the polymer can further be exploited by use of serial desorptions, in order to obtain the ultimate retention.

For example, the desorption cycle for Cr, Fe, Ni and Zn (Figure 5.9) gave a gradual decrease of 1.577 mg g^{-1} to 0.262 mg g^{-1} for Cr; 1.545 mg g^{-1} to 0.719 mg g^{-1} for Fe; 1.312 mg g^{-1} to 0.081 mg g^{-1} for Ni and 1.573 mg g^{-1} to 0.608 mg g^{-1} for Zn.

The decrease of the adsorption by the reused polymer is because of the loss of the active sides; as the regeneration of the polymer could not result in a full retention.

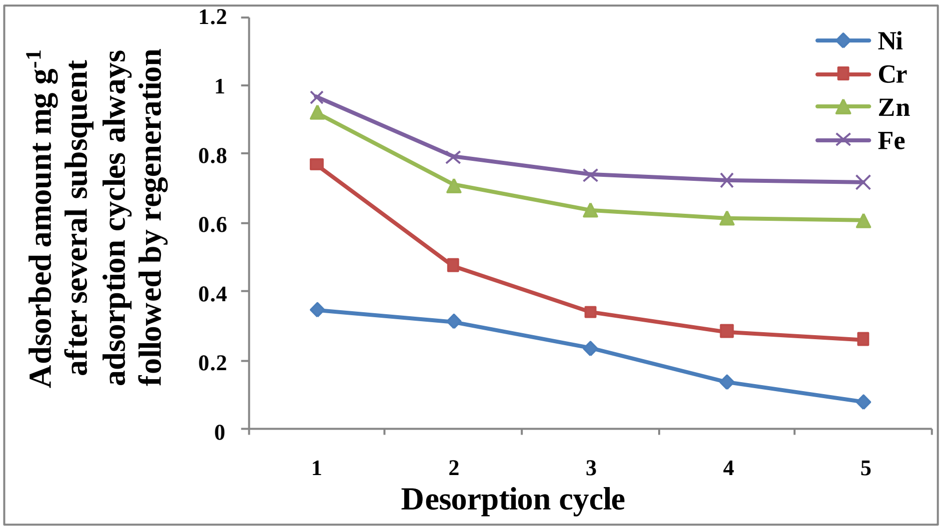


Figure 5.9. Regeneration of CPEI by serial desorptions

5.1.10. Removal of heavy metal and metalloid ions from wastewater samples by CPEI

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 wastewater (not analysed 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 analysed. Thus the effect of enhancement, dilution and/or precipitation cannot be conclusively attributed to in this case. Further, the contribution of 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 fresh CPEI are given in Table 5.6.

Table 5.6. Removal of metal and metalloid ions from mining wastewater samples (1 g CPEI in 40 mL wastewater)

Samples	Metals	C_i (mg l^{-1})	RSD(n = 3)	C_f (mg l^{-1})	RSD (n =3)	Ads %
SW 1	Fe	6.100	0.087	0.154	8.132	97%
pH (3.8)	Ni	6.000	7.003	2.062	6.479	66%
SO_4^{-2} (383.2 mg L^{-1})	Zn	4.300	9.873	0.143	1.490	97%
	Mn	111.7	3.775	17.30	5.556	85%
SW 2	As	0.117	2.590	0.049	5.906	58%
pH (7.2)	Se	0.090	5.841	0.077	1.502	14%
SO_4^{-2} (19.80 mg L^{-1})	Ni	1.500	5.281	0.371	5.906	75%
SW 3	Cr	0.250	6.892	0.002	5.2	99%
pH (4)	As	0.280	2.056	0.127	5.621	55%

SO_4^{-2} (819.4 mg L^{-1})	Fe	4.480	6.509	0.183	2.562	96%
	Ni	1.790	1.722	0.885	4.730	51%
	Zn	1.570	5.015	0.401	5.240	74%
	Mn	22.00	8.823	4.700	9.330	79%
SW 4	Fe	5.840	8.972	0.186	9.606	97%
pH (5.6)	Ni	4.670	3.531	1.005	6.743	79%
SO_4^{-2} (653.6 mg L^{-1})	Zn	7.650	7.073	0.746	7.664	90%
	Mn	179.2	2.707	20.38	1.909	89%
Pit water	Cr	0.038	7.745	0.002	2.395	95%
pH (3)	Fe	0.600	3.543	0.031	3.707	95%
SO_4^{-2} (1669 mg L^{-1})	Hg	0.275	1.835	0.120	1.817	56%
	Ni	10.70	7.968	2.400	1.860	78%
	Zn	14.75	8.400	0.027	5.157	99%

Mn	136.4	7.990	34.25	4.727	86%
U	0.161	6.700	0.090	5.048	44%
Se	0.047	8.662	0.044	1.304	6%

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; SO42- - 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; SO42- - 0.03 (by ion chromatography).

SW- surface water; Ci - initial concentration before adsorption; Cf – final concentration after adsorption.

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 to be used in tandem with another material that can extract these elements better should these elements be encountered in polluted waters.

5.2. Phosphonated cross-linked polyethylenimine PCPEI

5.2.1. Characterization of phosphonated polyethylenimine

Fourier Transform Infra Red spectroscopy was used to characterize the phosphonated derivative of cross-linked polyethylenimine (PCPEI) in order to confirm the presence of phosphorous group (H_3PO_3). The FTIR spectrum is given in Figure 5.10.

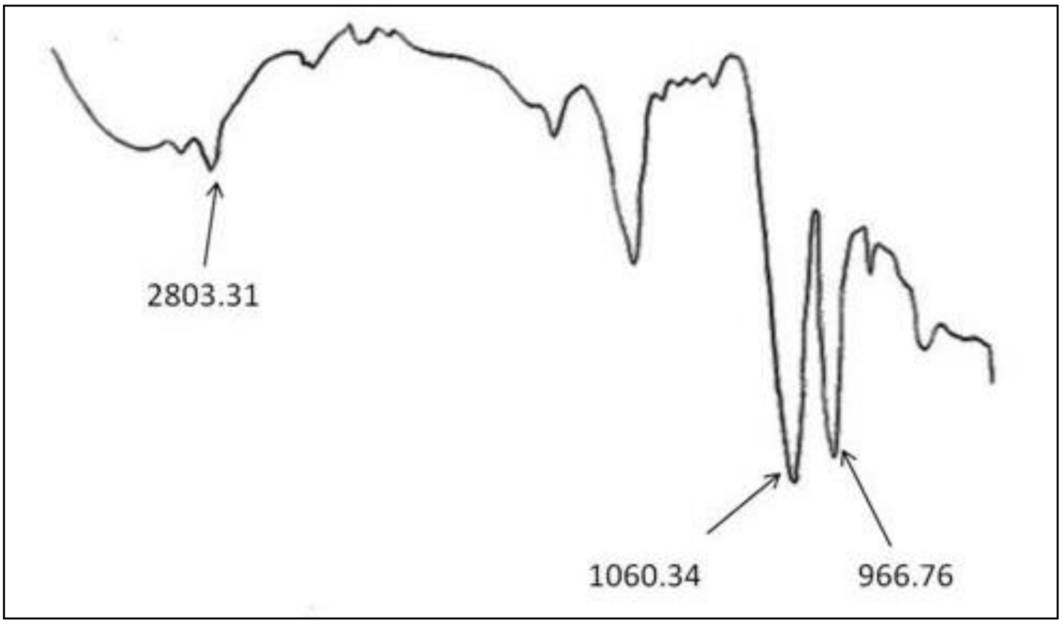


Figure 5.10. IR spectrum of PCPEI

The major peaks of importance on the IR spectrum of PCPEI are: 966.76 cm^{-1} indicating the presence of P—OH bond; 1060.34 cm^{-1} corresponding to the presence of P-O bond; and 2803.31 cm^{-1} signifies the presence of PO—H bond.

The absence of the N- H absorption intensively confirms the reaction of the secondary amine and hence confirms the phosphonation.

5.2.2. Removal of heavy metal and metalloid ions from synthetic solutions by PCPEI

The adsorption performance of PCPEI was investigated according to the procedure given in section 4.3.3.1. The adsorption capacity, adsorption percentages and the relative standard deviation (RSD) are given in Table 5.7.

The table shows the final metal concentrations obtained (C_f) after adsorption from an initial multi-metal solution of concentration 40 mg L^{-1} at two different pHs; the adsorption capacity as well as the adsorption percentages.

Table 5.7. Removal of metal and metalloid ions from synthetic solution by PCPEI

pH		Cr	As	Fe	Hg	Ni	Zn	Mn	U	Pb	Se
3	C_f (mg L^{-1})	12.80	9.660	15.07	17.40	6.22	11.58	3.91	0.770	15.70	29.76
	RSD (n = 3)	1.595	0.226	1.822	5.505	1.225	1.088	1.875	6.227	1.122	0.506
	Ads. Capacity (mg g^{-1})	1.088	1.213	0.997	0.904	1.351	1.136	1.443	1.569	0.972	0.409
	Ads percentage	68%	76%	62%	57%	84%	71%	90%	98%	61%	26%
8	Cf (mg l-1)	11.71	7.810	13.03	13.95	3.73	9.231	2.110	0.600	12.41	29.60
	RSD (n = 3)	1.357	0.786	2.014	3.319	7.784	7.554	5.387	0.333	2.173	0.220
	Ads. Capacity (mg g^{-1})	1.132	1.288	1.079	1.042	1.451	1.231	1.516	1.576	1.104	0.416
	Ads percentage	71%	80%	67%	65%	91%	77%	95%	99%	69%	26%
	LOD	0.009	0.018	0.003	0.024	0.006	0.003	0.0	0.078	216	0.024
	MQL	0.03	0.06	0.01	0.08	0.02	0.01	0.0	0.26	0.72	0.08

Initial concentration of the ions = 40 mg L^{-1}; C_i - initial concentration before adsorption; C_f – final concentration after adsorption

LOD: limit of detection in mg L^{-1}; MQL: method quantitation limit in mg L^{-1} ;RSD: relative standard deviation.

The results suggest that PCPEI has good ability to remove most of the trace elements. The adsorption trend varied as follows: U > Mn > Ni> Zn > As >> Cr > Pb > Fe>> Hg > Se.

Following the previously mentioned mechanism based on hard-soft Lewis acid-base theory, the high removal of U, Mn, Ni and Zn could be understandable as well as the low removal of Hg. The phosphorous atom in the chelating group ($-PO_3H_2$) in PCPEI is a hard Lewis base. So, in general, both the CPEI and PCPEI showed good performance toward hard metals with some differences in the ordering of removal which is also dependent on the affinity. For instance, although both PCPEI and CPEI have hard donor atoms (hard bases) their trend toward Cr and Fe as hard acids is different.

