

**PREPARATION OF MAGNETIC NANO COMPOSITE BEADS AND THEIR
APPLICATION TO REMEDIATION OF MINE WASTEWATERS**

Report to the
Water Research Commission

by

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EXECUTIVE SUMMARY

In this project, magnetic ion imprinted polymers with high recognition for uranyl (UO_2^{2+}) and chromium Cr(VI) ions were prepared for the first time. The prepared magnetic ion imprinted polymers were characterised and optimised in the laboratory. They were then applied to wastewaters from acid mine drainage and influent from wastewater treatment plant.

The optimum extraction parameters in batch format for magnetic ion imprinted polymers for uranyl ions were found to be sample pH of 4, 50 mg of magnetic ion imprinted polymers for a 25 ml sample volume. The optimum contact time was found to be 45 minutes at a stirring speed of 1500 rpm. The lower maximum extraction time implies that the magnetic ion imprinted polymers have fast binding kinetics. Under these optimum conditions, the recovery of uranyl ions was found to be above 80%. The binding of uranyl ions on the magnetic ion imprinted polymers were found to follow pseudo second order kinetics with rate constant (k_2) and correlation coefficient (R^2) ranging between 0.273-0.678 and 0.9811-0.9992 respectively. This implied a chemisorptions interaction of the uranyl ions with the magnetic polymers. The adsorption of uranyl ions onto the polymers fitted both Freundlich and Langmuir models. The maximum adsorption capacity was found to be around 1.2 mg g^{-1} which is in the same range as other magnetic ion imprinted polymers but lower than other ordinary polymers or imprinted polymers without magnetic ions. Despite low binding capacity, the prepared magnetic ion imprinted polymers when tested for selectivity were found to have superior selectivity for uranyl ions compared to major competitors of Fe^{3+} , Pb^{2+} , Ni^{2+} and Mg^{2+} that have similar ionic radius. The selectivity order observed was as follows: $\text{UO}_2^{2+} > \text{Fe}^{3+} > \text{Pb}^{2+} > \text{Ni}^{2+} > \text{Mg}^{2+}$. The same selectivity and recovery was observed when the magnetic ion imprinted polymers were applied to wastewaters from acid mine drainage and influent from wastewater treatment plant.

The optimum extraction conditions for the prepared magnetic ion imprinted polymers for Cr(VI) were found to be as follows; sample pH of 4, adsorbent amount of 20 mg for a 25 ml sample volume. The extraction time was 40 minutes at stirring speed of 1500 rpm. The low extraction time indicates fast binding kinetics of Cr(VI) to the prepared polymers. At optimum conditions, the recovery of Cr(VI) was above 80%. The maximum adsorption capacity for the magnetic polymers was found to be 6.20 mg g^{-1} . The optimum time for the adsorption of the Cr(VI) analyte was determined as 40 minutes at stirring speed of 600 rpm. The binding of Cr(VI) on the magnetic ion imprinted polymers were found to follow pseudo second order kinetics. This implied a chemisorptions interaction of the Cr(VI) ions with the magnetic polymers. The adsorption of Cr(VI) onto the polymers fitted neither Freundlich nor Langmuir models. The prepared magnetic ion imprinted polymers were found to very selective towards Cr(VI) compared to other ions such as SO_4^{2-} , F^- and NO_3^- . The order of selectivity of anions followed the trend: $\text{Cr}_2\text{O}_7^{2-} > \text{SO}_4^{2-} > \text{F}^- > \text{NO}_3^-$.

The prepared magnetic materials may not be suited for remediation of polluted wastewater for uranyl and Cr(VI) ions on a large scale because of high cost of preparing them but are very good as sample extraction materials before final quantification. This is very important because direct analysis of these metal ions from wastewaters is a huge challenge because of

other interfering ions. Since the materials can be reused more than six times, this makes them cheap materials for sample extraction purposes. Besides, in sample extraction, only few mg of material is used ranging from 25-500 mg depending on the sample volume.

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LIST OF ABBREVIATIONS AND ACRONYMS

AAS	Atomic absorption spectroscopy
Acac	Acetylacetone
AFM	Atomic force spectroscopy
AMD	Acid mine drainage
BET	Brunauer, Emmett and Teller
CDs	Cyclodextrins
CHNS	Carbon, hydrogen, nitrogen and sulphur
CNTs	Carbon nanotubes
DL	Detection limit
DMRB	Dissimilatory metal reducing bacteria
DRS	Diffuse reflective spectroscopy
DU	Depleted uranium
DVB	Divinylbenzene
EDS	Energy dispersive spectrometry
EGDMA	Ethylene glycol dimethacrylate
F	Force
FTIR	Fourier-transformed infra-red
FWHM	Full width at half maximum
GFAAS	Graphite furnace atomic absorption spectroscopy
GTF	Glucose-tolerance factor
ICP-OES	Inductively coupled plasma optical emission spectroscopy
IIP	Ion imprinted polymer
ISL	<i>In-situ</i> leaching
MAA	Methacrylic acid
MCL	Maximum contaminant level
MIP	Molecularly imprinted polymer
NECSA	Nuclear Energy Corporation of South Africa
NEMA	National Environmental Management Act
NIP	Non imprinted polymer
Nufcor	Nuclear Fuels Corporation of South Africa
OA	Oleic acid
ORNL	Oak Ridge National Laboratory
PRBs	Permeable Reactive Barriers
PXRD	Powdered X-ray diffraction
r.f	Radio frequency
rpm	Rotations per minute
SA	South Africa
SABS	South African Bureau of Standards
SALO	Salicylaldoxime
SD	Standard deviation
SEM	Scanning electron microscopy
SRB	Sulphate reducing bacteria

t yr ⁻¹	Tonnes per year
TEM	Transmission electron microscopy
TEOS	Tetraethyl orthosilicate
TGA	Thermo-gravimetric analysis
TRIM	Trimethylolpropane trimethacrylate
UNSCEAR	United Nations Scientific Committee on the Effects of Atomic Radiation
WHO	World Health Organization
4-VP	4-Vinyl pyridine
γ-MPS	γ-Methacryloxypropyltrimethoxysilane

Chapter One: Background

1.1 Introduction

One of the most critical global issues is water pollution (Brown, 1996; Ramakrishna *et al.*, 2006) and it has led to alteration of the physiochemical properties of water (Richardson, 1988). Pollution of water bodies due to the indiscriminate disposal of heavy metals has been a concern for a long time. The rapid increase in the levels of environmental pollution over recent decades has resulted in increasing concern for people's well-being and for global ecosystems (Kot and Namiesnèik, 2000). Inorganic pollutants of great physiological significance are heavy metals (Ramakrishna *et al.*, 2006), because of their toxicity towards aquatic-life, human beings and the environment (Qdaisa and Moussab, 2004, Luo *et al.*, 2011). Pollution due to heavy metals is now seen as a priority (Fu and Wang, 2011). There is a lot of evidence in literature that trace back pollution generation to anthropogenic sources in the quest for exploiting nature as a source of means of livelihood by man (Agbontalor, 2007). Industrialization and urbanization have caused excessive discharge of heavy metals into the environment (Khan *et al.*, 2004).

Mining industry accounts for major environmental threats in countries like South Africa because it has large reserves for several minerals (Ochieng *et al.*, 2010). As an example, South Africa is the world's largest producer of ferrochrome which holds about 70% of the world's total chrome reserves, mostly located in the Bushveld Igneous Complex (BIC) ores and produces 75% of the world's ferrochrome. In some cases, platinum group's metals (PGMs) contain chromium as well. The so called Witwatersrand Basin has a lot of gold tailing dumps that are source of pollution either from dust particles or from acid mine drainage. The issue of AMD is a hot subject in South Africa and is always in the media. This is because of the catastrophic effects of AMD on animals, plants and the environment. In order to assist the mining industry with the mitigation of AMD, the Department of Minerals and Energy (DMR) in South Africa had subsidies for the months of January, February and March 2010 worthy R7.5 million. However due to the extent of the problem, this amount fell dangerously short of the funds that are necessary to treat AMD.

Acid mine drainage (AMD) is highly acidic water, usually containing high concentrations of metals, sulphides and salts. AMD have been identified to be the single most significant threat to South Africa's environment. In South Africa, this is being driven home by the AMD problems being experienced at the East Rand operations of Pamodzi Gold. Pyrite (FeS_2) is responsible for starting acid generation. When pyrite is exposed to oxygen and water, it will be oxidized, resulting in protons release. Mining increases the exposed surface area of sulphur bearing rocks. The oxidation process occurs in undisturbed rocks as well but at a slower rate. These wastewaters containing heavy metals such as uranium and chromium are directly or indirectly discharged into the environment killing aquatic life

(Fu and Wang, 2011). Both uranium and chromium in their hexavalent states are very toxicity because they are very mobile and can easily cross the biological membranes. Direct water contamination also arises from many other industries such as metal cleaning; metal finishing (Luo *et al.*, 2011), textile industry (Halimoon and Yin, 2010) and wastewater treatment plant influents.

The most common remediation techniques in the removal of heavy metals from water include chemical precipitation (Pavlović *et al.*, 2007), ion exchange (Mier *et al.*, 2001; Wojtówicz and Stokłosa, 2002; Bai and Bartkiewicz, 2009), electrodeposition (Meunier *et al.*, 2006; Lewinsky, 2007), membrane technology (Sanga *et al.*, 2008; Ahmad *et al.*, 2011), lime neutralization and phytoremediation (Lone *et al.*, 2008; Liao and Chang, 2004; Raskin *et al.*, 1997). Most of these remediation techniques have got disadvantages such as creating by products that are toxic, expensive in terms capital and operational costs and requires specialised personnel (Nameni *et al.*, 2008; Luo *et al.*, 2011; Zhan *et al.*, 2011).

This has led to the search of new techniques and/or materials that can be used for remediation of such polluted wastewaters. Most of the research now is focused on new materials that are selective and cheap that can be used for removal of metal ions from wastewater streams. These materials are usually contained in a large column and wastewater is pumped through trapping the target compounds. The trapped metals ions are eluted and the column is regenerated for further use. Magnetic synthetic polymeric sorbents are such new materials that are currently studied for use in remediation of wastewaters (Zhao *et al.*, 2010; Wang *et al.*, 2011; Fan *et al.*, 2012). However, many of the studied magnetic polymers are not selective because they are synthesized without a template molecule (Zhao *et al.*, 2010; Wang *et al.*, 2011; Fan *et al.*, 2012). The incorporation of a template during polymerisation allows to prepare polymers that are highly selective towards the target chemical during use (Oliveira *et al.*, 2004). This is because after polymerisation; the template is removed leaving a magnetic polymer that has cavities complimentary to the template in size, shape and functionality.

Chapter Two: Literature Review

2.1 Background on uranium

The main use of uranium in the civilian sector is to fuel commercial nuclear power plants as it is commonly understood as a material storing huge amounts of energy and its only commercial application is as nuclear fuel (Sarangi and Beri, 2000). This requires uranium to be enriched with the ^{235}U isotope and the chain reaction to be controlled so that the energy is released in a manageable way (Uranium-U). Sarangi and Beri (2000) noted that the growth of uranium mining normally follows the pattern of growth nuclear power generation capacity in most countries. This relationship of supply and demand of uranium over time is shown in Figure 2.1.

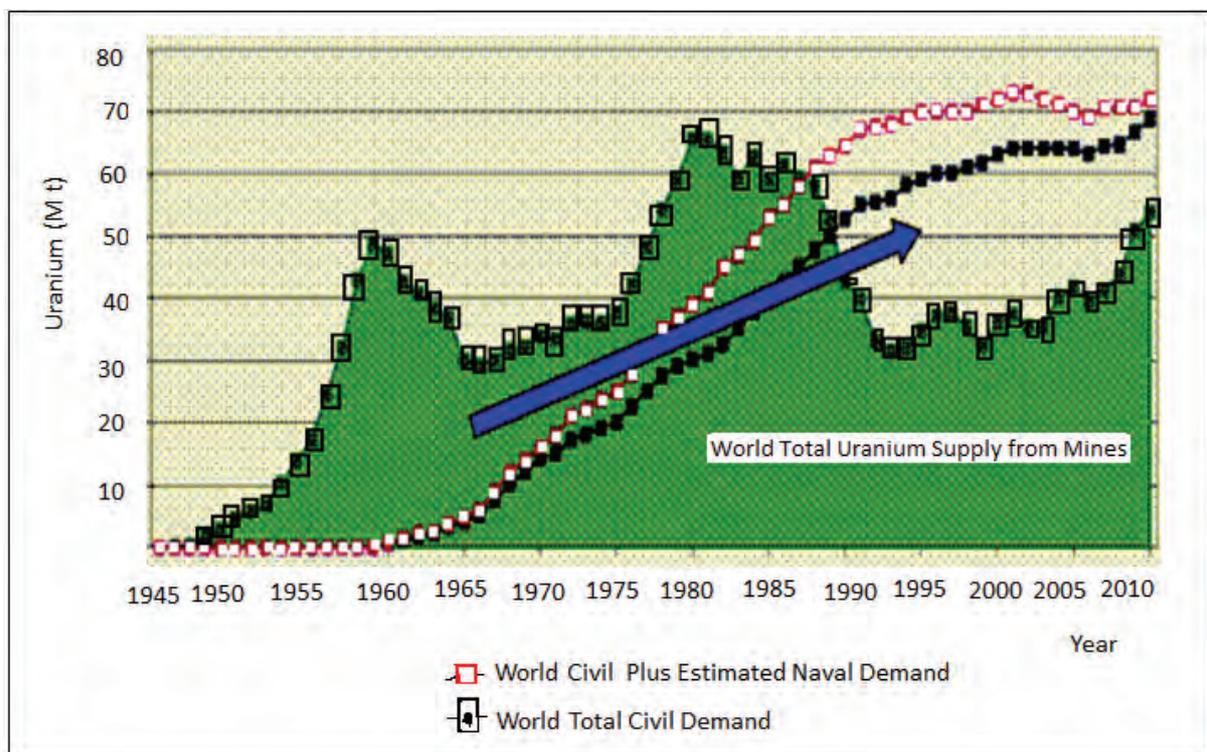


Figure 2.1: Supply and demand of uranium.

Uranium is widely distributed throughout the Earth's crust and almost all types of rocks contain some amount of uranium (Montgomery, 1995). Uranium is also present in river water, ground water and even seawater (Sarangi and Beri, 2000). The average uranium concentration in the Earth's crust is approximately 2.7 ppm (Brookins, 1988). Mining is, however, done in areas where concentration is high enough to make profit. This is therefore restricted to certain areas of various countries and while other countries have very little deposit and have to import enriched uranium for energy purposes. Table 2.1 shows some reported uranium concentration in different matrices.