The most noticeable difference between CPEI and PCPEI is the high removal of As by PCPEI compared to CPEI. This could be explained by the nature of existence of chelating groups in the polymer surface. While the (-NH) in CPEI exists as a ligand all along the polymer backbone, the ($-PO_3H_2$) exists as an anion pendent ligand along the polymer chain (Abd-El-Aziz, 2005). An example of a pendent ligand is given in Figure 5.11.

Figure 5.11. Complexation of pendent ligand

As such the replacement of anions easily occurs. The chemical similarities of phosphorus and arsenic mean that they can easily replace each other. Thus, the phosphorus is released from the polymer into the solution by replacing the arsenic ions.

5.2.3. pH effect on the adsorption process by PCPEI

Phosphonated cross-linked polyethylenimine showed variation in its performance at two different pH regimes. Figure 5.12 gives the adsorption percentages of metal ions by PCPEI at pH 3 and pH 8.

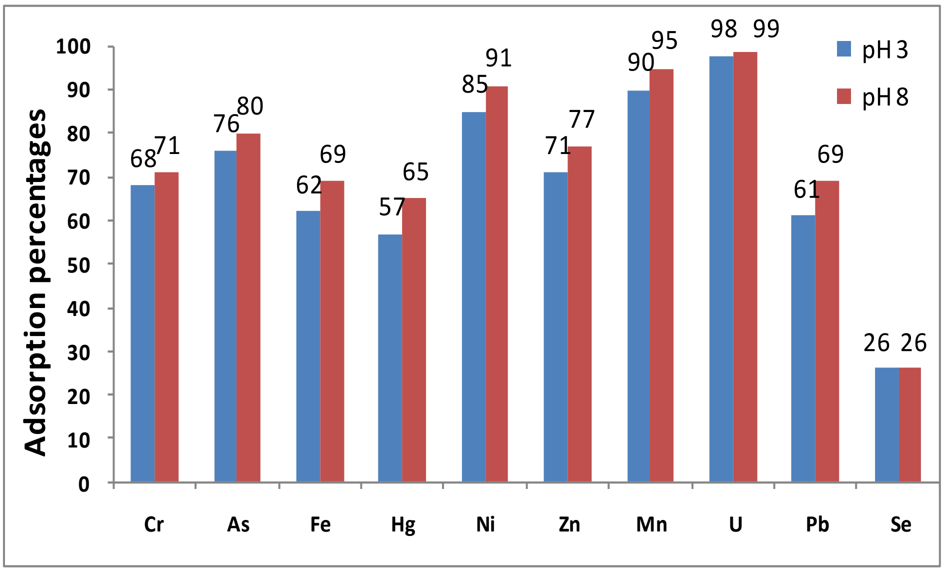
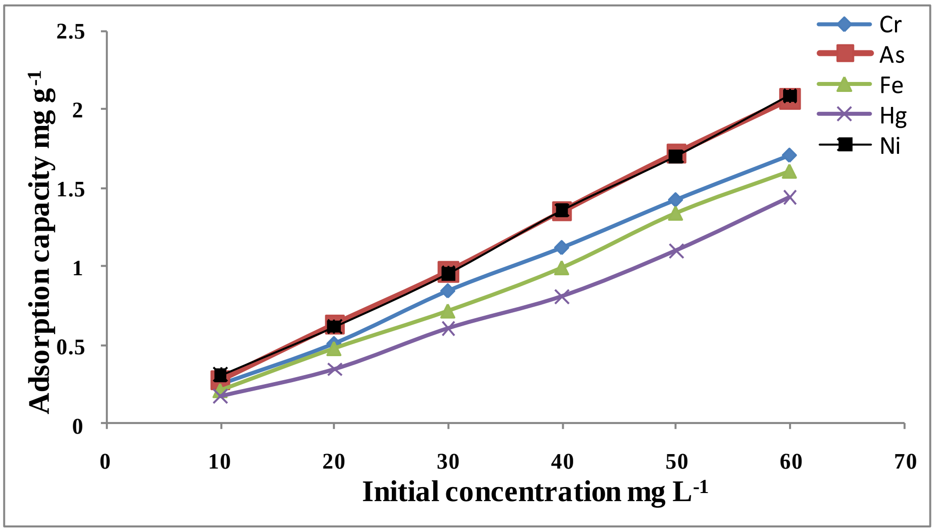


Figure 5.12. The pH effect on the adsorption process by PCPEI

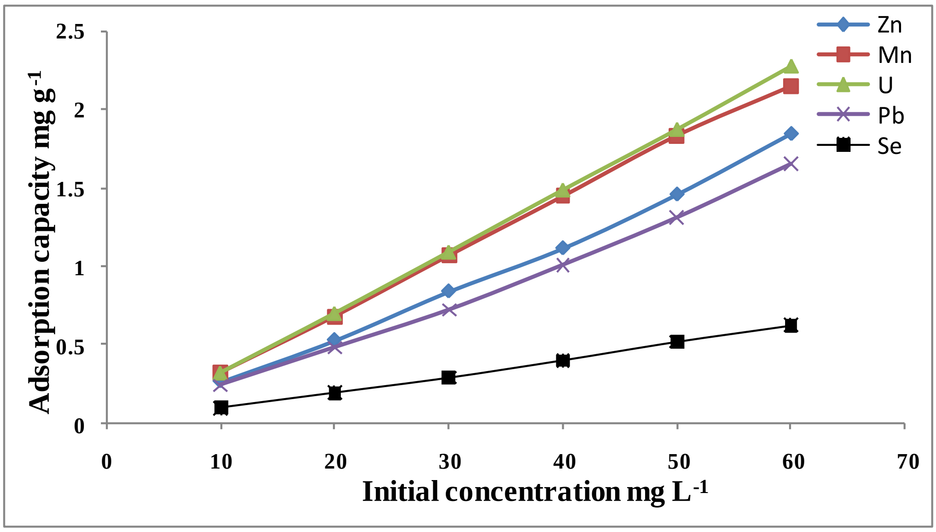
The adsorption percentages are a bit lower under acidic conditions (pH 3). For example, the removal percentage of As dropped by 4%; Mn dropped by 5% and Ni dropped by 6%. But in general, PCPEI still showed good removal efficiency at low pH, which is very important for its application for heavy metal removal from acidic mine wastewaters.

5.2.4. Effect of initial concentration on the adsorption process by PCPEI

The results for the dependence of adsorption capacity on metal ion concentrations are shown in Figure 5.13.



(a)



(b)

Figure 5.13. Effect of concentration on the adsorption of (a) Cr, As, Fe, Hg, Ni (b) Zn, Mn, U, Pb, Se by PCPEI

The adsorbed amount of the metal ions increased with increasing of concentration. U, Mn, As, and Ni showed high adsorption capacity even at very low concentrations. On the other hand, the rest of the metals showed very low removal at low concentrations which increased significantly at high concentrations, but still showing lower affinity compared to U, Mn, As, and Ni.

5.2.5. Adsorption isotherms for PCPEI

The calculated Langmuir constants (b and q_m) and Freundlich constants (n and K_f) as well as the coefficients of correlation (R^2) are shown in Table 5.8.

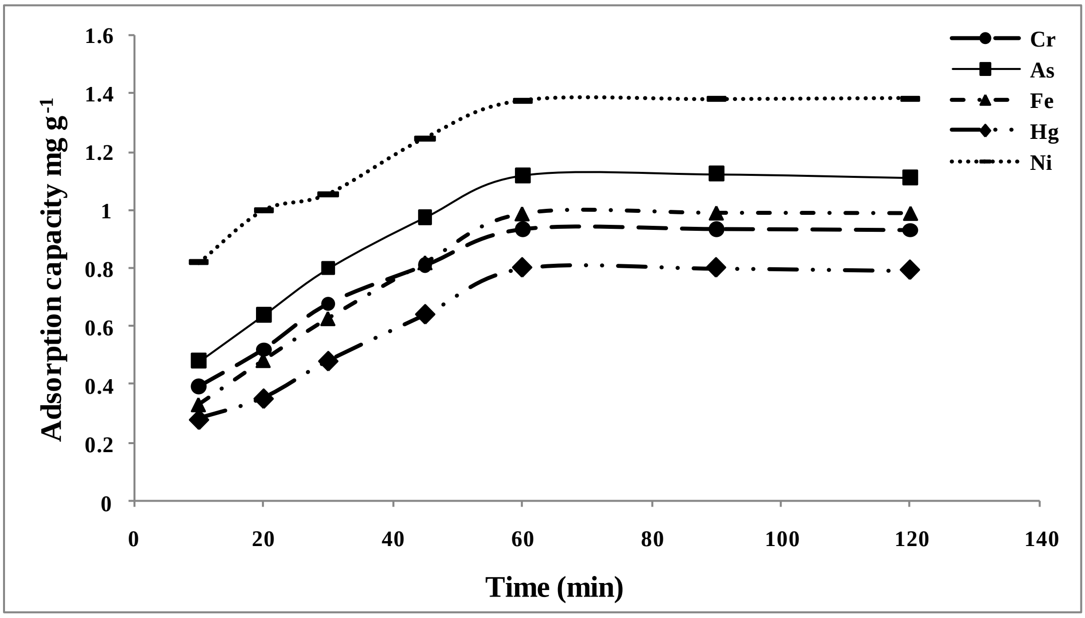
Table 5.8. Langmuir and Freundlich parameters for the adsorption of metal and metalloid ions on PCPEI

Metals	Langmuir			Freundlich		
	b	**R^2**	**q_m**	**K_f**	**R^2**	**n**
Cr	2.218	0.748	16.95	3.652	0.978	0.631
As	0.749	0.824	13.88	3.575	0.981	0.483
Fe	1.504	0.863	24.63	3.790	0.989	0.703
Hg	1.127	0.879	39.94	4.358	0.970	0.700
Ni	1.390	0.761	9.809	2.589	0.933	0.653
Zn	2.223	0.784	15.07	3.013	0.968	0.767
Mn	1.365	0.476	6.313	2.862	0.986	0.0.415
U	0.220	0.942	15.00	4.317	0.957	0.222
Pb	2.834	0.747	19.23	3.185	0.976	0.828
Se	3.05	0.850	82.70	4.533	0.998	0.938