Table 2.1: Typical concentration ranges in different environmental matrices.

Matrix	Typical concentration range (ppm)	Reference
Soil	0.0-11.7	UNSCEAR, 1993
Air	2.2×10^{-8} - 1.0×10^{-7}	NCRP, 1999
Surface water	3.0×10^{-5} - 2.1×10^{-3}	WHO, 2001
Groundwater	4.0×10^{-5} - 2.0×10^{-3}	WHO, 2001

Major sources of radioactive waste and contamination emanate from the production of electrical power and weapons from nuclear fuels, nuclear weapons' tests, fuel reprocessing, and nuclear accidents (Hu *at al.*, 2010). Other sources of uranium include by-products of mining activities of other minerals such as gold and copper (Ginder-Vogel *et al.*, 2006). The process of using uranium for nuclear fuels or nuclear weapons generates a lot of uranium waste that has always been a problem for long term storage. Every 900 kg of natural uranium enriched for nuclear energy purposes contains about 120 kg of enriched uranium and the remaining 780 kg is depleted uranium (DU). In order to make a nuclear reaction occur, there has to be a greater percentage of the more fissionable ^{235}U in the fuel than occurs in nature. The enrichment process converts U_3O_8 into a gas, uranium hexafluoride (UF_6), which enables the uranium to be enriched from a ^{235}U content of 0.7% to about 3 to 4%. The enriched UF_6 is converted back into UO_2 and formed into fuel pellets. For weapons grade uranium, this content can even go up to much higher levels of 90% ^{235}U . DU is obtained as a by-product in the enrichment process of natural uranium. DU is distinguished from natural uranium by lower relative concentrations of 0.25 to 0.30% ^{235}U (Bleise *et al.*, 2003).

2.1.1 Uranium mining as a source of pollution

Various technologies are available for mining of uranium as summarized in Table 2.2. These methods have been changing over time with evolving of new technologies coupled with mining challenges arising from reaching deep ores. In 1990, about 55% of world production came from underground mining, but this shrunk dramatically to 33% from 1999. ISL mining has been steadily increasing its share of the total. In 2010 production was as shown in Table 2.2.

Table 2.2: Methods used in the mining of uranium.

Method	tonnes U	%
Conventional underground	15,095	28
Conventional open pit	13,541	25
<i>In situ</i> leach (ISL)	22,108	41
By-product	2920	5

Conventional mining involves removing mineralized ore from the ground, breaking it up and treating it to remove the minerals being sought. These causes mine tailing dumps that are a source of AMD. On the other hand, ISL involves leaving the ore where it is in the ground, and recovering the minerals from it by dissolving it and pumping the pregnant solution to the surface where the minerals can be recovered. Consequently, there is little surface disturbance and no tailings or waste rock generated as with other methods such as open pit. However, if air and water enter the underground ISL and the ore is pyrite bearing, AMD drainage might result too. In conventional underground mining where shafts are drilled down the earth to reach the ore bearing minerals. The mined ore is taken to the surface for extraction and this also creates mining dumps that are a source of AMD. The production of uranium in South Africa has generally been a by-product of gold or copper mining. In Africa, gold and uranium mining are typically accomplished together, as both methods process large amounts of rocks for very small yields.

2.1.2 Toxicity and fate of uranium

Uranium atoms decay into other atoms that are also radioactive and commonly called "decay products." Radioactivity decay is a spontaneous process and cannot be accelerated or slowed down by any chemical or physical means (Montgomery, 2005). Uranium and its decay products primarily emit alpha radiation, however, lower levels of both beta and gamma radiations are also emitted. Alpha particles travel up to 50 mm in air and only a few microns in rocks before being absorbed and this makes them very safe. Beta particles have a travelling range of about 3 m in air and about 2 mm in rocks. Gamma rays have a high penetrating power and it can take a thick sheet of metal such as lead or concrete to reduce them significantly. ^{206}Pb , the last element on the list of uranium decay series is stable and non-radioactive. It does not decay, and therefore has no half-life. The half live of ^{238}U is about 4.5 billion years, ^{235}U about 700 million years, and ^{234}U about 250 thousand years. In general, ^{235}U and ^{234}U pose a greater radiological health risk than ^{238}U because they have much shorter half-lives. They decay more quickly and are therefore more radioactive as compared to ^{238}U . Naturally occurring uranium contains three isotopes, namely ^{238}U , ^{235}U , and ^{234}U (Bleise *et al.*, 2003). Krachler and Carol (2011) noted that the use of uranium needs an appropriate knowledge of the isotopic composition of the material considered. Of the naturally occurring uranium radioisotopes, ^{238}U is by far the most abundant in terms of mass composition with a composition of 99.28% followed by ^{235}U at 0.72% and ^{234}U at 0.006%.

On average, approximately 90 μg of uranium exists in the human body from which about 66% is found in the skeleton, 16% in the liver, 8% in the kidneys and 10% in other tissues (WHO, 2001). Excessive exposure of uranium and its compounds cause kidney toxicity. This exposure can be through breathing air containing uranium dusts or eating substances containing uranium, which then enters the bloodstream. Once in the bloodstream, uranium compounds are filtered by the kidneys where serious damage can be inflicted at high blood concentrations. Virtually all of the observed or expected effects are from nephrotoxicity associated with deposition in the kidney tubules and glomeruli damage at high blood concentrations of uranium (ranging from about 50 to 150 mg depending on the individual).

Studies have shown that uranium causes birth defects in fetuses and infants and that the risk of leukaemia is increased. Uranium also mutates human DNA and chromosomes and deforms them. Since uranium isotopes mainly emit alpha particles that have little penetrating ability, one possible radiological toxicity source can be from some of the radioactive decay products. This is indeed the case as it was already proved in the 1920`s that contamination with radon (Schuessberger disease), a decay product of ^{238}U , can cause bronchial and lung cancer. For these reasons, several research groups have been stimulated, for many years, to investigate the chemistry and toxicology of uranium in all its chemical forms in order to assess the potential chemical and radiological risk for the environment and human health (Berto *et al.*, 2011).

2.1.3 Uranium speciation

The need to determine different species of trace elements in environmental and biological materials is important since the effects or toxicity of an element and its behaviour depend to a great extent on its chemical form and concentration (Kot and Namiesnèik, 2000). The geochemical speciation of uranium influences its solubility, mobility and biological availability in the environment. Geochemical speciation information on uranium has been used to evaluate potential *in situ* remediation approaches (Lovely *et al.*, 1991; U.S. DOE, 1999; Fredrickson *et al.*, 2000).

Since the mobility and transport of uranium in soils occurs via water it is of great importance to investigate the aqueous chemistry of this element and its speciation in natural waters (Berto *et al.*, 2011). Some previous studies already underlined the importance and complexity of uranium speciation in ground waters mainly in the context of uranium milling for predicting radionuclide migration and for remediation strategies on contaminated sites (Teprat *et al.*, 2009). The distribution of uranium ions in aqueous solution is dependent on both the solution pH and the total uranium concentration (Kotrba *et al.*, 2011).

In nature, uranium ions normally occur in tetravalent and hexavalent form. The hexavalent form is easily soluble in acidic water (Sarangi and Beri, 2000). In oxygen-containing groundwater, uranium is most commonly found predominantly in the hexavalent oxidation state, U(VI), (Langmuir, 1978; Sandino *et al.*, 1992; Farrel *et al.*, 1999; Kilislioglu and Bilgin, 2003; Ginder-Vogel *et al.*, 2006; Konstantinou, 2007) a highly soluble, mobile and therefore troublesome form. In these oxidizing conditions, the uranyl predominates and behaves as strong acid in a Lewis acidity scale (Kotrba *et al.*, 2011). Uranyl ions show high capacity of interacting with a variety of organic and inorganic ligands to form complex species of different stabilities (Kotrba *et al.*, 2011). In systems with high dissolved carbonate concentrations, uranyl-carbonate complexes may become dominant (Gascoyne, 1992) and it forms soluble carbonate complexes in solution, Figure 2.2 (Langmuir, 1978; Pavel *et al.*, 2009). These stable dissolved ternary complexes can effectively compete with mineral surfaces as "reservoirs" for U(VI) (Grenthe *et al.*, 1992).

The hydrolysis of the uranyl ions in aqueous solution is significant at high pH values. A larger number of uranyl hydroxides, oxyhydrates and uranates are known, but

$(\text{UO}_2)_2(\text{OH})_2^{2+} \cdot \text{H}_2\text{O}$ is the most stable species in the presence of water at 25°C. These hydrolysed complexes represent a significant percentage of the overall speciation at high pH values (Baes and Mesmer, 1976).

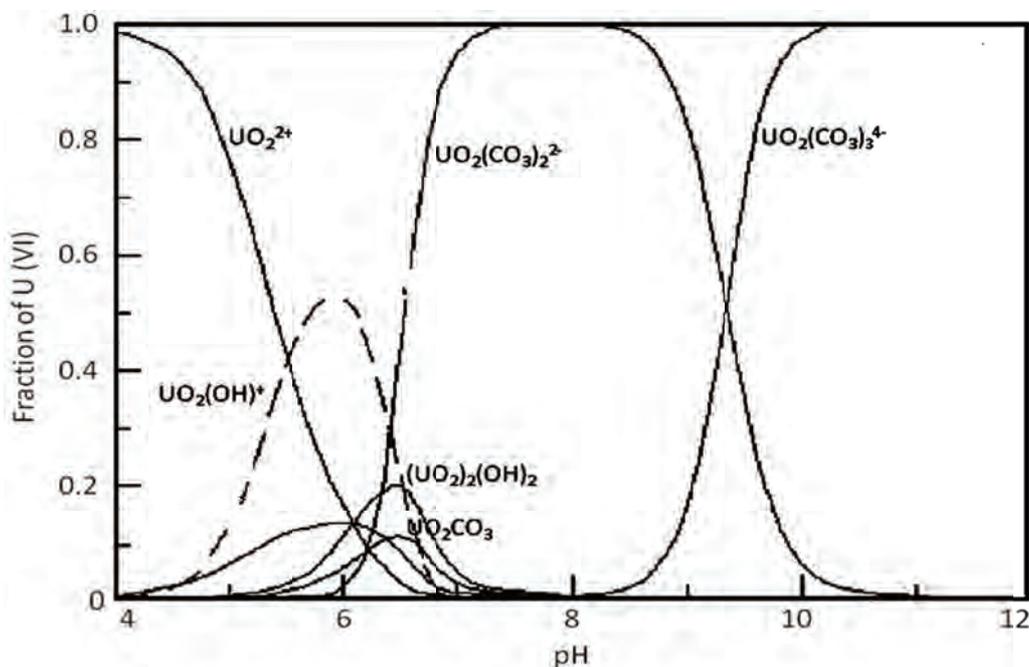


Figure 2.2: Species distribution of U(VI) (Choppin, 2006).

In concentrations below 10^{-6} M, $\text{UO}_2(\text{OH})^+$ is the dominant hydrolysis species in solution. Above this concentration, the study of uranyl (VI) hydrolysis is complicated by the formation of polymeric species such as $(\text{UO}_2)_2(\text{OH})_2^{2+}$, $(\text{UO}_2)_3(\text{OH})_4^{2+}$ and $(\text{UO}_2)_3(\text{OH})_5^+$. U(VI) bonds readily with minerals suspended in water and can spread easily over large areas. However, the tetravalent state, U (IV), resists combining with minerals and is highly stable and immobile (Ginder-Vogel *et al.*, 2006).

2.2 Background of chromium

Chromium exists primarily in the mineral chromite, which is present in soils, waters, rocks, fauna and flora, and volcanic dust and gases. Many chromium compounds are coloured as its name means many colours. Examples of these are; ammonium dichromate (orange crystalline solid), chromium nitrate nonahydrate (purple crystals), sodium dichromate dihydrate (orange colour) and chromic sulphate which is green (Shupack, 1991).

Chromium has many industrial applications, for example, its compounds can be added to cooling water to inhibit corrosion. Chromium and its compounds are also employed in the manufacturing of inks, industrial dyes and paint pigments (Aksu *et al.*, 2002). Other uses of chromium include stainless steel production, leather tanning, wood preservation, fertilizers, chrome tanning, textile, photography, etc., (Kannan, 1995). Chromium metal is also extensively used in ferrous alloys, mostly due its resistance to ordinary corrosive agents. The dichromate anions can also be used to oxidize various functional groups like the aldehydes

and alcohols, but their limited solubility in non-aqueous solutions has seen a continued interest in the development of new chromium(VI) reagents for the effective oxidation of organic substrates, especially under mild aprotic conditions. Considering this drawback, new polymer supported dichromates based on quaternised polyvinylpyridine were synthesized by several groups including that of Tamami and Kiasat (1997). Polymer supported solid phase organic reagents have an advantage that excess reagents and by-products can easily be separated from the reaction product which is not the case with their monomeric counterparts (Sherrington and Hodge, 1988).

2.2.1 Chromium mining as a source of pollution

The world has large reserves of chromite estimated to be 12 billion tons. Of this, over 95% of the world's chromium resources are concentrated in Southern Africa and Kazakhstan. The world's largest producer of ferrochrome is South Africa having about 70% of the world's total chrome reserves. Chromium is normally mined in the form of the mineral chromite (Cammarota, 1992). These are mostly located in the Bushveld Igneous Complex (BIC) ores covering an area of approximately 12 000 square kilometres. In total, there are 10 mining sites around South Africa (Mining industry of South Africa). In total, the combined chromium ore reserves exceed 450 million tons, calculated to a depth of 300 metres, with an annual production capacity of more than 4 million tons. An estimation of over 200 000 jobs and a contribution of over R42 billion in Gross Domestic Product per annum by South Africa's chrome value (www.meraferesources.co.za), underscores the importance of this chromium to the nation.

All of the mining activities of chromium that involves both underground and open pit produce a lot of mine tailing dumps that are a source of AMD. The dust particles from these mine tailing dumps is a source of air pollution.

2.2.2 Speciation and fate of chromium in the environment

Chromium is one of those heavy metals which exist in variable oxidation states of which the trivalent Cr(III) and hexavalent Cr(VI) oxidation states are the most common in the environment (Toral *et al.*, 2009). The oxidation states of chromium can go from -2 to +6. The electron configuration of the element in the ground state is $3d^5 4s^1$, while that for the trivalent state is $3d^3 4s^0$ and that for the hexavalent state is $3d^0 4s^0$. Chromium(III) oxidation state is the most stable form of chromium. Energy is required to convert the trivalent state to lower or higher states. The negative standard potential (E^0) of the Cr(III)/Cr (II) metal ion couple signifies that Cr (II) is readily oxidized to Cr(III), and Cr (II) species are stable only in the absence of any oxidant (Kotas and Stasicka, 2000). The reduction potential of Cr (II) is -0.91 V and that of Cr(III) is -0.74 V (De la Guardia and Morales-Rubio, 2003).

Just like other metals, chromium enters the environment as a result of effluents discharged from industries (Gómez and Callao, 2006). Once it enters the natural water system, chromium exists primarily in trivalent and hexavalent forms (Chen-Jen, 2002). The need to study chromium speciation emanates from drastic differences in biochemical properties of Cr(III)

and Cr(VI) compounds (Panichev *et al.*, 2008). For instance, Cr(III) is an essential element for humans and animals and plays an important role as the glucose-tolerance factor (GTF) in insulin metabolism (Langard and Norseth, 1990; Florence and Batley, 1980). Also Cr(III) is considered a micro nutrient for many living organisms while Cr(VI) is an irritant to plants and animal tissues. The hexavalent form of chromium is also known to be very toxic to humans and causes chronic adverse effects (Langard and Norseth, 1990). Cr(VI) is carcinogenic because of its high oxidation potential and its ability to penetrate biological membranes (Udy, 1956; Lin and Huang, 2001). The toxicity of Cr(VI) is as a result of its properties as an oxidant (Katz and Salem, 1992). The Eh-pH diagram for chromium, Figure 2.3, provides a generalized depiction of the aqueous species stabilities in different redox conditions.

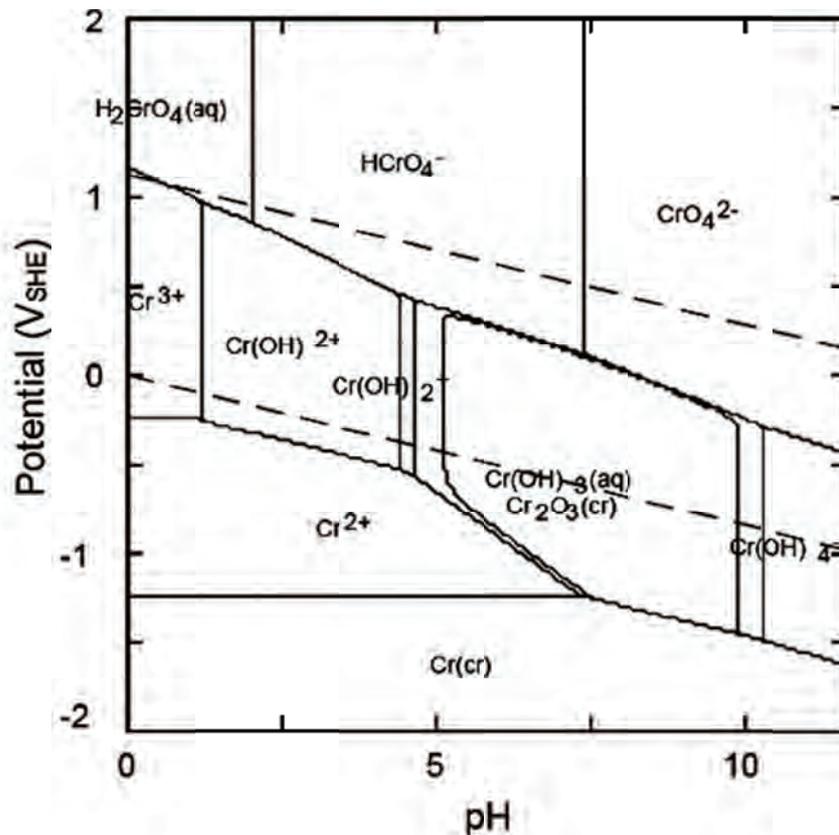


Figure 2.3: The pH-Eh diagram of stability of different chromium species (Ball and Nordstrom, 1998; Nieboer and Jusys, 1988; Richard and Bourg, 1991).

Trivalent chromium has a low solubility in aqueous medium in alkaline and neutral pH, (Petruzelli *et al.*, 1995; Zhao *et al.*, 1998). Low solubility of chromium(III) means it will be retained and adsorbed to solid particles or it precipitates, Johnson *et al.* (1992), thereby making it relatively immobile in the aquatic systems. On the other hand, Cr(VI) is highly soluble and can be transported over a great distance before it is reduced back to the trivalent state. In aqueous solution, the hexavalent chromium species may exist in a variety of oxospecies, namely, dichromate (Cr₂O₇²⁻), hydrochromate (HCrO₄⁻) or chromate (CrO₄²⁻)

depending on concentration and pH (Neagua and Mikhalovsky, 2010; Namasivayam and Sureshkumar, 2008; Chanda and Rempel, 1993), Figure 2.4.

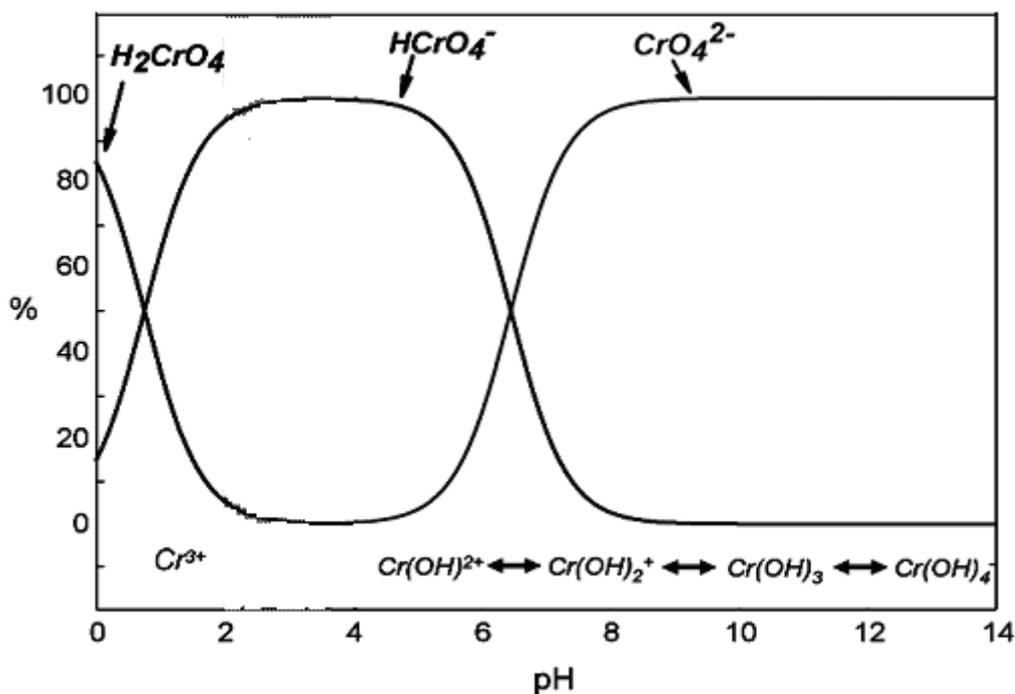


Figure 2.4: Species distribution diagram of Cr(III) and Cr(VI) in an aqueous system (Hagendorfer and Goessler, 2008).

According to Toral *et al.* (2009), the different species of Cr(VI) in aqueous solutions are given by equilibrium equations 2.1 and 2.2.



Changing between the chromate and dichromate requires making the solution acidic or alkaline. In acidic solution yellow dichromate is favoured while in alkaline solution, chromate blue colour is seen.

The structures of the chromate and dichromate anions shows that the Cr-O bond lengths are 166 pm and 163 pm, respectively, and the bridging Cr-O bond is 179 pm, while the Cr-O-Cr bond angle is 126° (Shupack, 1991). The structures of these two anionic forms of chromium are based on the sharing of a corner of the tetrahedral structure of the chromate ion as polymerization proceeds as pH is lowered, (Figure 2.5).

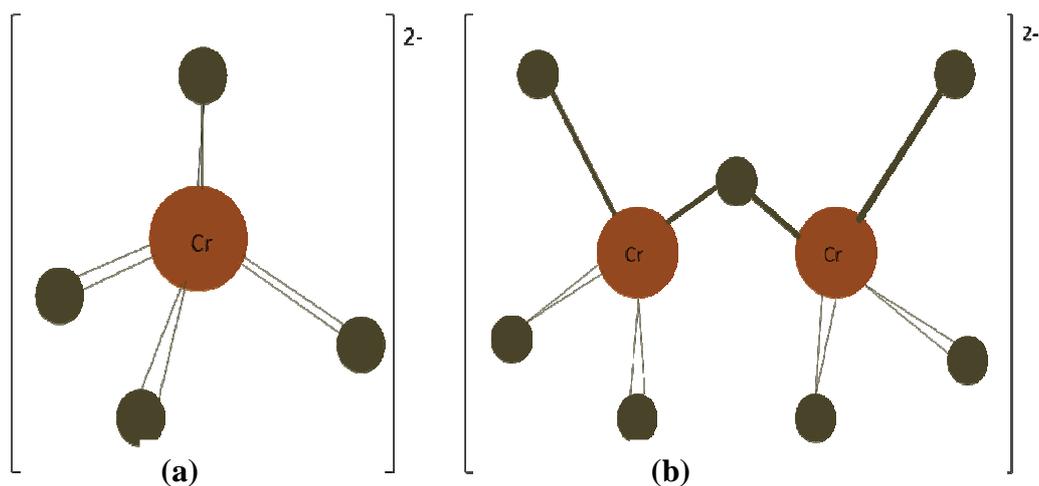


Figure 2.5: Structures of the (a) chromate and (b) dichromate anions.

2.2.3 Health and environmental concerns of chromium

One of the major causes of environmental pollution is the discharge of various heavy metals into the environment through various industrial wastewaters. These include chromium which is one of the most toxic and has become a serious health concern (Parka *et al.*, 2005). The consequences of ingesting Cr(VI) are severe and will generally occur immediately after the incident. However, the likelihood of carcinogenic and cancer effects of oral exposures to Cr(VI) are dependent on the doses taken. Ingestion of very high concentrations of Cr(VI) of normally greater than 200 mg L^{-1} by humans can result in gastritis, nephrotoxicity and hepatotoxicity (Paustenbach *et al.*, 2003). Because of the reductive conditions in the stomach, conversion of ingested Cr(VI) to Cr(III) prior to absorption is limited and this partly explains the lack of toxicity at lower pH (De Flora *et al.*, 1987). The respiratory system has a low efficiency and capacity in the reduction of Cr(VI). This implies that cells are protected from toxic effects. However continual exposure to chromium increases the chances of lung and nasal cancer. Owing to the corrosive nature of some chromium(VI) compounds, dermal exposure can lead to dermal ulcers and at high doses, systemic toxicity can lead to severe effects on the renal, haematological and cardiovascular system or even death.

2.3 South African regulation on waste and pollution

The National Environmental Management Act, 1998 (Act 107 of 1998) (NEMA), replacing the Environmental Conservation Act, 1989 (Act 73 of 1989), is the principal law through which environmental management is practiced and regulated in South Africa. However, NEMA is used in association with a lot of other Acts. Examples of these are; the White Paper on Integrated Pollution and Waste Management (2000), the National Water Act, 1998 (Act 36 of 1998), Air Quality Act, 2004 (Act 39 of 2004), Mining and Environmental impact guide (2008). The South African Constitution (1996) also stipulates that everyone has the right to an environment that is not harmful to their health and well-being. The Consumer

Protection Act, CPA, which came into effect on 1 April 2011 includes the regulation of goods and services with actual or potential environmental and/or health impacts.

The South African government published, in 1999, a National Waste Management Strategy, NWMS, which presented a long-term plan for addressing key issues, needs and problems experienced with waste management. The 2008 National Radioactive Waste Disposal Institute Act provides for the establishment of a National Radioactive Waste Disposal Institute which manages radioactive waste disposal in South Africa. The responsibility for nuclear waste disposal has been discharged by the South African Nuclear Energy Corporation, NECSA. NECSA is a state corporation responsible for most nuclear energy matters including wastes and safeguards. The South African Bureau of Standards also sets regulation limits of various pollutants in different environmental compartments.

2.4 Water contamination and permissible limits of U(VI) and Cr(VI)

Most anthropogenic uranium arises from gold and copper mining (Todorov and Ilieva, 2004). Each year, large amounts of AMD containing uranium are leached into river and streams (Wang *et al.*, 2011). Further, uranium contamination of groundwater is a widespread environmental problem (Riley and Zachara, 1992). Studies on groundwater at some contaminated sites have uranium contents up to 50 mg L⁻¹ (Junghans and Helling, 1998; Meinrath *et al.*, 2003; Jerden and Sinha, 2003). This value is more than 1600 times larger than the US EPA threshold value of 30 µg L⁻¹. Based on the risks posed by uranium and chromium, many countries and international organizations have proposed strict levels to limit discharge of these into water (Wang *et al.*, 2011). Some of the limits are shown in Table 2.3.

Table 2.3: Maximum allowable limits of uranium and chromium(VI) in water by different bodies.

Body	U maximum allowed limit (µg L ⁻¹)	Cr(VI) maximum allowed limit (µg L ⁻¹)
U.S. EPA [*]	30	50
Canada ^κ	20	50
WHO [‡]	20	50
South Africa [•]	≤ 15	≤ 7

^{*}(US EPA, 1999), ^κ(Health Canada, 1999) and [‡](Shin *et al.*, 2002), [•](DWA, 1999)

South Africa generally has problem of AMD from gold mining activities that also contain uranium (Tutu *et al.*, 2009; Bakatula *et al.*, 2012). The dust particles from tailing dumps are also blown by wind to nearby places and in the end are washed down into streams and rivers by rainfall and these contain uranium and chromium. Radionuclides contained in uranium tailings emit 20 to 100 times as much gamma-radiation as natural background levels on deposit surfaces. Some researchers have found out that gamma radiation levels decreasing rapidly with distance from the pile (Diehl, 2011).