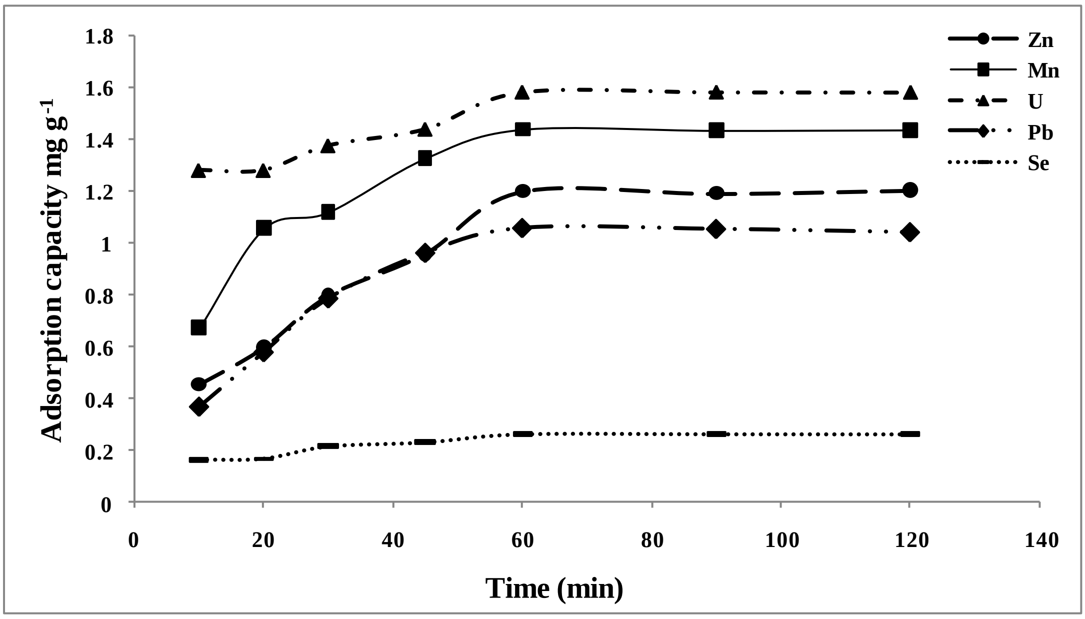
The results suggest that the Freundlich model best fits the data. All Freundlich correlation coefficients were found to be > 0.95 except for Ni which had an R^2 value of 0.993.

5.1.6. Effect of contact time on the adsorption process by PCPEI

Figure 5.14 shows the effect of contact time on the adsorption of metal ions onto PCPEI by plotting the adsorption capacity as a function of time. Results were obtained by running the adsorption experiments at different time intervals at fixed temperature and fixed concentration, in order to obtain the optimal time required for adsorption of metal ions by PCPEI.



(a)



(b)

Figure 5.14. Effect of time on the adsorption of (a) Cr, As, Fe, Hg, Ni (b) Zn, Mn, U, Pb, Se by PCPEI

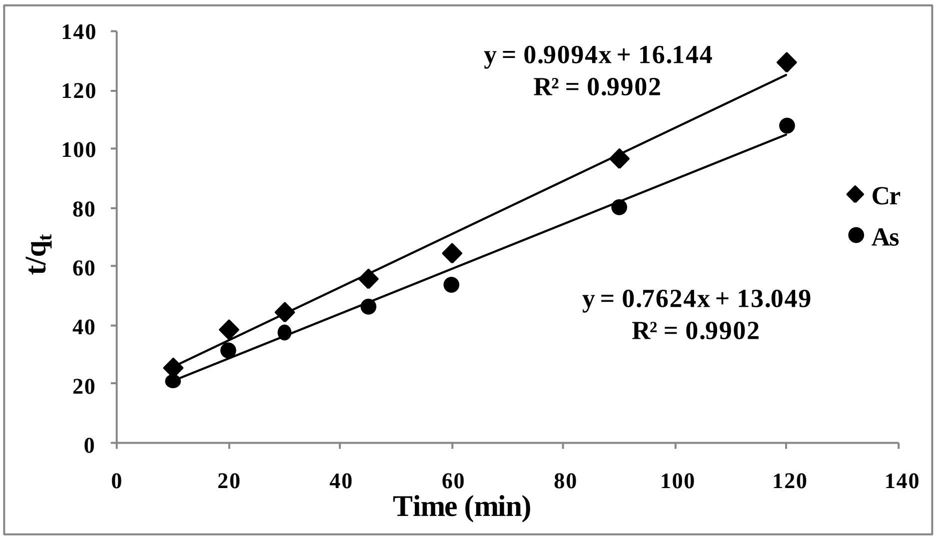
All the metals were observed to adsorb fast within the first 30 minutes, with a slow adsorption within the second 30 minutes and no further increase in adsorption beyond 60 minutes. This could be attributed to the unavailability of the reaction sites which depresses with time. Thus despite the increase in adsorption after 45 minutes being low, the minimum required time for the adsorption to be completed was 60 minutes.

5.2.7. Kinetic modelling of adsorption process by PCPEI

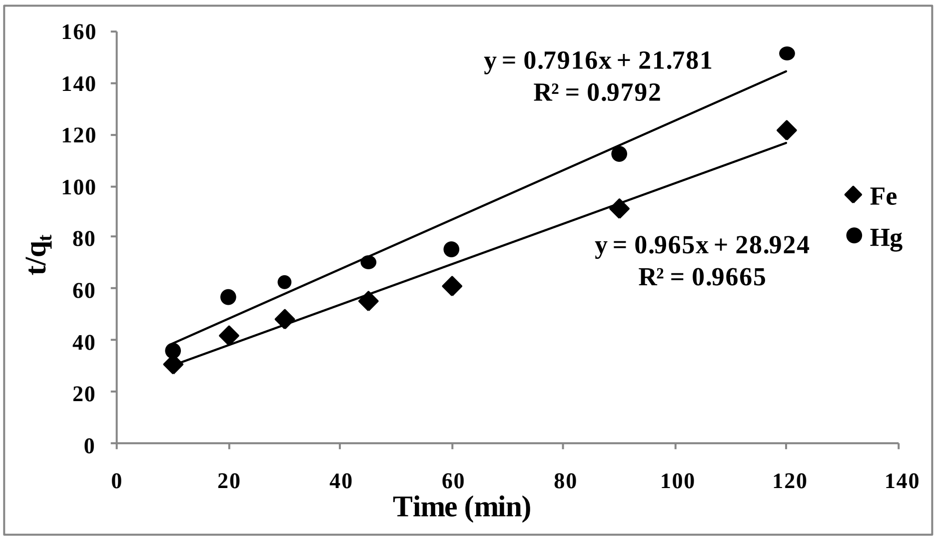
Pseudo first-order equation and pseudo second-order equation were used to investigate the kinetics of adsorption of metal ions onto PCPEI.

The experimental kinetic data showed better correlation with the pseudo second-order. The pseudo second-order rate constants (K_2) of the adsorption of metals were calculated from the slopes of the plots.

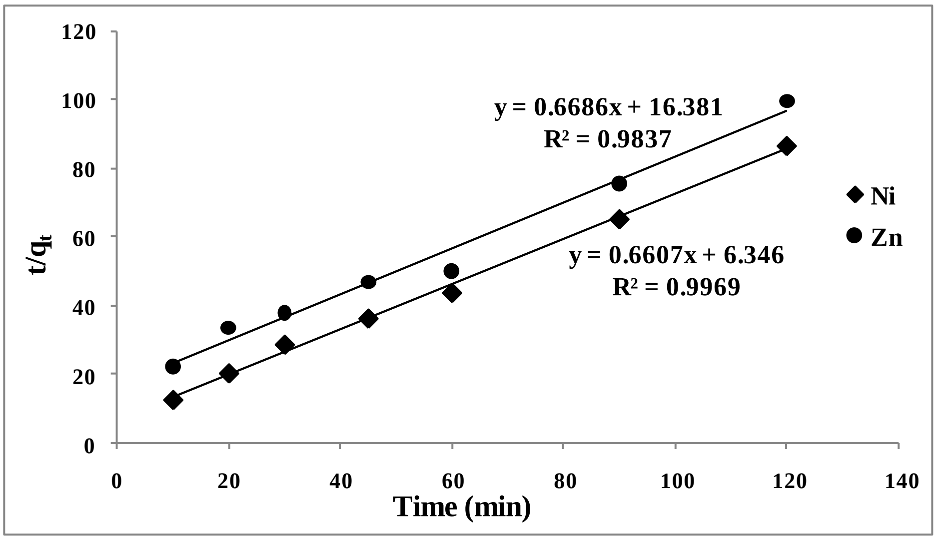
The plots of linearized form of pseudo second-order model (t/q_t vs. t) for metal adsorption by PCPEI are given in Figure 5.15.



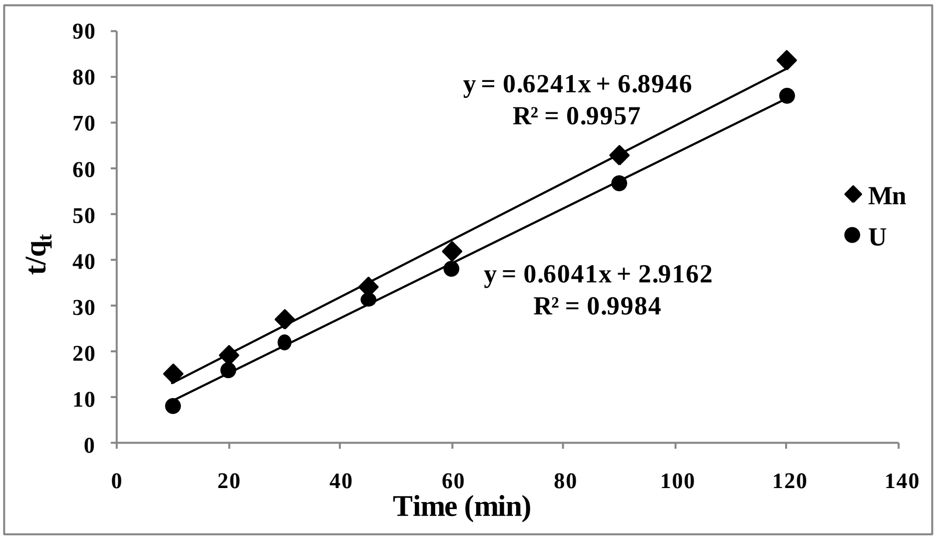
(a)