2.5 Conventional methods of uranium and chromium removal

A number of conventional methods have been used for the removal of both chromium and uranium in various environmental compartments. However, the conventional methods have both advantages and disadvantages. In some cases, disadvantages exceed the advantages as seen in Table 2.4. This has therefore led to continued research in removal technologies. Current research is focused on improving the existing ones or developing new ones altogether. Some of the conventional technologies are briefly discussed below.

Table 2.4: Advantages and disadvantages of some convectional removal techniques (Wang *et al.*, 2010).

Method	Disadvantages	Advantages
Chemical precipitation	pH dependence Difficult separation Adverse effect by chelating agents Result in sludges Chemical required	Simple and cheap
Ion exchange	Sensitive to particles High operational costs No selectivity to alkaline metals Membrane fouling	No sludge generation Pure effluent recovery possible
Membrane technology	Membrane fouling Limited life of membrane Expensive High pressure	Pure effluent
Flocculation	Chemicals required Depend on basin design	Generate very fine particles of precipitates
Flotation	Less selective for heavy metals	Costly
Electrodialysis	Takes time Large electrode surface area used Fouling Expensive	Metal selective

2.5.1 Bioremediation

This is the use microorganisms such as bacteria to remediate polluted environmental compartments. For uranium(VI) bioremediation, a possible viable alternative approach is that of reducing the soluble and thus mobile U(VI) to relatively insoluble U(IV) which precipitates in solution (Lovley *et al.*, 1991; Finneran *et al.*, 2002; Anderson *et al.*, 2003) using microorganisms. This can prevent further migration and spread of the uranium contamination (Kelvin *et al.*, 2005). Several researchers, like that at Stanford University and Oak Ridge National Laboratory (ORNL) have shown that several common types of bacteria can be used to convert an unstable form of uranium, U(VI), into a more stable form, U(IV). This reduces the environmental and health threat of uranium contamination (Ginder-Vogel *et al.*, 2006).

Numerous common dissimilatory metal reducing bacteria (DMRB) and sulphate reducing bacteria (SRB) are known. These include *Shewanella*, *Geobacteraceae*, and *Desulfovibrio* species. They couple the oxidation of organic matter and H₂ to the reduction of U(VI) resulting in U(IV) and the subsequent precipitation of uraninite (UO₂) (Gorby and Lovley, 1992; Fredrickson *et al.*, 2000) a sparingly soluble phase. Figure 2.6 demonstrates how *Geobacteraceae* species can be used to effectively remove uranium from contaminated groundwater by reducing soluble U(VI) to the relatively insoluble U(IV) with organic compounds serving as electron donors.

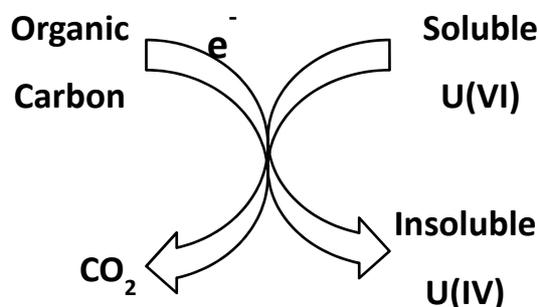


Figure 2.6: Uranium(VI) reduction driven by microbial respiration (modified from Ginder-Vogel *et al.*, 2006).

Polti *et al.* (2009) provided quantitative information on the reduction of Cr(VI) in soil samples by an indigenous actinomycete. *Streptomyces sp.* MC1. This species, previously isolated from sugarcane demonstrated its ability to reduce Cr(VI) in liquid minimal medium. Chatterjee *et al.* (2011) studied the Cr(VI) reduction capability of a bacterial strain *Cellulosimicrobium cellulans* in two environments, of nutrient-supplemented and non-supplemented. In the former, the bacterial strain was observed to reduce 54.89% Cr(VI) from the wastewater. In their study, Mishra *et al.* (2012) investigated the Cr (VI) resistance in

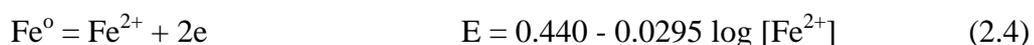
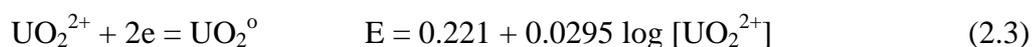
Lactobacillus strains and they also evaluated the reduction of Cr (VI) by the same species. A complete bacterial reduction of 32 mg L⁻¹ of Cr (VI) was observed within 6 to 8 hours.

2.5.2 Permeable reactive barriers (PRBs)

Permeable Reactive Barriers are trenches or fence-like arrays of non-pumping wells placed in the subsurface at depths of up to 45 m to intercept the flow of contaminated ground water (Freethy *et al.*, 2002). The fill materials contained within the PRBs react by degrading or sequestering the dissolved contaminants. The PRBs act as large *in-situ* filters for cleaning up ground water. Some of the advantages for the use of PRB technologies are that they offer lower operating costs, are highly energy efficient and require no surface facilities or ground water pumping (Freethy *et al.*, 2002; Morrison and Spangler, 1992; Shoemaker *et al.*, 1995). The use of PRBs is a relatively new technology that offers promise to overcome these problems encountered with conventional methods such as pump-and-treat which is ineffective especially when dealing with large contaminated areas. Two commonly used PRBs contaminant-removal mechanisms are: (a) precipitation reactions in which metal contaminants are sequestered within freshly formed mineral phases, and (b) oxidative degradation of contaminants by particulate iron metal. For PRBs to be cost-effective they should be reusable for a longer period of time. They should not be susceptible to clogging or rapid passivation by reaction products.

2.5.3 Chemical precipitation

Chemical precipitation is a method of wastewater treatment where chemicals are added to form particles which settle and remove contaminants. It is a favourable method especially when dealing with large volume of matter which contains heavy metal ions in low concentration (Eisazadeh, 2008). The solubility of precipitated metal compounds should be known for the successful implementation of the chemical precipitation approach. If a metal can form an insoluble compound, then the compound can be removed *via* clarification and filtration (Amer, 1998). However, this technique has a disadvantage that it produces a large amount of sludge precipitate that requires further treatment (Acheampong *et al.*, 2010). Iron mediated reductive precipitation of redox active metal species has been proposed for the removal of soluble metals and radionuclides from contaminated ground water (Cantrell *et al.*, 1995). Cantrell *et al.* (1995) and Gu *et al.* (1998), attributed the removal of the soluble uranium to reductive precipitation of U(VI) to less soluble U (IV) species and adsorption of the uranyl to iron corrosion products. Zero valent iron can reduce uranium species adsorbed on its surface (Fiedor *et al.*, 1998). Under anaerobic conditions, the thermodynamics of U(VI) reduction by zero valent iron can be described by the following redox couples (Pourbaix, 1966):



Iron can be used to precipitate chromium(VI). However, this is pH dependent as investigations of Olazabal *et al.* (1997) showed. Precipitation equilibria and spectroscopic studies of the Cr(VI)/Fe(III)/H₂O system have been performed and the identified precipitates which existed were FeOHCrO₄, FeOHCrO₄·2Fe(OH)₃ and Fe(OH)₃, depending on the pH used. Gheju and Balcu (2011) investigated the total removal of chromium from Cr(VI) aqueous solutions by reduction with scrap iron and subsequent precipitation of the resulted cations with NaOH. Another precipitation reagent is sodium metabisulphite which was used by Ramakrishnaiah and Prathima (2012) as reducing agent for the reduction of hexavalent chromium to trivalent chromium. Their results showed that total chromium can be removed from synthetic and industrial effluents by chemical.

2.5.4 Ion exchange

Ion exchange is an exchange of ions between two electrolytes or between an electrolyte solution and a complex using solid polymeric or materialistic ion exchangers. Synthetic resins have been widely reported to be efficient in removing uranium from contaminated groundwater. Pakalns (1980) stated that Chelex-100 resin (a weakly acidic metal-chelating resin) conditioned at pH 4.6 separated uranium from fresh and saline waters. Diphonix is also a chelating resin that was found to remove uranium from water at near-neutral pH conditions (Chiarizia *et al.*, 1997). At low pH conditions, uranium was found to be strongly adsorbed by strong-base anion exchange resins (DowexTM 1-X8 and Purolite A-520E) (Gu *et al.*, 2004).

2.5.5 Phytoextraction

Phytotechnologies involving use of plants for pollutant removal have gained importance during the last two decades. The sequestration of heavy metals in plants is achieved mainly by absorption and accumulation mechanisms (Dhir, 2010). Phytoremediation technology involving use of aquatic plants can provide an economical and eco-friendly option for treating wastewaters containing heavy metals (Dhir, 2010). Many plants have been used for the remediation of uranium from soils and aquatic environments and some of them are *Brassica juncea* and *Brassica chinensis* (Huang *et al.*, 1998), *Lemna gibba L.* (duckweed) (Mkandawire *et al.*, 2004).

Ipomoea aquatica exhibits uniform absorption characteristics showing over 75% removal of added Cr(VI) and this plant was selected due to its easy establishment, tolerance and growing easiness. Since in its use it showed no toxicity symptoms, it a potential phytoremediant (Weerasinghe *et al.*, 2008). Revathi *et al.* 2011 successfully used a hyperaccumulator, sorghum plant, phytoremediation of chromium metal from polluted soil of Ranipet Tanneries.

Phytoremediation has many limitations which include death of the plants if contaminant concentrations are too high. The toxicity and bioavailability of biodegradation products is not always known. The success of phytoremediation may be seasonal depending on location. Other climatic factors will also influence its effectiveness. If the plants contain high levels of heavy metals, disposal of harvested plants can be a problem.

2.5.6 Electrodialysis

Electrodialysis is a decontamination technique used to transport salt from one solution, the diluate, to another solution, the concentrate, by applying an electric current in an electrodialysis cell. Inside an electrodialysis unit, the solutions can be separated by alternately arranged anion exchange membranes, permeable only for anions and cation exchange membranes, permeable only for cations. By this, two kinds of compartments are formed. By applying a current, cations within the diluate move toward the cathode passing the cation exchange membrane facing this side and anions move towards the anode passing the anion exchange membrane. A further transport of these ions, now being in a chamber of the concentrate is stopped by the respective next membrane. Zaheri *et al.* (2010) investigated the ability of electrodialysis for continuous removal of uranium from aqueous solutions in a bench scale unit.

2.6 Adsorption techniques

The shortfalls of the conventional methods have prompted the use of adsorbents as an alternative approach. Adsorption techniques are used mainly for metal recovery from dilute solutions. Thus, to find out an effective adsorbent that can be used repeatedly to adsorb metals is particularly important (Wang *et al.*, 2011). Some of the common adsorbents that have been used to remove uranium(VI) and chromium from wastewaters are reviewed in the next section.

Zeolites are hydrated aluminosilicate materials having cage-like structures with internal and external surface areas of up to several hundred square meters per gram and cation exchange capacities of up to several milliequivalents per kilogram. At least 41 types of natural zeolites are known to exist, and many others have been synthesized. Both natural and synthetic zeolites are used in industry as adsorbents (Baker *et al.*, 2009). Camacho *et al.* (2010) used clinoptilolite zeolite to remove uranium from groundwater. Mongolian natural zeolite was applied to adsorptive removal of hexavalent chromium contained in tannery wastewater (Bolortamir and Egashira, 2008).

Activated carbon with low polar properties is a typical adsorbent commonly used for the removal of polar organic material in water and wastewater (Ying *et al.*, 1990). Adsorption using commercial activated carbon (CAC) can also remove heavy metals such as Cd, Ni, Cr and Cu from wastewater (Demirbas *et al.*, 2004, Ahn *et al.*, 2009). Pellet-600 and PVA-300 with high mesoporous volumes and surface area were used by Yue *et al.* (2009) as a low-cost, chemically activated carbon materials. Their findings were that these two showed more effective removal efficiency of Cr(VI) from water than commercially available activated carbons tested. Acharya *et al.* (2009) activated carbon prepared from *Tamarind wood* with zinc chloride. They also studied the uptake of chromium(VI) on this adsorbent and the results indicated effective adsorption of chromium(VI) from aqueous solutions.

Due to a large surface area, small, hollow and layered structures, carbon nanotubes (CNTs) have already been investigated as promising adsorbents (Chen *et al.*, 2009). Extensive efforts

have been put in the utilization of CNTs for removal of metal ions. Unlike many adsorbents, CNTs possess different features that contribute to the superior removal capacities such as fibrous shape with high aspect ratio, large accessible external surface area and well developed mesopores (Gupta *et al.*, 2011). Recently, it was shown that magnetic CNTs are very promising materials for efficient removal of heavy metal ions from aqueous solutions. Magnetic CNTs are composed of metallic cores of the diameter range of 5-100 nm, which are completely wrapped in carbon coatings of thickness range 1-5 nm. The carbon coatings perfectly isolate the encapsulated nanoparticles. The crystallinity of these coatings is similar to carbon nanotubes. The magnetic CNTs-based sorbents are fully mobile as they can be very easily moved and separated by external permanent magnets.

2.7 Magnetic nanoparticles

One of the most important research and development frontiers in modern science is nanoscience (Faraji *et al.*, 2010). Nanoparticle materials have drawn a lot of attention because most of their physical properties differ significantly from those of the corresponding bulk materials (Franco *et al.*, 2005; Burke *et al.*, 2002; Dimitrov and Wysin, 1994). These properties include electrical, optical, magnetic, and chemical properties (Hyeon, 2002). In literature, there are many nanoparticles that have been used and they include metals such as gold, iron, nickel, platinum, silver, cobalt, semiconductors like cadmium selenite, lead selenite, or hybrids like CdSe/Zn selenite (ZnS) (Burda *et al.*, 2005). Among these magnetic particles, metal oxides are often preferred over pure metals (Schmidt, 2007; Ramanujan and Yeow, 2005) because they are more stable to oxidation. An example of these metal oxides is magnetite, Fe₃O₄.

These magnetic nanoparticles, have attracted a lot of attention over the past years and have found wide applications in many biomedical fields such as bioseparation, site-specific drug delivery and magnetic resonance imaging (Pankhurst *et al.*, 2003). Good physicochemical properties of magnetic nanoparticles are taken advantage of in order to make full use of them. The ideal magnetic nanoparticles are expected to be of high magnetic properties, small size with narrow size distribution and superparamagnetic characteristics (Yang *et al.*, 2004). Magnetic susceptibility is normally used to characterize magnetic materials and these materials can be classified into three main categories namely, ferromagnetic, paramagnetic and diamagnetic. In antiferromagnetism, which includes certain metals and alloys in addition to some ionic solids, there is a spontaneously alignment of electrons at relatively low temperatures into opposite directions throughout the material. This antiparallel arrangement implies that there is no net spontaneous magnetization. Iron, Co and Ni are materials associated with ferromagnetism, together with their alloys. There are also many other materials which exhibit ferromagnetic behaviour. Typical ferromagnetic substances show permanent spontaneous magnetization even without external applied fields. For a ferromagnetic material, a material specific constant, magnetic susceptibility is greater than the susceptibility of paramagnetic or diamagnetic materials. In ionic compounds, such as oxides, more complex forms of magnetic ordering can occur as a result of crystal structures. One type of magnetic ordering is called ferrimagnetism where the magnetic structure is

composed of two magnetic sublattices separated by oxygen atoms. The exchange interactions are mediated by the oxygen anions. Superexchange interactions result in an antiparallel alignment of spins between the two sublattices. In ferrimagnetism, the magnetic moments of the sublattices are not equal to each other and as a result, there is a net magnetic moment. Figure 2.7 shows the orientation of electrons in different environments.

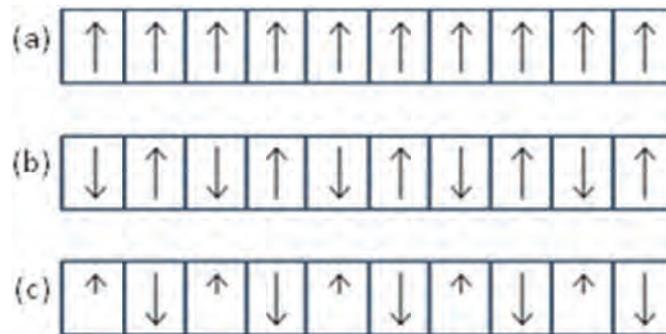


Figure 2.7: Orientation of domains in (a) ferromagnetism (b) antiferromagnetism and (c) ferrimagnetism.

2.7.1 Superparamagnetism

Lu *et al.* (2007) noted that, in most applications, the nanoparticles perform best when the size of the nanoparticles is below a critical value, which is dependent on the material but is typically around 10-20 nm. Below this critical value, each nanoparticle will become a single magnetic domain and shows superparamagnetic behaviour when the temperature is above the blocking temperature (Lu *et al.*, 2007) and this is contrary to bulk materials (Frey *et al.*, 2009). Nanoparticles can be easily magnetized and keep no remanent magnetization in the absence of the field.

By definition, superparamagnetism is a name given to a paramagnetic behaviour of small single-domain magnetic particles which are themselves internally coupled ferromagnetically or antiferromagnetically (Shaw and Heasley, 1967). Other new physical behaviours exhibited by nanoparticles apart from superparamagnetism are high field irreversibility, high saturation field, extra anisotropy contributions or shifted loops after field cooling. All these phenomena arise from finite size and surface effects that dominate the magnetic behaviour of individual nanoparticles (Tartaj *et al.*, 2003).

2.7.2 Magnetic properties of magnetic particles

Instead of the ferromagnetic behaviour observed in bulk magnetic materials, the nanometre magnetic composition of a magnetic particle can lead to a superparamagnetic behaviour (Ganguly, 2005). The hysteresis loop or magnetization curve can be used to characterize magnetic materials and an illustration of this is shown in Figure 2.8.

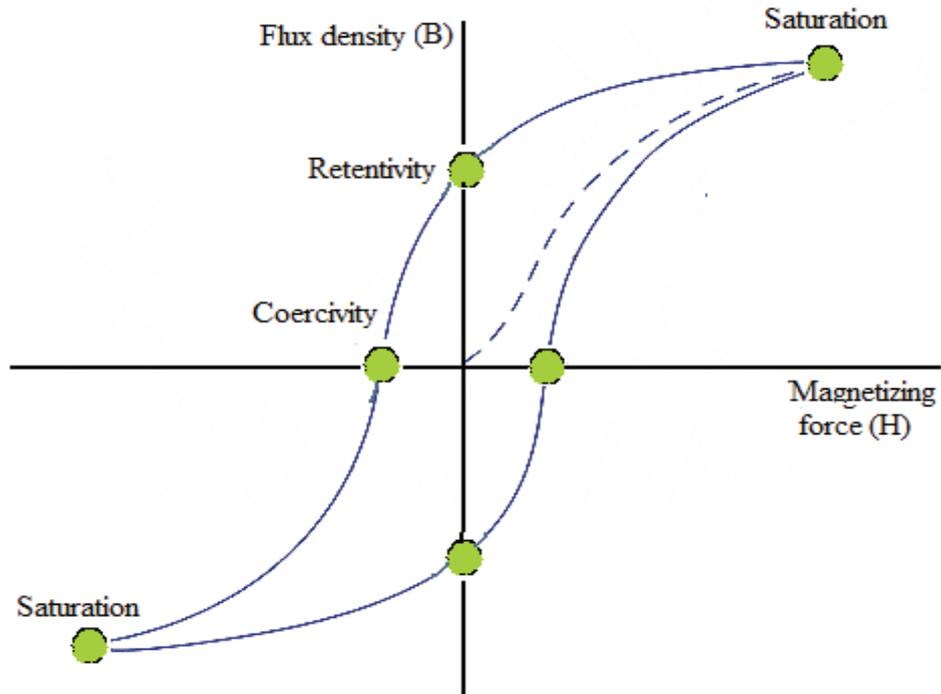


Figure 2.8: The Hysteresis loop of a superparamagnetic material.

From the hysteresis loop, a number of primary magnetic properties of a material can be determined, and these include coercivity and remanence. In superparamagnetism, magnetization does not return to zero and hysteresis behaviour is observed. The intercept of the magnetization curve with the flux density (B) axis gives the remanent magnetization, while the intercept with the magnetizing force (H) axis gives the coercivity. Superparamagnetic materials have high saturation magnetization and zero coercivity and remanence which make them distinguishable from ferromagnetism and paramagnetism.

2.7.3 Magnetite and its magnetic properties

Among all known iron oxides, magnetite, Fe_3O_4 , presents the most interesting and unusual behaviour because of the presence of both divalent and trivalent iron states, Fe^{2+} and Fe^{3+} , in the cubic inverse spinel structure (Daou *et al.*, 2006; Ravikumar and Bandyopadhyaya, 2011). Its formula can be written as $[\text{Fe}^{3+}][\text{Fe}^{3+}\text{Fe}^{2+}]\text{O}_4$. In stoichiometric magnetite, the ratio of $\text{Fe}^{3+}/\text{Fe}^{2+} = 2$. Both Fe^{2+} and Fe^{3+} are present in the final product. The magnetic properties reflect the splitting of the 5d orbitals, as shown in Figure 2.9 for octahedral and tetrahedral coordination of the Fe atoms by oxygen atoms. The small splitting between the two sets of d orbitals caused by oxide ligands means that all Fe^{3+} ions have five unpaired electrons and all Fe^{2+} ions have four unpaired electrons, Figure 2.9. Fe^{3+} and Fe^{2+} ions that are in octahedral sites are ferromagnetically coupled through a double exchange mechanism. The electrons spin of the Fe^{3+} and Fe^{2+} in the octahedral interstices are aligned in a parallel manner.

The hopping of electrons between Fe^{2+} and Fe^{3+} ions in the octahedral sites at room temperature renders magnetic and metallic properties to magnetite. The Fe^{3+} ions in tetrahedral and octahedral sites are antiferromagnetically coupled through the intervening

oxygen atom and their spins are anti-parallel. Thus, the Fe^{3+} spins in the tetrahedral and octahedral sites cancel and what remains are unpaired spins from the Fe^{2+} ions in octahedral sites.

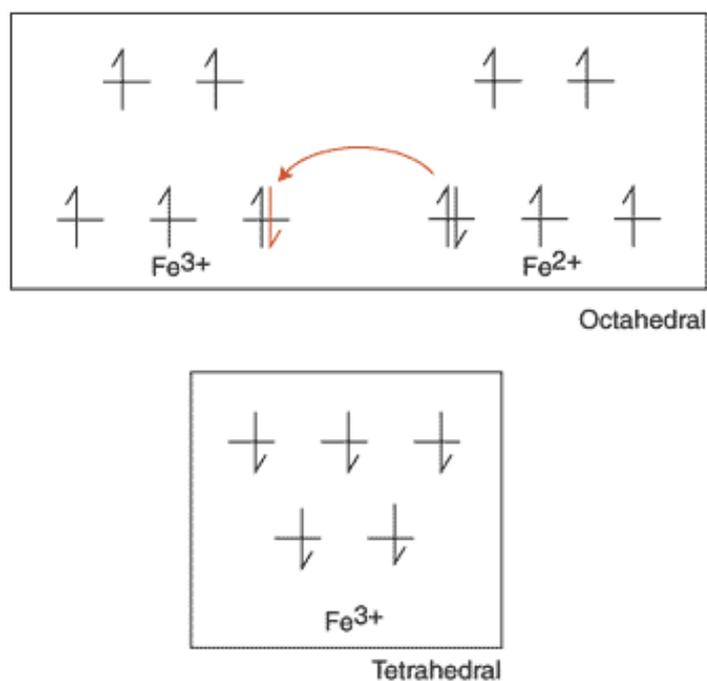


Figure 2.9: Electronic configuration in magnetite.

2.7.4 Synthesis of magnetic nanoparticles

Magnetic properties of magnetic nanoparticles can be tailored by their particle sizes and size distributions. The particle sizes and size distributions of magnetic nanoparticles are in turn, affected by their synthetic routes (Chin *et al.*, 2011). Tartaj *et al.* (2003) further noted that the performance of nanoparticles will be dependent on their chemical and physical characteristics. In order to take maximum advantage of those novel properties, synthetic protocols are needed in which significant control can be exercised over those parameters (Chen *et al.*, 2007). For these reasons, numerous physical and chemical synthesis approaches have been developed to produce Fe_3O_4 nanoparticles in order to obtain the desired properties (Chin *et al.*, 2011). Some of these synthetic routes are briefly discussed in the following section.

2.7.4.1 Co-Precipitation

Co-precipitation is the simplest chemical pathway to synthesize magnetite (Burda *et al.*, 2005; Laurent *et al.*, 2008). This method has attracted a lot attention as it is environmental friendly because the synthesis is carried out in aqueous solutions without using any organic solvents under mild reaction conditions at relatively low temperatures (Iwasaki *et al.*, 2009). The synthesis involves addition of the ferrous and ferric salts to an aqueous solution followed by the addition of a base, equation 2.5, in an alkaline hydrolysis reaction (Finotelli *et al.*, 2008). A black Fe_3O_4 precipitate forms upon addition of a base.



Magnetite can be formed over a wide pH range for given concentrations of Fe^{2+} and Fe^{3+} . A complete precipitation of Fe_3O_4 is expected in the pH range of 7.5-14 while maintaining a molar ratio of $\text{Fe}^{2+}:\text{Fe}^{3+}$ at 1:2 under an inert atmosphere. However, under oxidative environment, Fe_3O_4 may be oxidized to other forms of iron oxide as given by the equations 2.6 and 2.7 (Kim *et al.*, 2003).



2.7.4.2 Thermal decomposition

Highly crystalline and monodisperse Fe_3O_4 nanoparticles have been synthesized by conducting reactions at high temperature ($>200^\circ\text{C}$) through thermal decomposition of organometallic precursors in nonpolar organic solvents (Sun *et al.*, 2003; Park *et al.*, 2005). Park *et al.* (2005), performed a thermal decomposition of iron pentacarbonyl, $[\text{Fe}(\text{CO})_5]$, for the preparation of monodisperse $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles with average diameters in the nanoscale range. They achieved this by controlling the molar ratio of $[\text{Fe}(\text{CO})_5]$ and the surfactant, oleic acid. This synthetic route is however unpopular since $[\text{Fe}(\text{CO})_5]$ is very expensive and toxic. Chin *et al.* (2011) used different concentrations of iron (III) acetylacetonate, $\text{Fe}(\text{acac})_3$ and varied volumes of polyethylene oxide in a quest to study their effects on the particle size of Fe_3O_4 nanoparticles formed. In their research, Maity *et al.* (2009) proposed a mechanism for solubility of the as-prepared by using surface charges and surface coating of the magnetite nanoparticles in aqueous suspension. They also used thermal decomposition of $\text{Fe}(\text{acac})_3$ in tri(ethyleneglycol).

2.7.4.3 Microemulsion

For microemulsion to occur, the mixture system has to consist of an oil phase, a surfactant phase and an aqueous phase (Koutzarova *et al.*, 2006). Generally in this method, nanoparticles are synthesized in oil-in-water micro-emulsions by suspending a ferrous salt-surfactant to a water solution. The magnetic precipitate will then form as soon as a base is added to the reaction mixture (Thorek *et al.*, 2006). In water-in-oil micro-emulsions, the aqueous phase is dispersed as micro-droplets surrounded by a monolayer of surfactant molecules in a continuous non-aqueous (hydrocarbon) phase. The soluble metal salt will reside within the aqueous droplets surrounded by the oil (Ha *et al.*, 2008). In this method, coprecipitation occurs in tiny droplets of water embedded with a surfactant, so-called reverse micelles, which are distributed in an oil phase (Makovec *et al.*, 2005). Nassar and Husein (2005) subjected FeCl_3 bulk solid powder to the action of microemulsion formed with sodium bis (2-ethylhexyl) sulfosuccinate. Iron chloride was first solubilized in water of the microemulsions and then reacted with sodium hydroxide to eventually form the iron oxide nanoparticles.

2.7.4.4 Hydrothermal synthesis

Hydrothermal synthesis is a method to produce metal oxide crystals from metal salt aqueous solutions by application of heat (Dawson, 1988; Matijevic and Hsu, 1987). For example, hydrothermal treatment of iron salt could generate iron oxides when the applied conditions are appropriate (Mohapatra and Anand, 2010).

Hu *et al.* (2010) developed a hydrothermal method to fabricate sheet-like and pseudo-octahedral magnetite crystals. NaOH was added to $K_4[Fe(CN)_6]$ aqueous solution with constant stirring. Hydrothermal treatment was done at 160°C after which magnetite precipitate was collected. In another study, Togashi *et al.* (2012) synthesized water dispersible magnetite (Fe_3O_4) nanoparticles in an aqueous environment under high temperature and pressure in the presence of 3, 4-dihydroxyhydrocinnamic acid by using a tubular flow reactor. Haw *et al.* (2010) synthesized Fe_3O_4 nanoparticles by precipitating $FeSO_4 \cdot 7H_2O$ and $FeCl_3$ in NaOH. However, prior to the addition of a base, dilute HCl was used to prevent the formation of other iron oxides. The precipitated black product was immediately added into a Teflon-lined stainless steel autoclave which was then placed in a furnace at 200°C for 1 h.