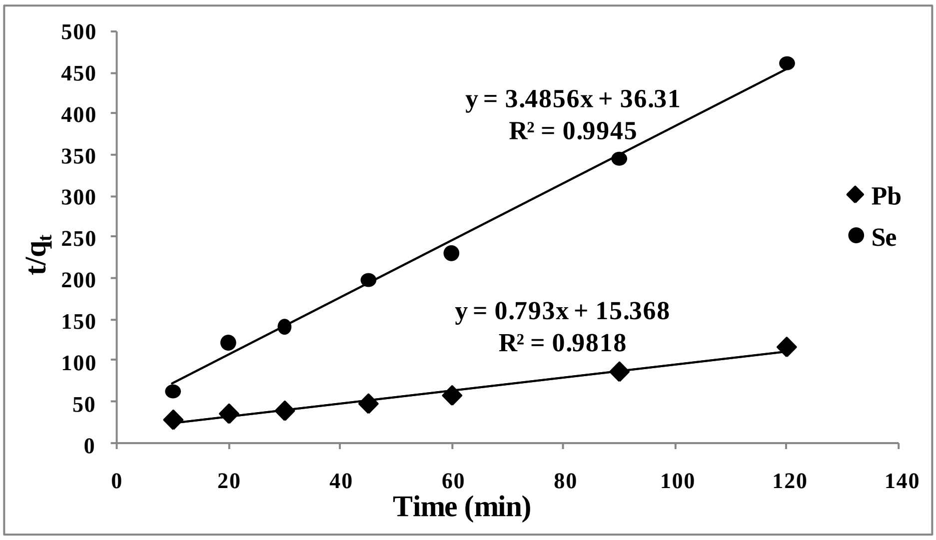
(b)


120
100
80
60
40
20
0
0
20
40
60
80
100
120
140
t/q_t
Time (min)
y = 0.6686x + 16.381
R² = 0.9837
y = 0.6607x + 6.346
R² = 0.9969
◆ Ni
● Zn

(c)


90
80
70
60
50
40
30
20
10
0
0
20
40
60
80
100
120
140
t/q_t
Time (min)
y = 0.6241x + 6.8946
R² = 0.9957
y = 0.6041x + 2.9162
R² = 0.9984
◆ Mn
● U

(d)



(e)

Figure 5.15. Pseudo second-order plots for the adsorption of (a) Cr and As, (b) Fe and Hg, (c) Ni and Zn, (d) Mn and U, (e) Pb and Se by PCPEI

5.2.8. Thermodynamic modelling of adsorption process by PCPEI

The calculated activation energy values (Ea) for the adsorption of metal and metalloid ions onto PCPEI surface as well as the calculated constants K_1 and K_2 are presented in Table 5.9.

Table 5.9. Activation energy values of the adsorption of metal and metalloid ions by PCPEI

Metals	K_1	K_2	Ea J mol^{-1}	Ea K J mol^{-1}
Cr	0.013	0.009	55187	55.19
As	0.011	0.008	55912	55.91
Fe	0.011	0.008	55912	55.913
Hg	0.003	0.002	55955	55.96
Ni	0.015	0.012	56840	56.84
Zn	0.011	0.008	55912	55.91
Mn	0.017	0.013	56163	56.16
U	0.004	0.003	56896	56.90
Pb	0.003	0.002	55955	55.96
Se	0.003	0.001	50340	50.34

The activation energies for the adsorption of all metals and metalloids onto PCPEI are high indicating chemisorptions. Overall the activation energy values are comparable to those for CPE.

5.2.9. Regeneration of PCPEI

Desorption results for PCPEI by different concentrations of HNO_3 are shown in Figure 5.16. The results show the concentrations of metals desorbed by 2 mol L^{-1}, 3 mol L^{-1}, 5 mol L^{-1}, and 7 mol L^{-1} of HNO_3.

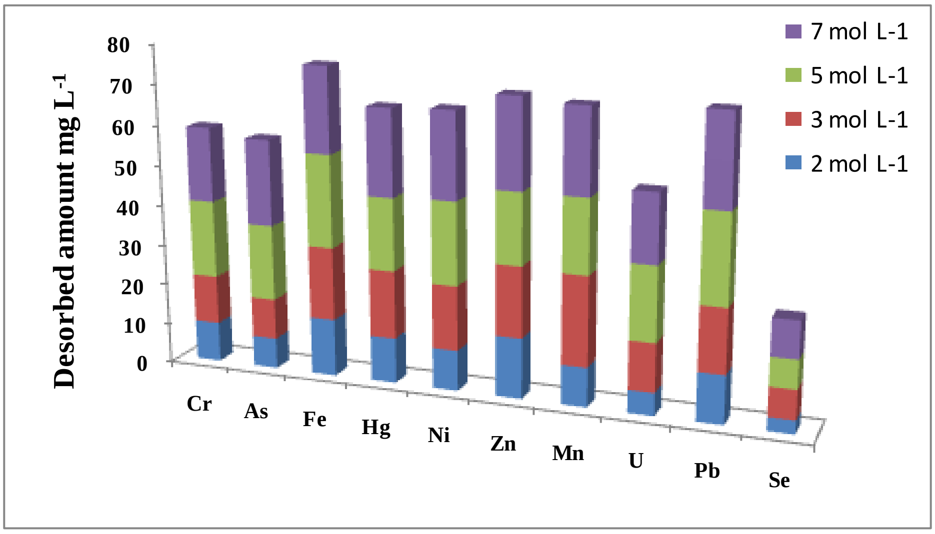


Figure 5.16. Desorption of metal and metalloid ions from PCPEI by different concentrations of HNO_3

For most metal ions, the most effective HNO_3 acid concentration was 7 mol L^{-1}.Subsequently, regeneration of the used PCPEI was carried out using 7 mol L^{-1} acid concentration. The desorption percentages are given in figure 5.17.

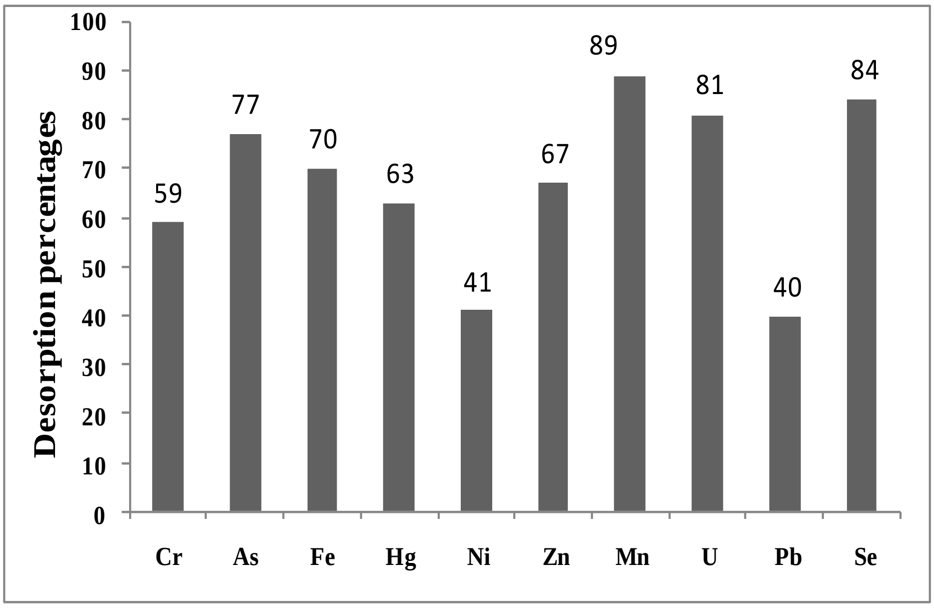


Figure 5.17. Desorption of metal and metalloid ions from PCPEI by 7 mol L^{-1} HNO_3

The adsorption percentages for the regenerated PCPEI are given in Table 5.10.

Table 5.10. Removal of metal and metalloid ions from synthetic solutions by regenerated PCPEI

pH		Cr	As	Fe	Hg	Ni	Zn	Mn	U	Pb	Se
3	C_f (mg l^{-1})	28.60	13.63	26.10	30.00	12.50	18.02	9.080	2.200	26.83	36.90
	RSD (n = 3)	0.504	2.284	2.989	6.600	0.779	0.245	0.778	1.797	1.186	1.803
	Ads. Capacity (mg g^{-1})	0.456	1.055	0.556	0.400	1.100	0.879	1.237	1.512	0.527	0.124
	Ads percentage	29%	66%	35%	25%	69%	55%	77%	95%	33%	8%
8	Cf (mg l-1)	26.00	10.61	25.87	29.83	10.91	14.00	7.91	1.970	24.24	37.50
	RSD (n = 3)	0.426	1.983	3.202	4.180	0.267	0.505	1.156	3.335	3.467	2.020
	Ads. Capacity (mg g^{-1})	0.56	1.176	0.565	0.407	1.164	1.040	1.284	1.521	0.630	0.100
	Ads percentage	35%	73%	35%	25%	73%	65%	80%	95%	39%	6%
	LOD	0.026	0.003	0.081	0.048	0.061	0.017	0.022	0.090	0.034	0.003
	MQL	0.007	0.010	0.023	0.050	0.067	0.045	0.011	0.001	0.055	0.003

Initial concentration of the ions = 40 mg L^{-1}; C_i - initial concentration before adsorption; C_f – final concentration after adsorption

LOD: limit of detection in mg L^{-1}; MQL: method quantitation limit in mg L^{-1}; RSD: relative standard deviation.

The percentages, though lower, still portrayed good recoveries. The performance of PCPEI decreased as follows: the adsorption of U dropped by 3%; As dropped by 3%; and Mn dropped by 4% just to mention a few.

Since the regenerated PCPEI showed good removal efficiency, it could exhibit better removal after serial desorptions. Figure 5.18 demonstrates the desorption cycle of As, U, Ni and Mn from PCPEI.

After a cycle of five desorptions, the adsorbed amount on PCPEI was decreased by 0.826 mg g^{-1} for As; 1.246 mg g^{-1} for Ni; 1.511 mg g^{-1} for Mn and 1.477 mg g^{-1} for U.

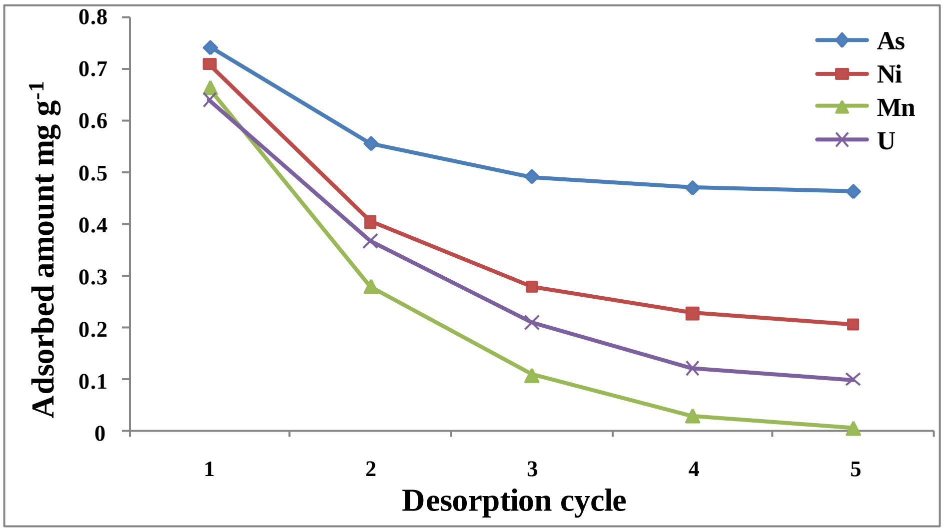


Figure 5.18. Regeneration of PCPEI by serial desorption

5.2.10. Removal of heavy metal and metalloid ions from wastewater samples by PCPEI

PCPEI was employed to remove metal and metalloid ions from wastewater samples according to the procedure stated in section 4.2.4.