2.7.5 Coating of magnetite

Due to the van der Waals' forces and magnetic dipole-dipole interactions resulting from residual magnetic moments, unmodified magnetite nanoparticles have a tendency to agglomerate and flocculate, Kim *et al.* (2003), thereby inhibiting the advantages of the specific properties by single-domain (Sun *et al.*, 2005). This is also true for ferrofluids which are stable colloidal suspensions of single domain ferro or ferrimagnetic particles in a liquid carrier (Voit *et al.*, 2001). Among other parameters, Häfeli *et al.* (2002) noted that surface coating and aggregation tendencies can influence the overall magnetic responsiveness of magnetic particles. Coating of the magnetite particle surfaces can effectively prevent agglomeration and this is achieved by covering the magnetite with a surfactant or coating layer. Coating of the ferrofluids enables stabilization of the particles against gravimetric forces and to avoid strong interaction and also agglomeration of the particles (Voit *et al.*, 2001).

Selection of the appropriate core and monolayer material will then become critical as each layer or coating agent dictates a specific function (Lodhia *et al.*, 2010). There are several choices of coating agents which include organosilanes, having C_{18} or aminopropyl groups, polymers (Inoue *et al.*, 1990), biomass, hemimicelles/admicelles of ionic surfactant, alkyl carboxylates and many others.

As already mentioned, these polymeric networks of the coating agents or surfactants encapsulate oxide monodomains and hold them apart against clustering together. Apart from this, the formation of a polymer layer on the surface of the magnetite nano-particles prevents further oxidation (Kim *et al.*, 2003). According to Lee *et al.* (2003), if not properly coated, iron oxide can produce secondary contaminants when it comes into contact with water and

oxygen. However, as noted by Niu *et al.* (2012), these coating agents cannot totally prevent the agglomeration and oxidation of nanoparticles in certain conditions such as in acidic solutions.

For coating with silicon alkoxide, a well-known Stöber process can be used (Ohmori and Matijevic, 1992), which comprises the hydrolysis and condensation of a sol-gel silicon alkoxide-based precursor (Cui *et al.*, 2009), e.g. tetraethyl orthosilicate (TEOS). This method has been used to coat iron oxide nanoparticles by a number of researchers (Lu *et al.*, 2002).

2.8 Ion imprinted polymers

Molecular imprinting can be defined as the assembly of a cross-linked polymer matrix around an imprint molecule that is held in place, either covalently or non-covalently or semi-covalently, by judiciously chosen functional monomers. The removal of the imprint molecule yields an imprint cavity of a specific size (Lofgreen *et al.*, 2011) and shape complementary to the imprint molecule. When the interaction between the template and monomers within is due to ionic interaction, this is called ion imprinting producing ion imprinted polymers. The product polymer, after template removal, thus contains the specific chemical "memory" in sites that selectively and discriminately recognize the imprint and are thus capable of its reuptake (Mosha and Mkayula, 2005). This product is the one which is generally called the molecularly imprinted polymer, MIP. In some cases, before polymerization reaction is complete and while it is still in a gel form, it can be used to form various shapes of MIPs like polymer monoliths, membranes, microspheres and nanospheres for different applications (Esfandyari-Manesh *et al.*, 2011). The general technique of MIP synthesis is summarized in Figure 2.10.

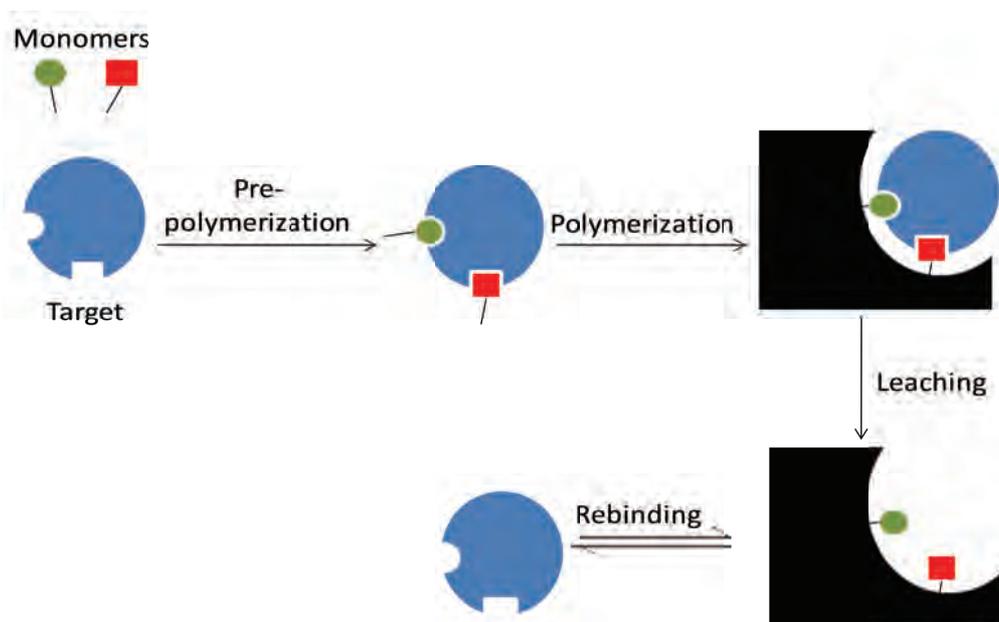


Figure 2.10: Schematic diagram depicting imprinting polymerization (Haupt and Belmont, 2008).

These recognition sites mimic the binding sites of biological receptor molecules such as antibodies and enzymes (Karim *et al.*, 2005; Haupt and Belmont, 2008). The concept of molecular imprinting was first introduced in 1931 and has attracted wide interest from the beginning of the 1970s. Organic polymers with predetermined ligand selectivities were prepared independently in 1972 by Wulff and Sarhan (1972) and Klots and Takagishi (1972) (Park and Seo, 2002). Over decades of research, molecularly imprinted polymers (MIPs) have gained more and more acceptance with respect to their application as polymeric antibodies in analytical chemistry and separation science (Yu and Lai, 2010).

The use of MIP sorbents was firstly directed at extracting of organic chemicals from complex samples. Pichon and Chapuis-Hugon (2008) and Turiel and Martin-Esteban (2010) have reviewed the role of MIPs for selective extraction of various organic compounds. Recently, a lot of publications have also been reported on selective extraction of metal ions using ion imprinted polymers, IIPs. IIPs are similar to MIPs but they can recognize metal ions after imprinting and retain all the advantages of MIPs (Daniel *et al.*, 2005). Roa *et al.* (2004; 2006) have reviewed the metal ion imprinted polymers as novel materials for selective recognition of inorganics. Metal ion-imprinted resins which could adsorb the target metal ion from weakly acidic solutions were first reported by Nishide *et al.* (1976). Ion imprinted polymers are currently being increasingly explored in many techniques because of many outstanding advantages such as predetermined selectivity in addition to being simple and convenient to prepare (Metilda *et al.*, 2004). The selectivity of these IIPs comes from the specificity of the ligand on the coordination geometry of the ion-template complex, coordination number of the ions, charges on the ions and on their sizes (Zhan *et al.*, 2011). The synthesis process of IIPs is easy, low-cost and the resulting polymers are stable, versatile and resistant to a wide range of pHs, solvents and temperatures (Scorrano *et al.*, 2011).

2.8.1 Magnetic ion imprinted polymers

Ion-imprinted polymers cannot be separated rapidly and effectively after treatment from polluted water. If the ion-imprinted polymers encapsulating Fe_3O_4 as magnetic cores could be synthesized, the adsorbing polymers would be separated easily by use of external magnetic fields replacing the centrifugation and filtration process in a convenient and economical way (Zhan *et al.*, 2011; Philippova *et al.*, 2011; Ansell, 2008; Pan *et al.*, 2011). Synthesis and properties of magnetic polymer beads constitute a new topic of research rapidly developing in the last 15 years. The magneto responsive polymeric beads benefit from the combination of features inherent to both their components: magnetic particles and polymers. Magnetic separation method is considered rapid and effective as compared to the traditional centrifugation and filtration techniques. Synthesis of magnetic polymer beads is generally performed in three different ways (Philippova *et al.*, 2011):

- Synthesis of magnetic particles inside polymer matrix.
- Synthesis of the polymer in the presence of magnetic particles.
- Preparation of from pre-formed polymer and magnetic particles.

2.8.2 Types of template/monomer interactions

A crucial step in the synthesis of imprinted polymers is the prearrangement stage. At this stage, a complex is formed between the template and a functional monomer or a number of functional monomers. This complex is formed through a pre-polymerization reaction. The quantity and quality of the imprinted polymer recognition sites relates directly to the function of the mechanisms and extent the functional monomer-template interactions present in the pre-polymerization mixture (Karim *et al.*, 2005). Depending on the type of interaction between functional monomer(s) and template involved in the imprinting and binding processes, molecular imprinting can be classified into three different categories (Esfandyari-Manesh *et al.*, 2011; Turiel and Martín-Esteban, 2010) namely, the covalent, the semicovalent or sacrificial spacer and the non-covalent approaches.

In the covalent approach, reversible covalent bonds are formed between the template and the functional monomer(s). However, this approach is not so popular since it is not easy to come up with an appropriate template-monomer complex in which covalent bond formation and cleavage are readily reversible under mild conditions. Non-covalent imprinting is based on the formation of relatively weak non-covalent interactions between selected monomer(s) and template molecule before polymerization. The monomer(s) and template are simply mixed together and allowed to interact *via* self assembly (Cai and Gupta, 2004). Non-covalent imprinting approach uses intermolecular forces such as hydrogen bonding, electrostatic, hydrophobic interactions, ion pairs, dipole-dipole interactions, and van der Waals forces to form template-functional monomer(s) species in solution (Mayes and Whitcombe, 2005). This technique of non-covalent approach is most widely used because of the easiness of removing the template from the MIP resulting in greater number of affinity sites (Jiang *et al.*, 2007). The imprinting process in semi-covalent imprinting is approached in the same way as the covalent method (Tulla-Puche and Albericio, 2008). However, this approach differs from covalent imprinting in that the rebinding step is non-covalent in nature (Qi *et al.*, 2010). When the template, covalently embedded in the polymer matrix is removed from the MIP, functional groups capable of interacting non-covalently with the template species are left behind in the MIP at the cleavage site (Tulla-Puche and Albericio, 2008).

2.8.3 Polymerization reagents

There are several factors and reagents that influence polymerization, and hence the subsequent performance of the imprinted polymers. These include the nature of monomers, crosslinkers, porogen, template, initiator used, method of initiation, polymerization time and the dielectric constant of the porogens employed. Some of these reagents are reviewed in the following section.

2.8.3.1 Functional monomers

Excess of functional monomers will result in the presence of monomer units that are not complexed to templates. These monomers can undergo dimerization on their own. In their study to establish the effect of dimerization of the monomers, Zhang *et al.* (2010) used excess methacrylic acid (MAA) and realized that the accessible recognition sites were effectively diminished, thereby reducing the efficiency of the imprinting process. This was so because MAA has a strong tendency to form hydrogen-bonded dimers (Malosse, *et al.*, 2008; Ansell *et al.*, 2008 and Ansell and Wang, 2009).

Methacrylic acid is the most commonly used functional monomer because it can be used to synthesize MIPs of high selectivity for a large number of target molecules. It however fails for some targets, and therefore, other monomer combinations need to be found (Lanza and Sellergren, 2004). Figure 2.11 shows some other common functional monomers that can be used.

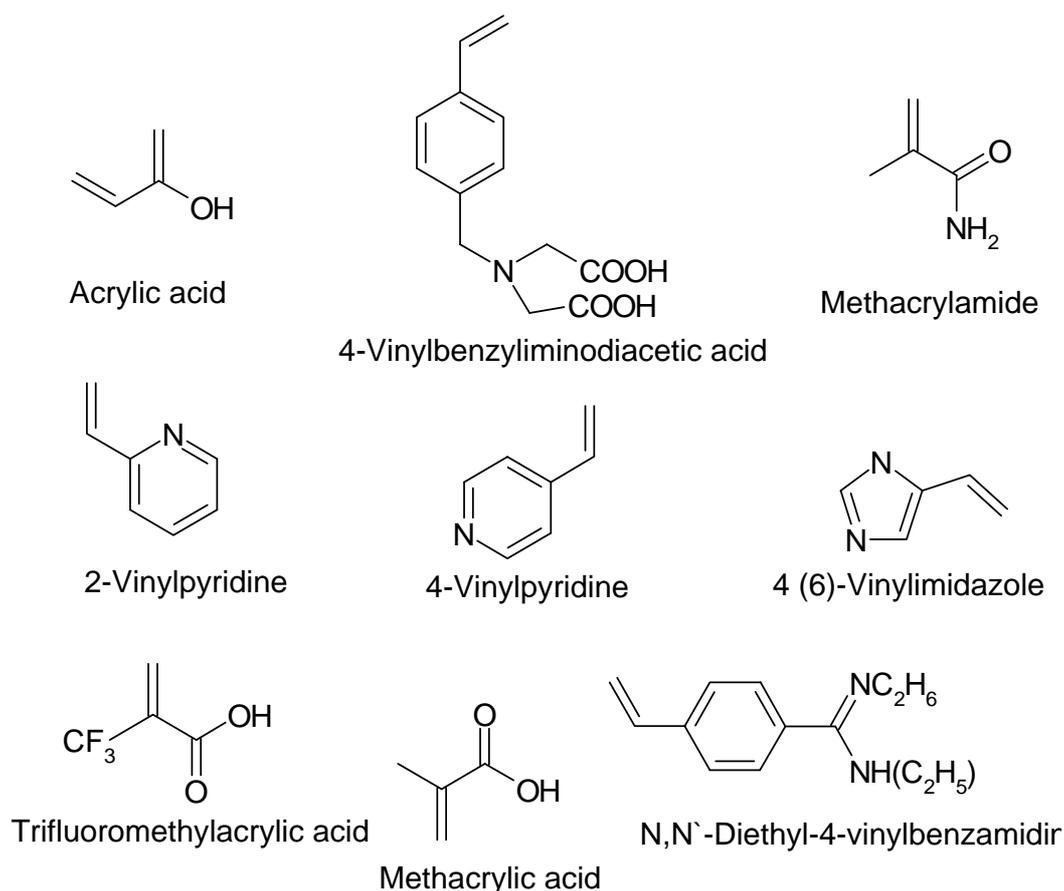


Figure 2.11: Common functional monomers used in imprinted polymerizations.