The adsorption results of metal ions from wastewater samples by PCPEI are given in Table 5.11.

Table 5.11. Removal of metal and metalloid ions from mining wastewater samples by PCPEI (1 g PCPEI in 40 mL wastewater)

Samples	Metals	C_i (mg l^{-1})	RSD(n = 3)	C_f (mg l^{-1})	RSD (n =3)	Ads %
S W 1	Fe	6.100	0.087	1.623	5.507	73%
pH (3.8)	Ni	6.000	7.003	0.830	1.885	86%
SO_4^{-2} (383.2 mg l^{-1})	Zn	4.300	9.873	1.220	3.487	72%
	Mn	111.7	3.775	17.08	1.956	85%
S W 2	As	0.117	2.590	0.020	2.946	83%
pH (7.2)	Se	0.090	5.841	0.055	5.456	14%
SO_4^{-2} (19.80 mg l^{-1})	Ni	1.500	5.281	0.372	2.164	75%
S W 3	Cr	0.250	6.892	0.110	1.458	56%
pH (4)	As	0.280	2.056	0.024	6.245	91%

SO_4^{-2} (819.4 mg l^{-1})	Fe	4.480	6.509	1.38	2.056	69%
	Ni	1.790	1.722	0.859	1.387	57%
	Zn	1.570	5.015	0.510	1.585	67%
	Mn	22.00	8.823	3.360	2.395	85%
S W 4	Fe	5.840	8.972	1.5	6.765	74%
pH (5.6)	Ni	4.670	3.531	0.88	2.061	81%
SO_4^{-2} (653.6 mg l^{-1})	Zn	7.650	7.073	1.76	2.078	77%
	Mn	179.2	2.707	19.05	5.638	90%
Pit water	Cr	0.038	7.745	0.015	2.395	61%
pH (3)	Fe	0.600	3.543	0.138	3.707	77%
SO_4^{-2} (1669 mg l^{-1})	Hg	0.275	1.835	0.063	1.817	77%
	Ni	10.70	7.968	2.030	1.860	81%
	Zn	14.75	8.400	0.823	5.157	94%

Mn	136.4	7.990	4.400	4.727	96%
U	0.161	6.700	0.001	5.048	99%
Se	0.047	8.662	0.033	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).

5.3. Sulphonated cross-linked polyethylenimine

5.3.1. Physiochemical characterization of sulphonated cross-linked polyethylenimine

The sulphonated cross-linked polyethylenimine was characterized by Fourier transform infra-red spectroscopy in order to confirm the introduction of new chelating group (SO_3H). The FTIR spectrum is given in Figure 5.19.

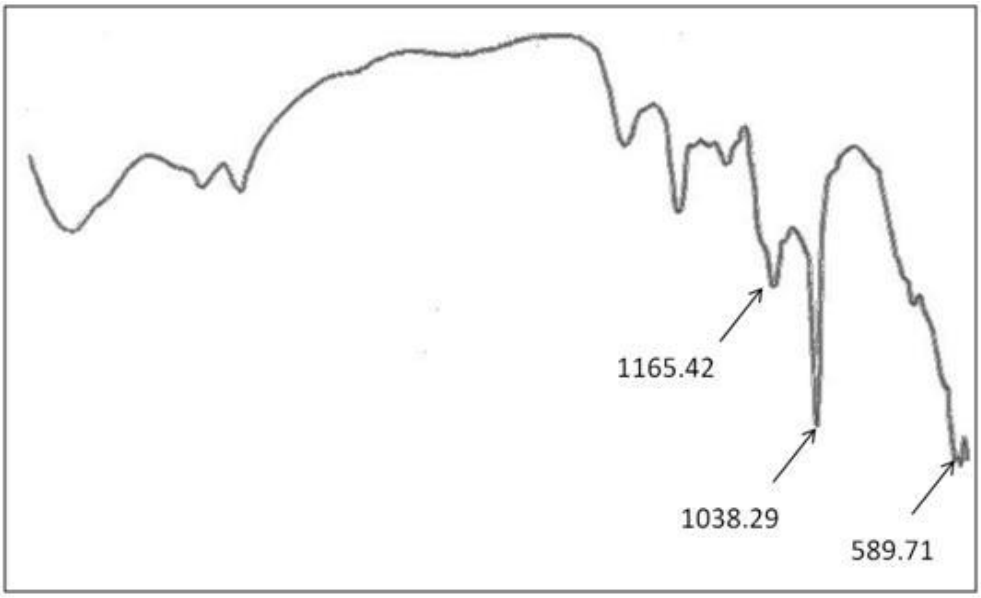


Figure 5.19. IR spectrum of SCPEI

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

5.3.2. Removal of heavy metal and metalloid ions from synthetic solutions by SCPEI

Removal of metal and metalloid ions from aqueous solution by SCPEI was performed using the procedure set out in section 4.3.3.1 and the results for the adsorption of metal ions in synthetic solutions are given in Table 5.12.

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).

Table 5.12. Removal of metal and metalloid ions from synthetic solutions by SCPEI

pH		Cr	As	Fe	Hg	Ni	Zn	Mn	U	Pb	Se
3	C_f (mg l^{-1})	18.90	12.90	20.50	6.600	13.30	14.90	18.80	9.70	12.80	7.900
	RSD	1.242	0.728	1.025	7.29	5.202	2.047	0.542	8.084	0.98	0.642
	Ads. Capacity (mg g^{-1})	0.844	1.084	0.780	1.336	1.068	1.004	0.848	1.212	1.088	1.284
	Ads percentage	53%	68%	49%	84%	67%	63%	53%	76%	68%	80%
8	Cf (mg l-1)	16.50	13.00	19.00	6.001	11.90	10.40	18.51	8.301	11.60	7.600
	RSD	2.004	2.078	0.68	0.469	0.469	0.873	2.782	7.076	1.883	1.725
	Ads. Capacity (mg g^{-1})	0.940	1.080	0.840	1.360	1.124	1.184	0.869	1.268	1.136	1.296
	Ads percentage	59%	68%	53%	85%	70%	74%	54%	79%	71%	81%
	LOD	0.003	0.009	0.0	0.018	0.0	0.0	0.0	0.09	0.003	0.024
	MQL	0.01	0.03	0.0	0.06	0.0	0.0	0.0	0.3	0.01	0.08

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

SCPEI showed good performance towards some elements with Hg and Se giving the highest adsorption capacities of 85% and 81%, respectively.

The high removal of Hg could be understandable since Hg is a soft acid and sulphur as is a soft base. It is also noticeable here the poor removal of hard acids (hard metals) such as Cr, Fe, and Mn as well as the good removal of moderate acids (Ni, Zn, and Pb)

The oxo-anions Se and As showed different affinity to SCPEI. Whereas Se was effectively removed by SCPEI, As showed low affinity. As both Se and As exist as bases in solution, the anion replacement could occur. Se exists in same group in periodic table with S thus the 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).

5.3.3. pH effect on the adsorption process by SCPEI

The effect of pH on the performance of SCPEI could be clearly observed from the difference in the adsorption percentages at two different pH values 3 and 8. This is shown in Figure 5.20.

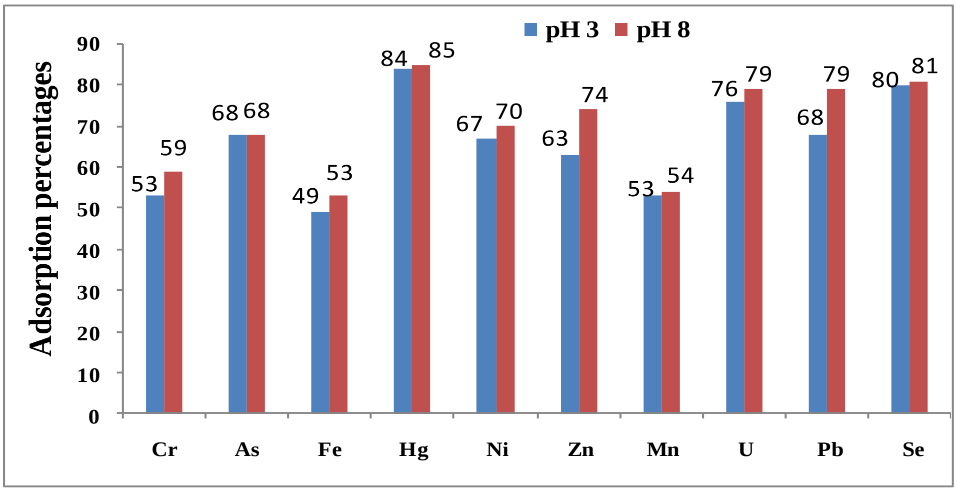


Figure 5.20. The pH effect on SCPEI

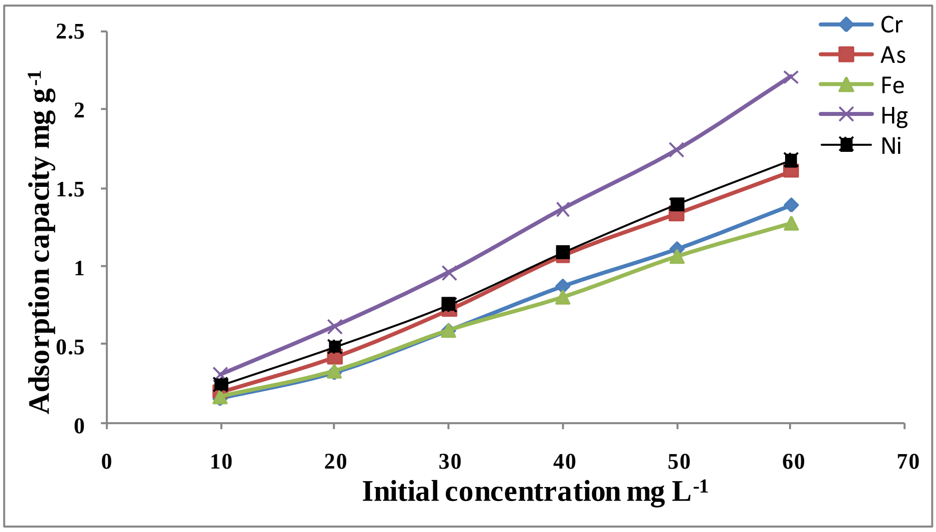
The removal efficiency of most elements dropped from high percentages at high pH to a bit lower percentages at low pH. The adsorption percentages of some metals such as Pb and Zn dropped significantly with their removal efficiencies dropping by 11% and 9%, respectively. The efficiency of others such as Se, Fe, U, Mn and Hg dropped by 1%, 4%, 3%, 1% and 1%, respectively which are trivial values.

Although the removal efficiency of SCPEI is a pH dependent to some extent, it is still showing good performance at low pH. This is a significant advantage as the application of the synthesized SCPEI for heavy metal removal entails application in acid mine drainage-impacted waters.

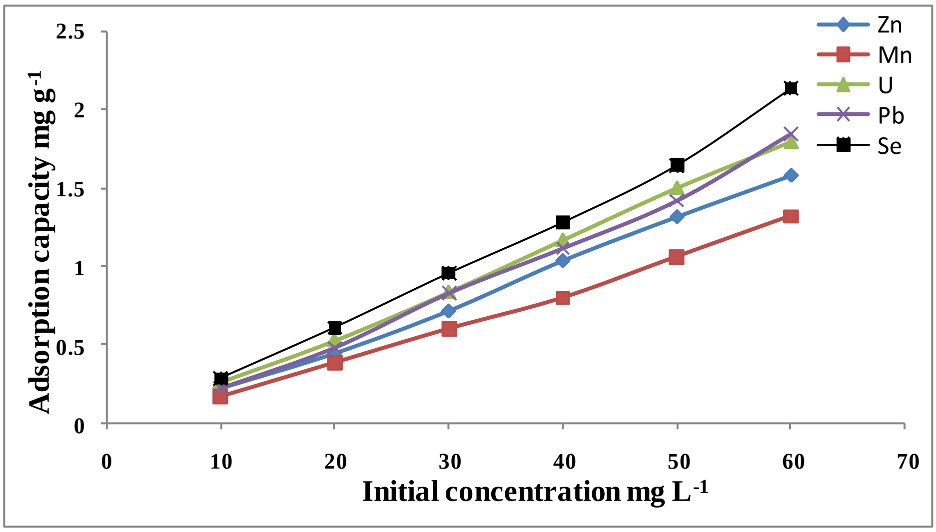
5.3.4. Effect of initial concentration on adsorption of metals by SCPEI

In order to observe the effect of the initial concentration of metal ions on the adsorption of SCPEI, the adsorption experiments were conducted using different metal ion concentrations at fixed time and at room temperature following the procedure set out in section 4.3.3.1.

The results for the dependence of adsorption on metal ion concentrations were obtained by plotting the adsorption capacity as a function of concentration. The results are given in Figure 5.21.



(a)



(b)

Figure 5.21. Effect of concentration on the adsorption of (a) Cr, As, Fe, Hg, Ni (b) Zn, Mn, U, Pb, Se by SCPEI

The results show that as the initial concentration increases; the adsorbed amount of the metal ions increases.

5.3.5. Adsorption isotherms for SCPEI

The experimental data of the adsorption of metal and metalloid ions onto SCPEI were analyzed using the linearized expressions of

Langmuir and Freundlich models. The results for the Langmuir model are presented in Table 5.13.

Table 5.13. Parameters of the Langmuir model for the adsorption by SCPEI

	Cr	As	Fe	Hg	Ni	Zn	Mn	U	Pb	Se
b	0.752	1.045	1.378	1.381	2.230	1.915	1.770	2.134	0.862	1.247
R^2	0.888	0.790	0.832	0.258	0.844	0.845	0.862	0.871	0.856	0.536
q_m	49.25	28.80	40.55	8.869	18.49	22.54	35.32	14.95	24.85	11.58

From the results, the low values of the correlation coefficient illustrate that the Langmuir model does not describe the nature of the interaction between the metal ions (adsorbate) and SCPEI (adsorbent) and hence it is not a good model to describe the adsorption isotherms.

The linearized form of the Freundlich equation was then used to analyze these data by plotting ln q_e versus C_e in order to investigate if the data fit Freundlich model or still need more analysis. The calculated Freundlich constants (n and K_f) as well as the correlation coefficient (R^2) obtained from the plots are presented in Table 5.14.

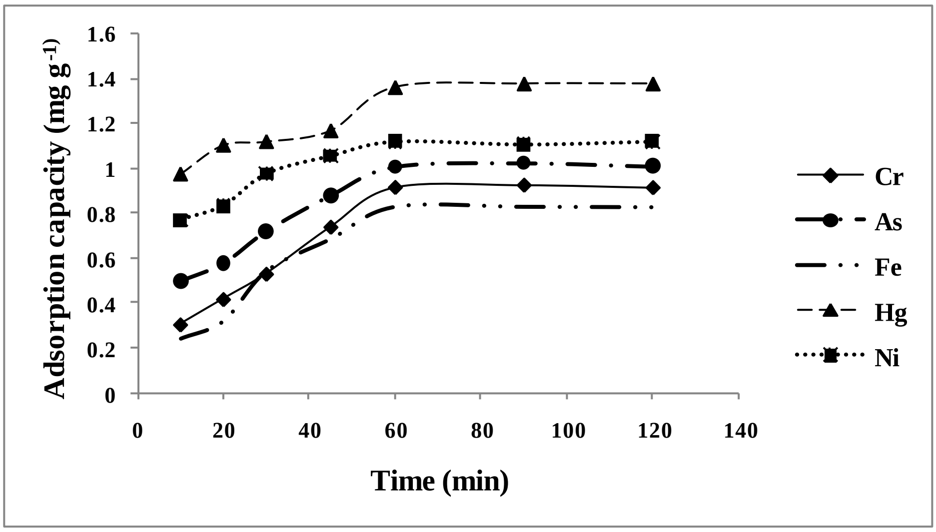
Table 5.14. Freundlich model parameters for the adsorption by SCPEI

	Cr	As	Fe	Hg	Ni	Zn	Mn	U	Pb	Se
n	0.613	0.483	0.736	0.339	0.841	0.834	0.769	0.751	0.571	0.340
R^2	0.977	0.981	0.986	0.951	0.990	0.992	0.996	0.983	0.963	0.963
K_f	4.966	3.575	4.290	4.072	2.591	2.742	4.055	3.044	4.199	4.204

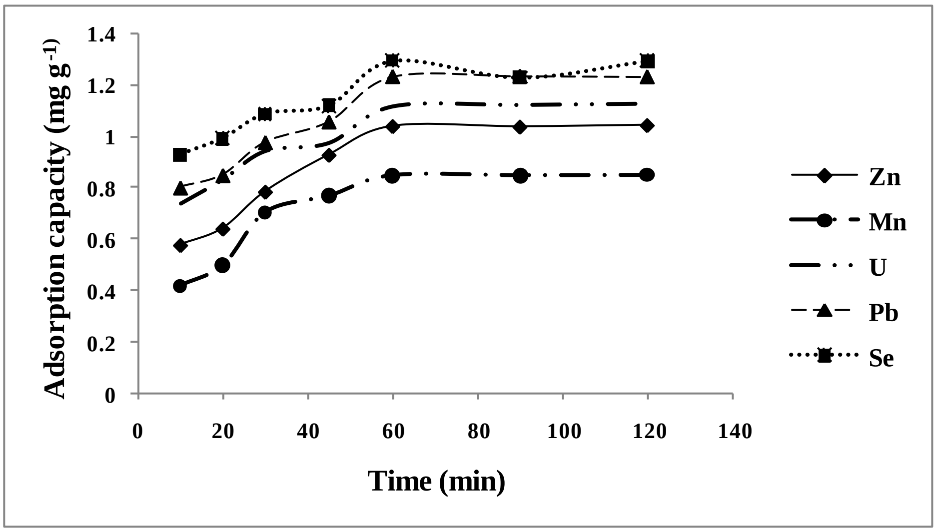
The high correlation coefficient values of Freundlich plotted linearized form implies good model to describe the adsorption isotherm of SCPEI; suggesting adsorption on a heterogeneous surface.

5.3.6. Effect of contact time on the adsorption process by SCPEI

The effect of contact time on adsorption of metal and metalloid ions by SCPEI was investigated by conducting the adsorption experiments using synthetic multi-component solution at fixed temperature and fixed concentration of 40 mg L^{-1}. The results of the time dependency of the adsorption of metals onto SCPEI are presented in Figures 5.22.



(a)



(b)

Figure 5.22. Effect of time on the adsorption of (a) Cr, As, Fe, Hg, and Ni (b) Zn, Mn, U, Pb, and Se by SCPEI

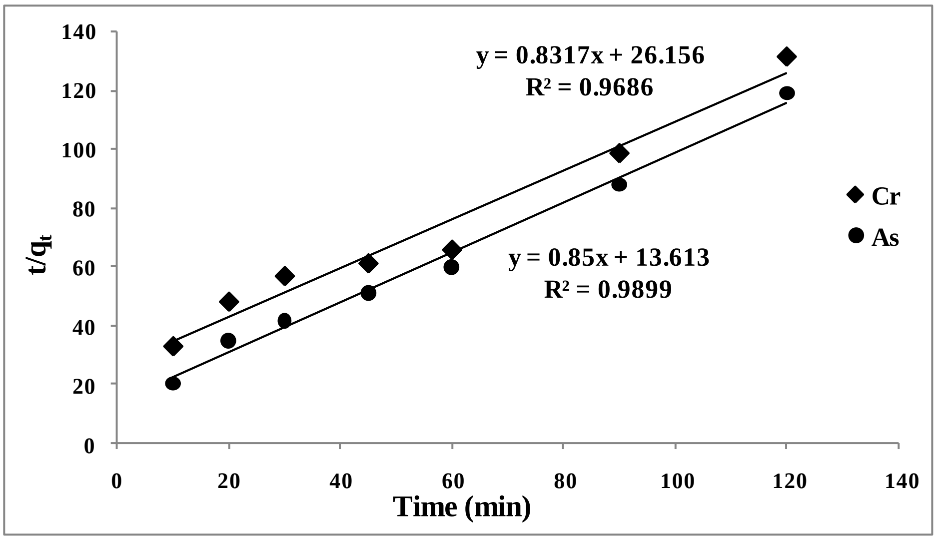
The results illustrate that the optimum contact time required for completed adsorption is 60 minutes. Hence the adsorption increased significantly within the first 30-45 minutes until it reached equilibrium after 60 minutes.