2.8.3.2 Cross-linkers

In order to have a permanent induced memory, the imprinted polymer needs to be rigid enough and the polymer needs to be macro-porous so as to allow the template molecules to easily diffuse in and out. To satisfy this, 80 mol% of the crosslinking monomer needs to be

added as a reagent in the polymerization mixture (Idziak, 2000). Cross-linking monomers have two or more functional groups that are able to bind with the polymer chain to form a rigid three dimensional structure (Arnold *et al.*, 1999; Moreno-Bondi *et al.*, 2008). The control of the morphology of the polymer matrix by cross-linking monomers is found in all types of polymer forms.

Approximately 80-90% of the imprinted polymers are composed of the cross-linking monomers and the other 10-20% comprises of other polymerization reagents. Having realized this large proportion of the cross-linking monomer in the polymer, Spivak and Sibrian-Vazquez (2002) directed their focus on the designing of cross-linking monomers for molecular imprinting in order to improve the performance of MIPs.

The most common cross-linking monomers have been EGDMA and DVB, which are commercially available. These cross-linking monomers are inexpensive and readily available in large quantities. In other applications of imprinted polymers, economic prices considerations are of less concern. Instead, cross-linking materials which give the best performance are used. Cross-linkers also control the hydrophobicity of the imprinted polymers. Hydrophobicity of the polymer is important in imprinted polymers because it influences the target analyte mass transfer into the cavity of the polymer. For example, non-polar analytes require a hydrophobic background. Since diffusion of the porogenic solvent is also dependant on the degree of cross-linking, the cross-linking monomers, together with their concentrations should be carefully selected in order to give maximum performance. Figure 2.12 shows some commonly used cross-linkers.

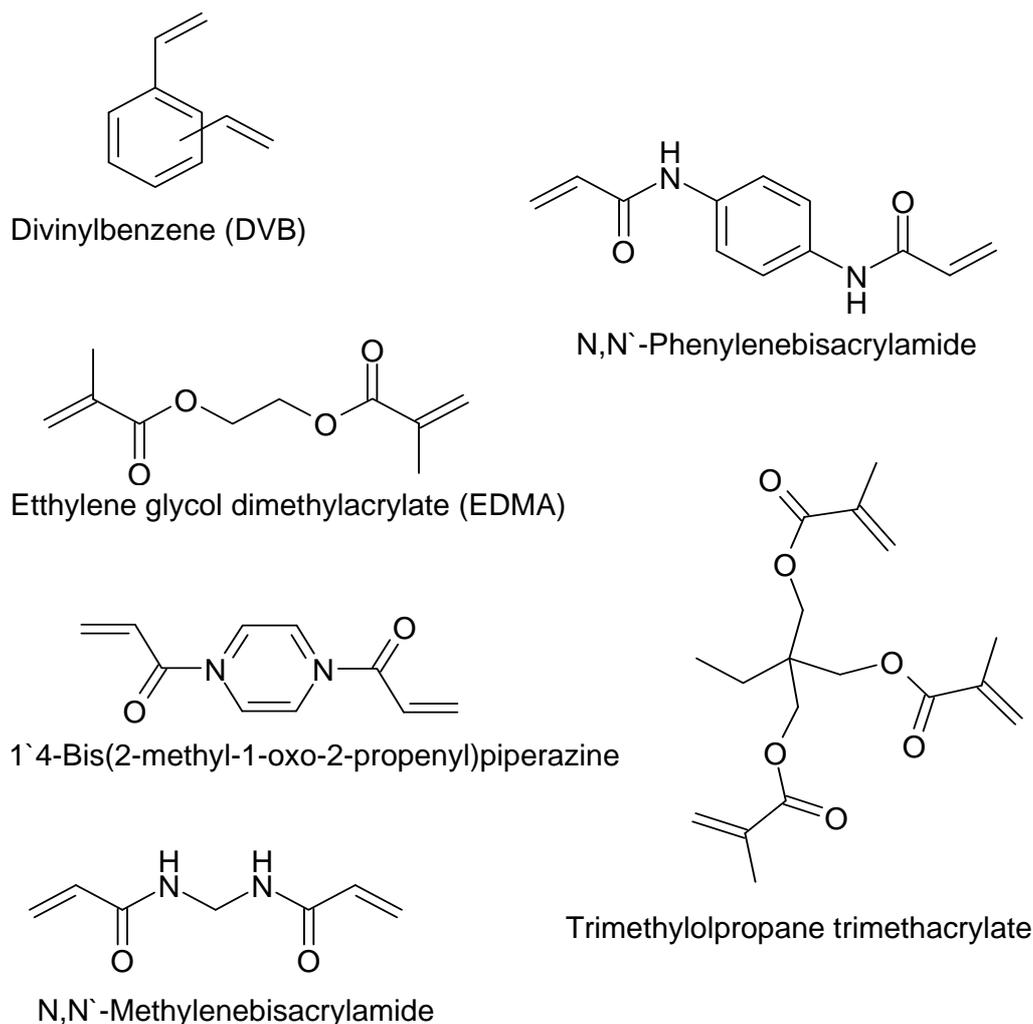


Figure 2.12: Common cross-linkers used in imprinted polymerization.

2.8.3.3 Initiators

The initiation step within the polymerization reaction is a two part process in which the initiator breaks up into free radicals. These radicals will then attach themselves onto monomers, thereby forming monomeric radicals. The cleavage of the radicals is normally as a result of subjecting them to heat, electromagnetic radiation or chemical reaction, which will homolyse them to radicals with higher reactivity than the monomer radicals. However the reactivity must be low enough to allow the initiator radical to react with the monomer.

Azo and peroxide initiators with bond energies of $105\text{-}170\text{ kJ mol}^{-1}$ are particularly useful in this regard and are the mostly used initiators in the synthesis of molecular imprinted polymers (Sellergre, 2003). Azoinitiators (R-N=N-R) normally have tertiary R groups that are able to stabilize the incipient radicals (Moad and Solomon, 1995).

2.8.3.4 Porogen

Most imprinting techniques reported to date have employed relatively apolar and aprotic porogens such as toluene or chloroform (Yoshizako *et al.*, 1998). These choices of porogens

are clearly useful for obtaining accurate formation of the assembly (Yoshizako *et al.*, 1998). In their investigations, Gladis and Rao (2004) found out that the selectivity varies with the polarity of the porogen used during polymerization. Uranyl-IIPs prepared in 2-methoxyethanol porogen gave high retention capacity and selectivity over thorium as compared to other porogens which were methanol, tetrahydrofuran, acetic acid, dichloroethane, N, N-dimethyl formamide and toluene.

Haginaka *et al.* (2008) also investigated the effect and influence of various porogens on the performance of the MIPs on the uptake of *d*-chlorpheniramine. Of the four porogens used, the specific surface areas and pore volumes followed the order toluene > phenylacetonitrile > benzylacetonitrile > chloroform.

In general, a low polarity solvent is normally chosen to preserve the interaction between the functional monomer(s) and the template during the pre-polymerization reaction. This came as an observation that there is a high correlation between the dielectric constant and the hydrogen bond donor/acceptor ability of the porogen (Mirsky and Yatsimirsky, 2011), Table 2.5.

Table 2.5: Examples of porogens used in molecular imprinting preparation and their physical properties.

Name	Chemical structure	Dielectric constant (20°C)	H-Bonding
Toluene		2.4	Poor
Chloroform		4.8	Poor
Acetone		21.0	Moderate
Acetonitrile		36.6	Moderate
Dimethyl sulfoxide		47.2	Moderate
Methanol		33.0	Strong
Water		80.1	Strong
*Benzene		2.3	Poor
*Dimethylformamide		36.7	Poor
*1-Propanol		20.1	Strong

*Mirsky and Yatsimirsky, 2011

2.8.4 Approaches in preparation of IIPs

2.8.4.1 Cross-linking of bifunctional reagents with linear chain polymers

In this approach, a linear polymer is formed with one ligand (with two functional groups) capable of forming metal-ligand complex. The ligand has functional groups that can help to polymerize at the same. A good example is 4-vinyl pyridine. Polymerization is performed in the presence of a metal ion in a suitable solvent. The ligand therefore acts both as monomer and cross linker forming a linear polymer. Nishide *et al.* (1976) cross linked poly (4-vinylpyridine) with 1, 4-dibromobutane in the presence of metal ions such as Cu(II), Zn(II), Co(II), Ni(II), Hg(II) and Cd(II) as templates. The linear polymer can also be made up of two different monomers. Both or one of the monomers can act as a ligand for the metal ion. Kabanov *et al.* (1979) is reported to have cross linked a copolymer of diethyl vinyl phosphonate and acrylic acid with N, N-methylene diacrylamide in the presence of metals. Figure 2.13 shows a typical linear chain polymer from bifunctional reagent.

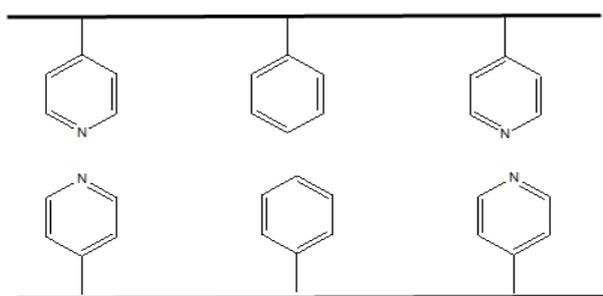


Figure 2.13: An example of a linear polymer with 4-VP anchored in the polymer matrix.

2.8.4.2 Chemical immobilization

In this approach, a vinylated ligand is chemically immobilized in the polymer matrix Figure 2.14. The ligand is chemically anchored to the cross linked polymer. It is the common used method for preparing IIPs (Rao *et al.*, 2006). A new IIP based on chemical immobilization has been reported for palladium ions by Rao *et al.* (2006). The IIP was synthesized by bulk polymerization using palladium iodide/thiocyanate-4-vinyl pyridinium ternary ion association complex in the presence of 2-hydroxyethylmethacrylate and ethylene glycol diamine methacrylic acid (Daniel *et al.*, 2006). Along the same lines, platinum IIP has been reported (Daniel *et al.*, 2005). Many other IIPs based on this approach have been prepared for metal ions such as those of copper (Say *et al.*, 2003), nickel (Ersoz *et al.*, 2004), calcium and magnesium (Rosatzin *et al.*, 1991) and zinc (Chen *et al.*, 1997).

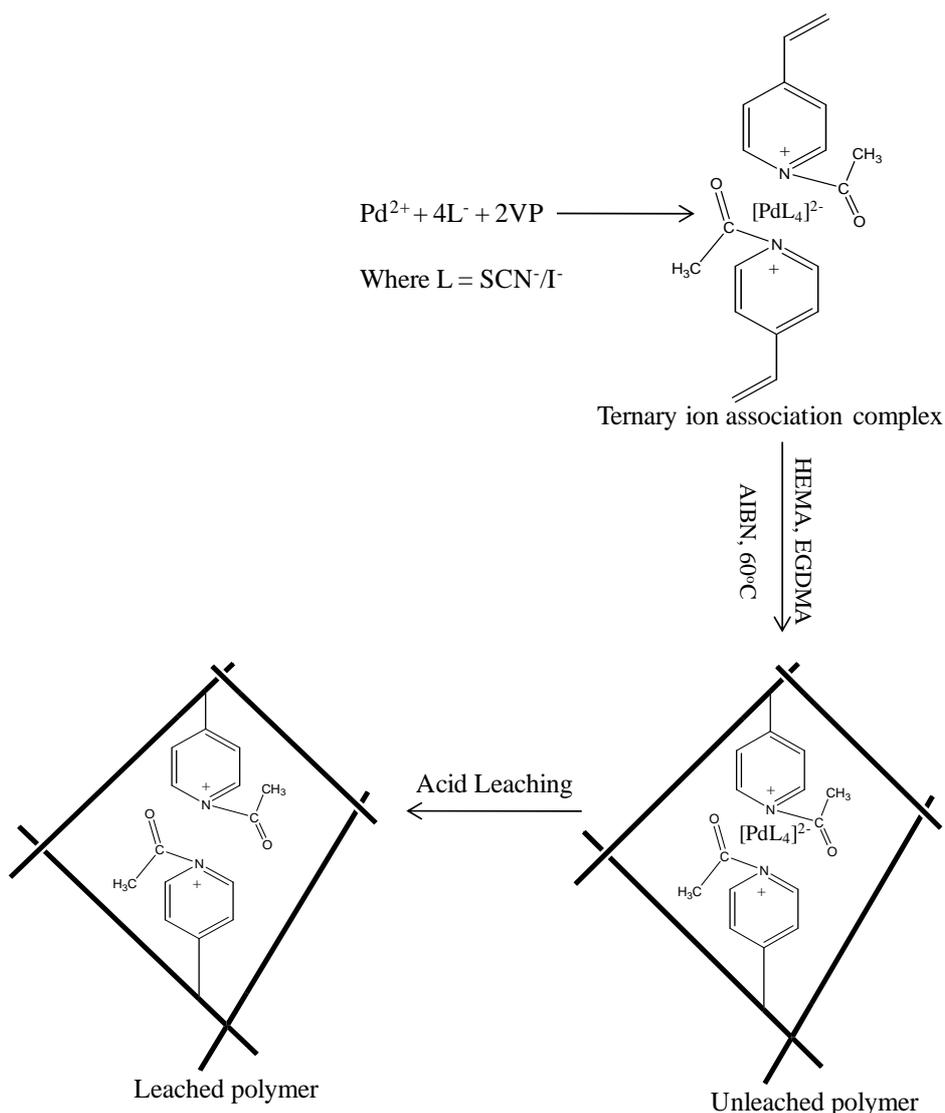


Figure 2.14: An example of the chemical immobilization approach in IIP preparation (Rao *et al.*, 2006).