5.3.7. Kinetic modelling of adsorption process by SCPEI

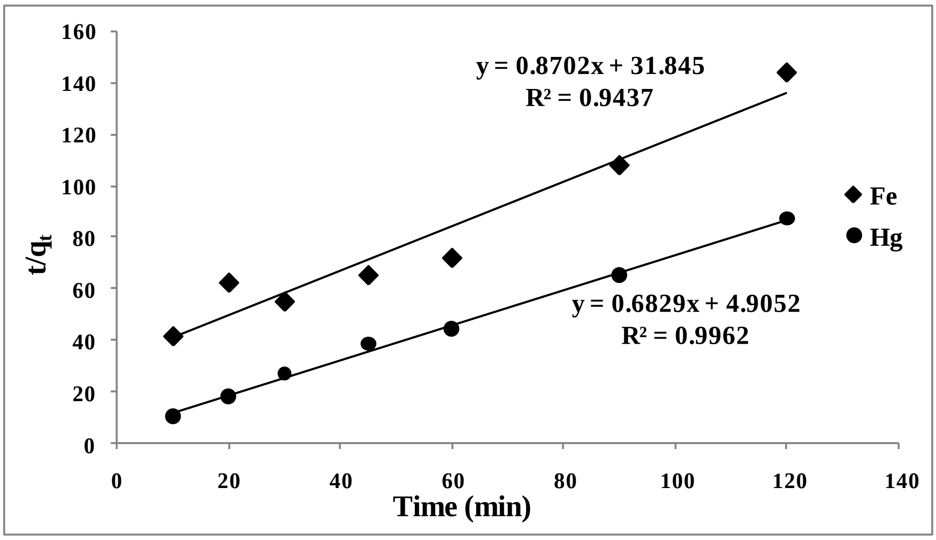
The pseudo-first-order equation and pseudo second-order equation were used as kinetic models to investigate the kinetics of adsorption of metal and metalloid ions onto SCPEI in order to describe the mechanism and rate controlling steps affecting the kinetics of the adsorption.

The plots of the linearized form of pseudo second order model (t/q_t vs. t) for metals adsorption by SCPEI are given in Figure 5.23.

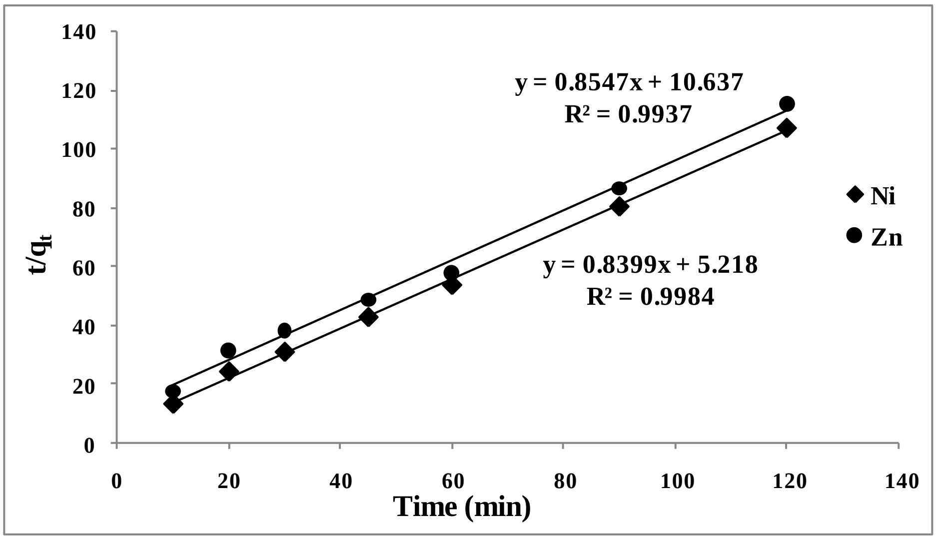
The experimental kinetic data showed better correlation with the pseudo second-order model because of the high values of correlation coefficients based on the linear regression $R^2 > 0.95$. The pseudo second-order rate constants (K_2) and the coefficient correlation values (R^2) were calculated from the slopes of the plots.



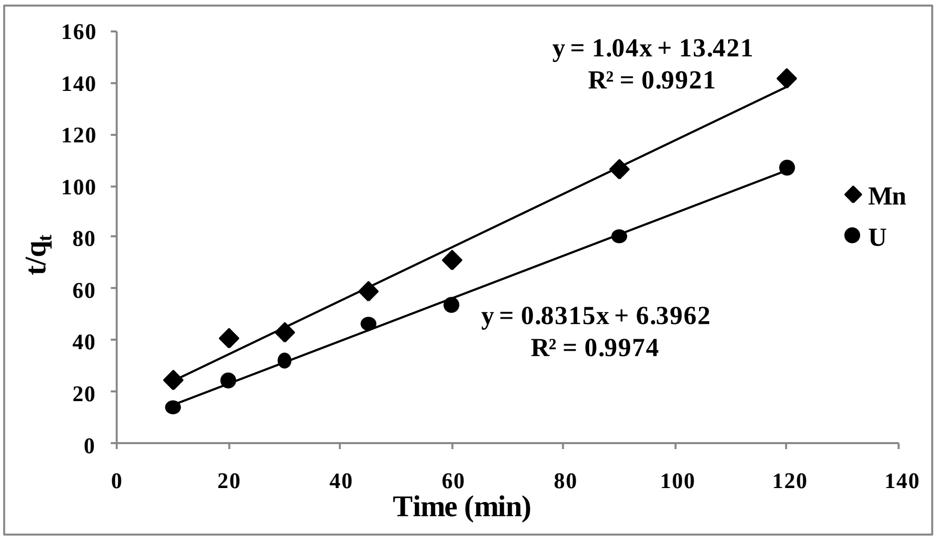
(a)


y = 0.8702x + 31.845
R² = 0.9437
y = 0.6829x + 4.9052
R² = 0.9962
Fe
Hg
t/q_t
Time (min)
0
20
40
60
80
100
120
140
160
0
20
40
60
80
100
120
140

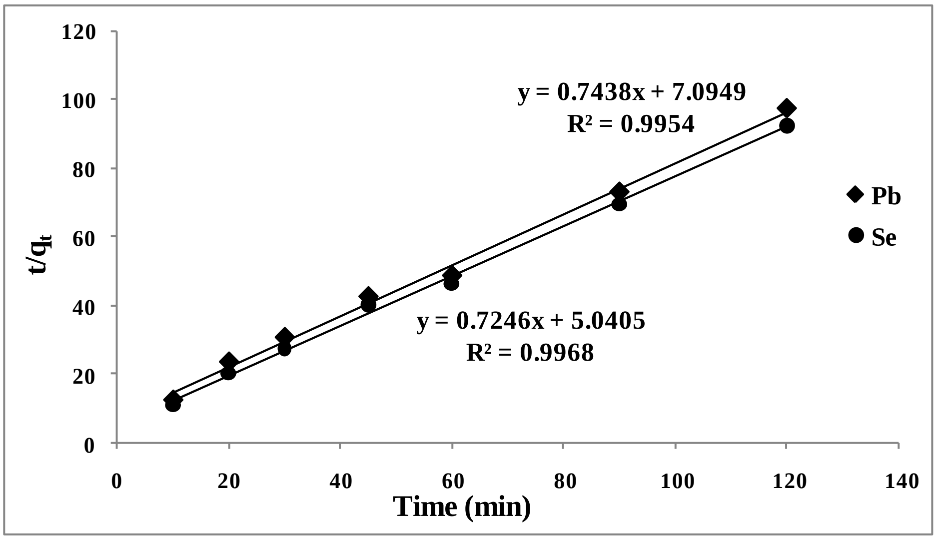
(b)


y = 0.8547x + 10.637
R² = 0.9937
y = 0.8399x + 5.218
R² = 0.9984
Ni
Zn
t/q_t
Time (min)
0
20
40
60
80
100
120
140
0
20
40
60
80
100
120
140

(c)



(d)



(e)

Figure 5.23. Pseudo second-order plots for the adsorption of (a) Cr and As, (b) Fe and Hg, (c) Ni and Zn, (d) Mn and U, (e) Pb and Se

5.3.8. Thermodynamic modelling of adsorption process by SCPEI

The results for the thermodynamic study of the adsorption of metal and metalloid ions onto SCPEI surface are tabulated in Table 5.15.

Table 5.15. Activation energy values of the adsorption of metal and metalloid ions by SCPEI

Metals	K_1	K_2	E_a J mol^{-1}	E_a K J mol^{-1}
Cr	0.011	0.006	52768	52.768
As	0.009	0.006	55116	55.11
Fe	0.009	0.005	53219	53.21
Hg	0.004	0.003	56896	56.89
Ni	0.012	0.01	57490	57.49
Zn	0.011	0.009	57310	57.31
Mn	0.009	0.005	53219	53.21
U	0.003	0.002	55955	55.95
Pb	0.003	0.003	59860	59.86
Se	0.01	0.009	58521	58.52

The high activation energy (Ea) values obtained in Table 5.15 show that all metal and metalloids adsorb onto SPEI by chemisorption.

5.3.9. Regeneration of SCPEI

Desorption results for SCPEI by different nitric acid concentrations are shown in Figure 5.24. The results show the concentrations of metals desorbed by 3 mol L^{-1}, 5 mol L^{-1}, and 7 mol L^{-1} of HNO_3.

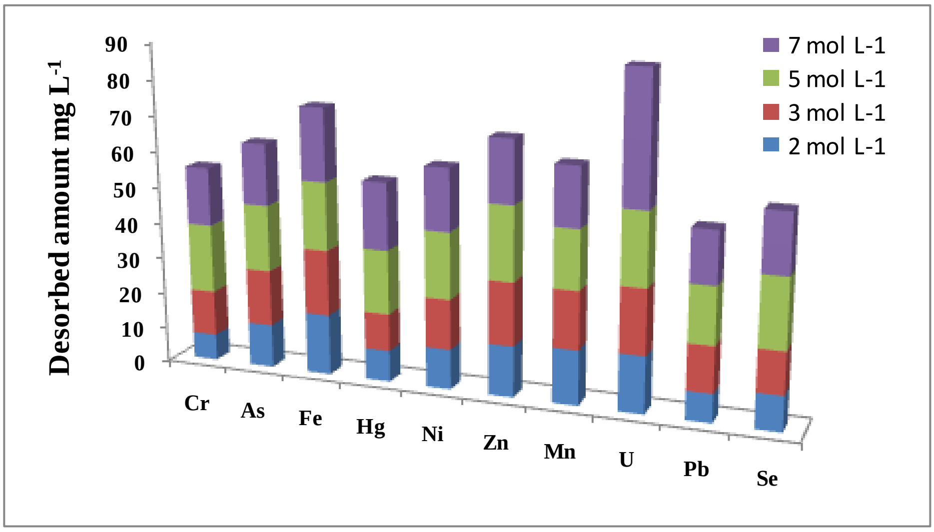


Figure 5.24. Desorption of metal and metalloid ions from SCPEI by different HNO_3 concentrations

For most ions, the most effective HNO_3 acid concentration was 5 mol L^{-1}. Subsequently, regeneration of the used polymer was carried out using 5 mol L^{-1} acid concentration.

The adsorption percentages for the recovered SCPEI on the same synthetic solutions are given in Table 5.16.

Table 5.16. Removal of metal and metalloid ions from synthetic solutions by regenerated SCPEI

pH		Cr	As	Fe	Hg	Ni	Zn	Mn	U	Pb	Se
3	C_f (mg l^{-1})	26.55	21.30	26.20	13.80	20.90	22.60	26.80	19.20	18.98	11.10
	RSD	0.945	1.779	0.612	5.183	3.077	0.997	0.764	7.677	1.689	10.57
	Ads Capacity (mg g^{-1})	0.538	0.748	0.552	1.048	0.764	0.696	0.528	0.832	0.841	1.156
	Ads percentage	34%	47%	35%	66%	48%	44%	33%	52%	53%	72%
8	C_f (mg l^{-1})	24.12	18.60	25.90	11.22	18.70	20.14	24.00	16.70	15.73	11.40
	RSD	1.009	4.446	0.589	1.254	0.3	0.795	0.77	*11.258*	*0.3*	8.103
	Ads Capacity (mg g^{-1})	0.635	0.856	0.564	1.152	0.852	0.794	0.640	0.932	0.971	1.144
	Ads percentage	40%	54%	35%	72%	53%	50%	40%	58%	61%	72%
	LOD	0.012	0.015	0.051	0.093	0.021	0.009	0.024	0.09	0.057	0.048
	MQL	0.12	0.15	0.51	0.93	0.21	0.09	0.24	0.9	0.57	0.48

Initial concentration of the ions = 40 mg L^{-1}; Ci – initial concentration before adsorption; C_f – final concentration after adsorption; LOD: limit of detection in mg L^{-1}; MQL: method quantitation limit in mg L^{-1}; RSD: relative standard deviation

The regenerated SCPEI still performing well, although its performance was decreased comparing with the fresh one.

The adsorption percentages of all ions decreased but maintained the same trend as the fresh polymer, as the regenerated SCPEI showed high removal to those metals which are highly adsorbed by the fresh SCPEI.

A cycle of five serial desorptions of Hg, Se, Pb and U from SCPEI (Figure 5.25) resulted in a decrease of: 1.360 mg g^{-1} to 0.178 mg g^{-1} for Hg; 1.296 mg g^{-1} to 0.183 mg g^{-1} for Se; 1.136 mg g^{-1} to 0.004 mg g^{-1} for Pb and 1.268 mg g^{-1} to 0.381 mg g^{-1} for U.

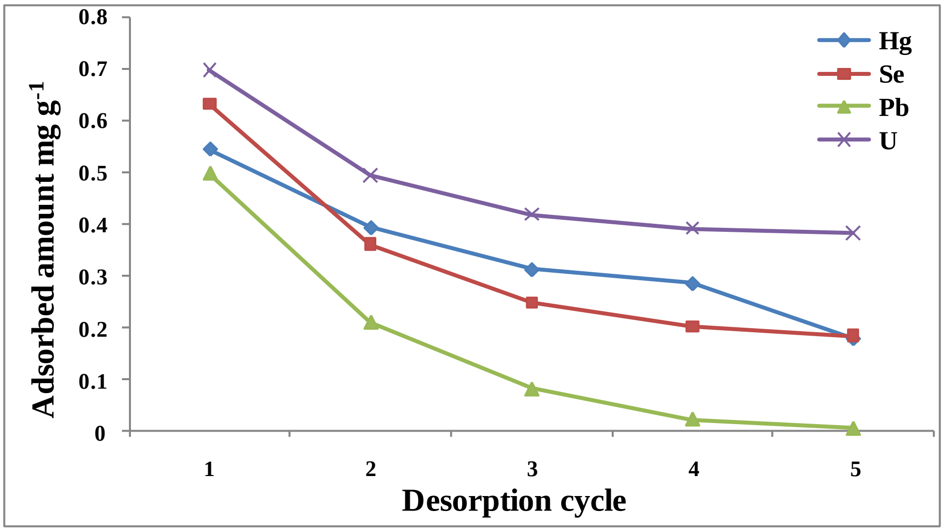


Figure 5.25. Regeneration of SCPEI by serial desorptions

5.3.5. Removal of heavy metal and metalloid ions from wastewater samples by SCPEI

The performance of SCPEI on metal and metalloid ions removal from wastewater samples is presented in Table 5.17 in term of adsorption percentages.

Table 5.17. Removal of metal and metalloid ions from wastewater samples by SCPEI (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 %
S W 1	Fe	6.100	0.087	4.5	3.095	26%
pH (3.8)	Ni	6.000	7.003	2.9	3.199	52%
SO_4^{-2} (383.2 mg l^{-1})	Zn	4.300	9.873	1.9	0.204	56%
	Mn	111.7	3.775	50.0	2.878	55%
S W 2	As	0.117	2.590	0.05	1.533	57%
pH (7.2)	Se	0.090	5.841	0.016	1.502	82%
SO_4^{-2} (19.80 mg l^{-1})	Ni	1.500	5.281	0.389	9.922	75%
S W 3	Cr	0.250	6.892	0.132	7.3	47%

pH (4)	As	0.280	2.056	0.099	3.514	65%
SO_4^{-2} (819.4 mg l^{-1})	Fe	4.480	6.509	1.98	2.562	56%
	Ni	1.790	1.722	0.891	2.367	50%
	Zn	1.570	5.015	0.62	6.676	61%
	Mn	22.00	8.823	10.97	3.002	50%
S W 4	Fe	5.840	8.972	4.0	5.045	32%
pH (5.6)	Ni	4.670	3.531	1.21	3.15	74%
SO_4^{-2} (653.6 mg l^{-1})	Zn	7.650	7.073	2.78	2.971	64%
	Mn	179.2	2.707	89.0	6.307	50%
Pit water	Cr	0.038	7.745	0.022	3.592	42%
pH (3)	Fe	0.600	3.543	0.356	7.037	41%
SO_4^{-2} (1669 mg l^{-1})	Hg	0.275	1.835	0.004	1.718	99%

Ni	10.70	7.968	2.2	6.32	79%
Zn	14.75	8.400	5.55	1.757	62%
Mn	136.4	7.990	66.0	5.32	52%
U	0.161	6.700	0.047	4.805	71%
Se	0.047	8.662	0.002	7.56	96%

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).

SW- surface water; C_i - initial concentration before adsorption; C_f – final concentration after adsorption.

The similarity in SCPEI trend between its performance towards metal and metalloid ions removal from synthetic solution and real wastewater samples is very clear.

CHAPTER SIX

CONCLUSION

This chapter summarizes the outputs of the study on the abstraction capacity of the synthesized cross-linked polyethylenimine and its functionalized derivatives (phosphonated and sulphonated) towards heavy metal and metalloid ions from wastewaters. It compares their potential, efficiency, affinity, selectivity, and removal mechanism as well as a brief comparison between the three polymers based on their functionality.

This study has proven that the synthesized polymeric materials represented in the modified (functionalized) cross-linked polyethylenimine can be successfully employed in the removal of metal and metalloid ions from wastewaters by taking advantage of their high selectivity, kinetics and reusability as well as their low cost.

Water-insoluble resins were synthesized by cross-linking polyethylenimine using epichlorohydrin as a cross-linker and then functionalizing the surface of the resulted cross-linked polyethylenimine by introducing both phosphorous and sulphur as donor atoms in order to have different chelating groups (ligands) for selective removal.The synthesized polymers were successfully employed in the removal of metals and metalloids from standard synthetic solutions and wastewater samples. The removal of ions as well as the mechanism of their removal hinges on the functional groups present in the cross-linked polyethylenimine (CPEI) and its functionalized derivatives sulfonated polyethylenimine (SCPEI) and phosphonated polyethylenimine (PCPEI); largely the amine groups in CPEI, sulfur atoms in SCPEI, and phosphorus atoms in PCPEI.

The synthesized polymers exhibited commendable potential for re-use through regeneration which is a very significant factor influencing the cost of the removal process as well as waste disposal.

While the adsorption of some metals onto one of the polymers was poor; it was quite superior onto the other one. This explains the role of the functional groups on the adsorption process and implies that the difference in the selectivity is attributed to the functionality of the adsorbents.

The study has shown that the water-insoluble form of polyethylenimine (cross-linked polyethylenimine CPEI) can perform comparably to the water-soluble form of polyethylenimine (PEI) which has commonly been used for the abstraction of heavy metal ions. CPEI selectively removed Cr, Fe, Zn, and Ni and it showed superior removal of Cr compared to the other two polymers. On the other hand, the removal of metalloids was very poor. CPEI was successfully regenerated using 5 mol L^{-1} HNO_3 for reuse.

The phosphonated polyethylenimine (PCPEI) performed very well towards some metals such as, Ni, Mn, Zn, and Pb; but among the three adsorbents it was unique in the removal of U and to some extent As. It was successfully recovered by 7 mol L^{-1} HNO_3 for reuse.

The sulphonated derivative exhibited unrivalled affinity for Hg and Se unlike the cross-linked polyethylenimine and its phosphonated derivative. It was successfully recovered by 7 mol L^{-1} HNO_3.

The Freundlich isotherm was found to best fit and describe the experimental data describing the adsorption process of metal ions onto the synthesized polymeric materials. The pseudo-second-order equation was found to explain the adsorption kinetics most effectively. The high activation energy values obtained from the thermodynamic studies were high indicating chemisorption.

The variation in selectivity and affinity of the developed materials presents them as potential adsorbents in the recovery of metals and metalloids from wastewaters.

Generally, the designed polymers are intended for use in filters in 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. The filtration system will thus enable removal of trace elements from the water before use. Their advantage, as pointed out in the previous sections, is that they can be modified to be selective for particular elements e.g. uranium.

The regeneration step can be conducted selectively as well through the use of different desorbing solutions, thus creating the possibility of collecting the desorbed metals for use in other metal processing industries. This, combined with the possibility of recovering low concentrations of gold in the waste streams, can be an effective self-financing process.

CHAPTER SEVEN

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