2.8.4.3 Surface imprinting

This approach involves emulsion polymerization using a functional monomer, an emulsion stabilizer, a polymer matrix forming co-monomer and print template. It is thus specific to emulsion polymerization. It is called surface imprinting because the microspheres are allowed first to form but before they are fully swollen, a metal ion is added to achieve complexation with ligand on the surface and then polymerization proceeds at room temperature. After polymerization, the template is removed which results in polymeric resins with functional groups on the surface giving recognition sites with preferential rebinding potential for the template ions. Surface imprinting is also called water-in-oil or oil-in-water emulsion IIPs. A number of IIPs have been reported for various metal ions such as Cu(II), Ni(II) and Co(II) (Tsukaghoshi *et al.*, 1993; 1995; Yu *et al.*, 1992; Okubo *et al.*, 1987; Watanabe and Bunseki, 1977). It is however not as popular as chemical immobilization approach. Figure 2.15 shows an example of the preparation using this approach.

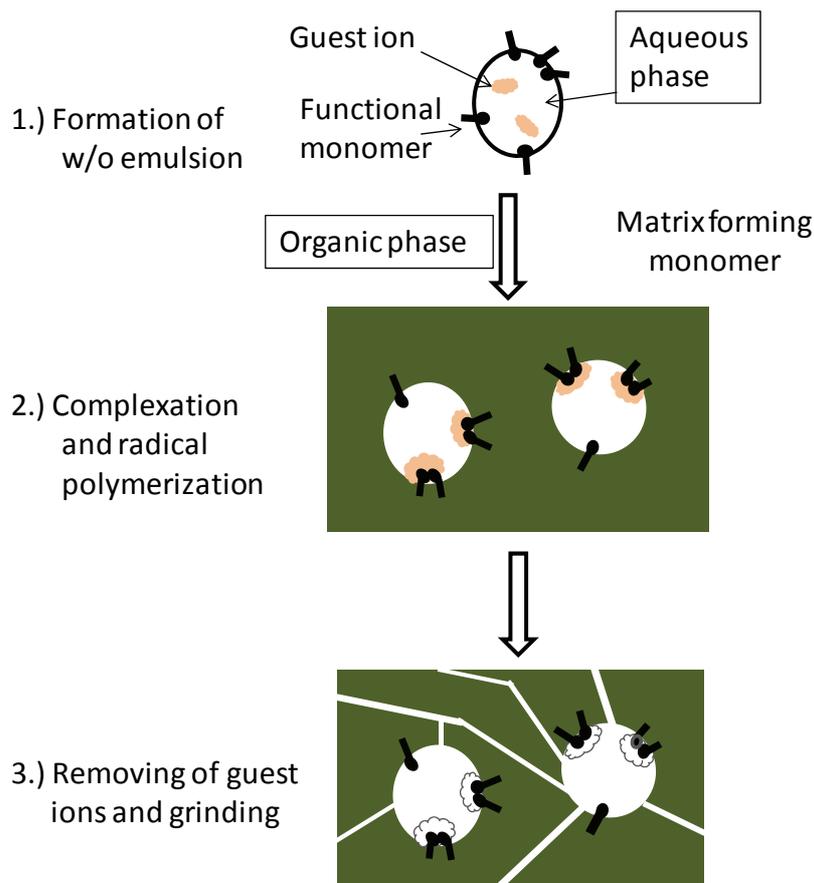


Figure 2.15: An example of surface imprinting approach in IIP preparation (Uezu *et al.*, 1998).

2.8.4.4 Trapping

This is a method that involves a vinylated and non vinylated chelating agent (Rao *et al.*, 2006). Polymerization results in chemical bonding of the vinylated ligand as in chemical immobilization. However, the non-vinylated ligand does not have any polymerizable groups and is just trapped inside the polymer matrix. This method is also very common. Perhaps it is as common as chemical immobilization. Many IIPs have been prepared for various ions such as those of dysprosium (Biju *et al.*, 2003), erbium (Kala *et al.*, 2004), neodymium (Gopikrishna *et al.*, 2005), uranium (Gladis and Rao, 2003; 2004), palladium (Daniel *et al.*, 2003; 2004), mercury (Liu *et al.*, 2005), etc. Figure 2.16 shows the example of the preparation using this approach.

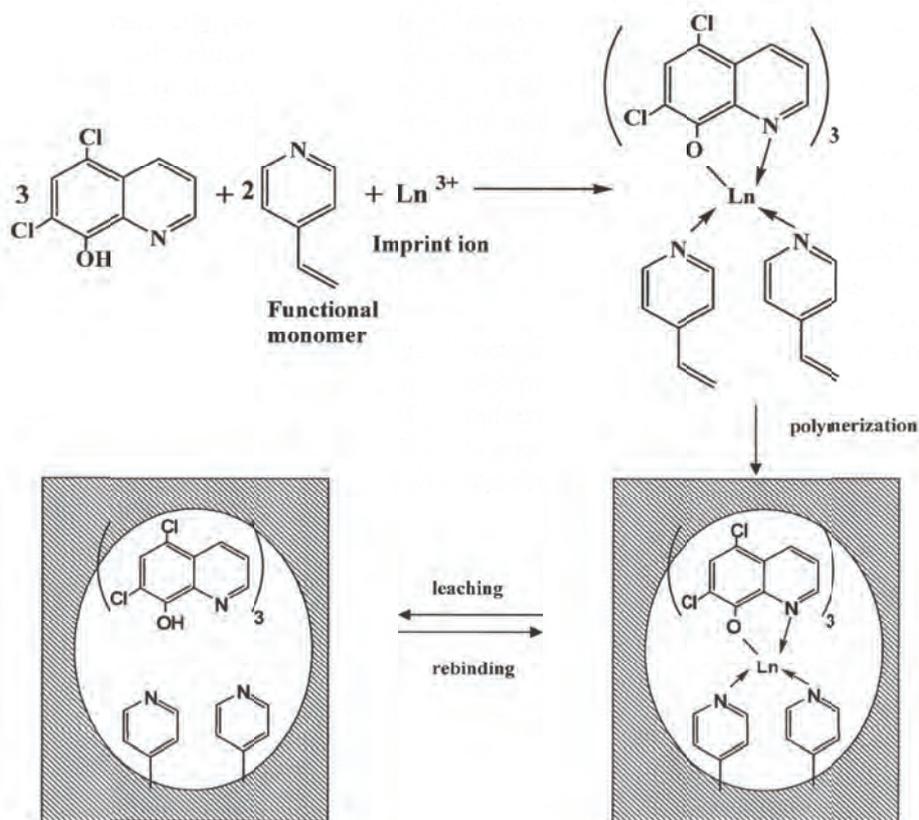


Figure 2.16: An example of trapping approach in IIP preparation (Rao *et al.*, 2006).

2.8.4.5 Metal coordination

In metal coordination, the template ion is a central ion surrounded by an array of ligand where it is bound. These ligands at least donate one pair of electrons to the central ion. This approach has been reported for IIP for zinc ions (Fan and Wang, 2010). The schematic representation is shown in Figure 2.17.

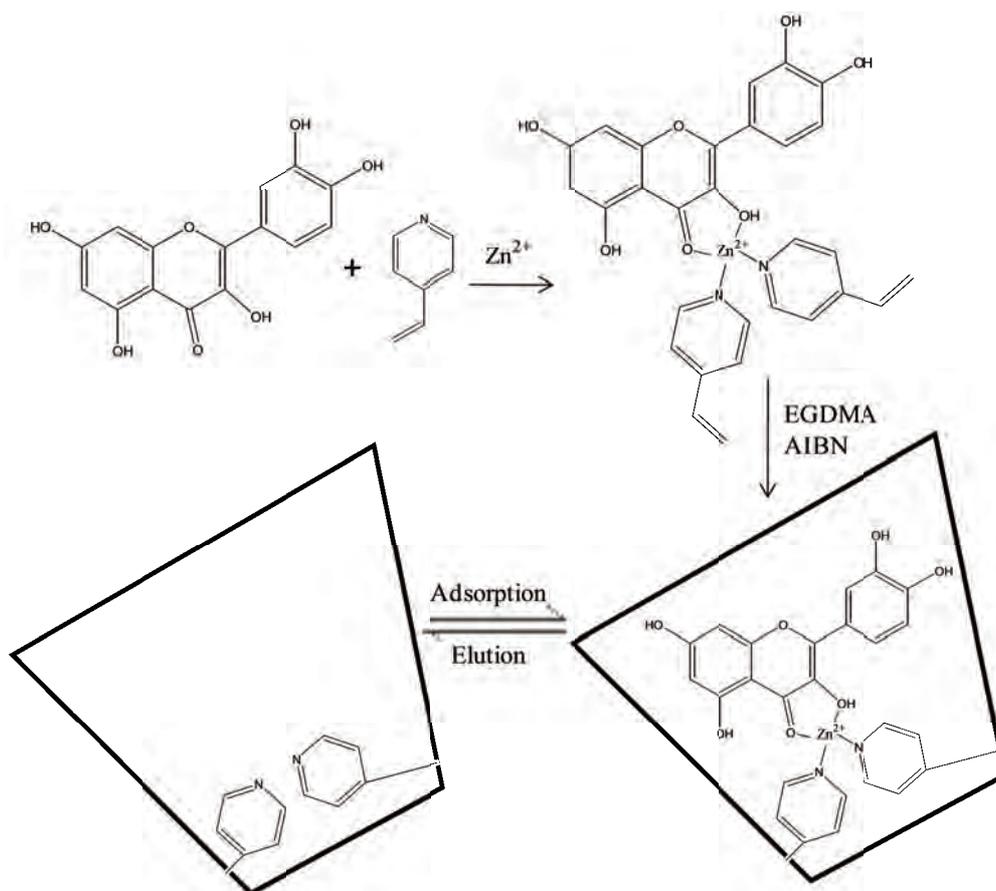


Figure 2.17: A scheme showing the metal coordination approach for zinc ion imprinted polymers (Fan and Wang, 2010).

The strength of the interaction depends on the oxidation state of the metal ion and on the ligand characteristics but it can be as strong as a covalent bond (Moreno-Bondi *et al.*, 2008). This approach has also been used by Matsui *et al.* (1996) in their research on the removal of Co^{2+} where they used dibenzoyl methane, cobalt(II) ion, styrene, divinylbenzene and 4-vinyl pyridine as pre-polymerization reagents. Uranyl ions have a unique shape and coordination geometry and can strongly interact with oxygen donating ligands according to hard-hard interaction concept as compared to other actinide ions (Fasihi *et al.*, 2011). As such, there have been a lot of investigations and reports on the complexation of uranium with different organic and inorganic ligands in solutions (Guillaumont *et al.*, 2006). Oxygen donor organic ligands are present in most of naturally occurring organic compounds, like carboxylic and amino carboxylic acids, lipids, (poly) phenols, acidic (poly) saccharides, humic substances, etc. (Berto *et al.*, 2011). UO_2^{2+} has also a tendency of reacting with nitrogen and sulfur donor ligands, showing a partial “soft” behaviour (Berto *et al.*, 2011).

2.8.5 Types of polymerizations

The polymerization techniques in IIPs are similar for MIPs for organic and ionic compounds. Bulk polymerization has been the most commonly used method though it is seen as time consuming and labour intensive. Other methods such as precipitation and emulsion

polymerizations have been used (Rao *et al.*, 2004; 2006). Table 2.6 gives a summary of the various polymerization techniques that have been reported. Various types of polymerization are briefly discussed below.

Table 2.6: Summary of some reported IIPs and polymerization techniques used.

Template	Polymerization approach	Polymerization technique	Reference
Cu(II)	Chemical immobilization	Suspension	Qi <i>et al.</i> , 2008
Cr(III)	Chemical immobilization	Suspension	Birlik <i>et al.</i> , 2007
Pb(II)	Chemical immobilization	Suspension	Zhu <i>et al.</i> , 2009
Hg(II)	Chemical immobilization	Suspension	Wu <i>et al.</i> , 2007
CH ₃ -Hg	Chemical immobilization	Suspension	Buyuktiryaki <i>et al.</i> , 2007
UO ₂ ²⁺	Chemical immobilization	Bulk	Preetha <i>et al.</i> , 2006
UO ₂ ²⁺	Trapping	Suspension	Sadeghi and Mofrad <i>et al.</i> , 2007
Zn(II)	Surface imprinting	Emulsion	Uezu <i>et al.</i> , 1998
Cd(II)	Surface imprinting	Emulsion	Fang <i>et al.</i> , 2005

2.8.5.1 Bulk polymerization

Presently, most MIPs are synthesized by the classical bulk polymerization method (Pérez *et al.*, 2000). The formed bulk polymers will then be crushed, ground and sieved to obtain particles mainly in the 25-50 µm size range (Pichon and Chapuis-Hugon, 2008). Grinding of the polymers normally produce particles that are irregularly shaped, polydisperse and usually include a large portion of fine particulate materials which are of no real use. Extensive sieving and sedimentation is done to achieve a narrower size distribution and to remove fine particles (Wang *et al.*, 2006). With all the steps involved, it is evident that bulk polymerization is time consuming, labour-intensive and wasteful as well since only 30-40% of the ground polymer is recovered as useable material. A polymer yield of useful particles can be even as low as 20% (Brüggemann *et al.*, 2000).

2.8.5.2 Precipitation polymerization

The main difference between bulk polymerization and precipitation polymerization is in the amount of the volume of the porogenic solvent used (Mohajeri *et al.*, 2011). The key point in precipitation polymerization is the use of a porogen in which the monomers are soluble in it but the resulting polymers are not (Biffis *et al.*, 2012).

2.8.5.3 Suspension polymerization

Suspension polymerization is an important process in industrial polymerization practice (Polacco *et al.*, 2000). In aqueous suspension polymerization systems, one or more monomers are dispersed into droplets. This is normally achieved by rapid stirring as well as addition of small amounts of water-soluble dispersing agents (Kalfas *et al.*, 1993). The size of the monomer droplets can be controlled by adjusting the stirring speed. Oil soluble initiators are normally used and the polymers are produced inside the drops in the same manner bulk polymers are produced (Brooks, 2010).

The function of the stabilizers in suspension polymerization is to hinder the coalescence of the functional monomer(s) droplets and of the formed polymer particles whose tendency to agglomerate may become critical when the polymerization has advanced (Kalfas *et al.*, 1993). Wang *et al.* (2006) used liquid paraffin as a dispersing agent. Water and liquid perfluorocarbon have generally been used as an aqueous continuous phase and an organic phase respectively (Wang *et al.*, 2006).

The temperature that is normally used for suspension polymerizations is usually in the range of 40-90°C under atmospheric pressure or it can be elevated to around 160°C but at elevated pressure since operation must always be below the boiling point of the continuous phase (Kalfas *et al.*, 1993).

2.8.5.4 Emulsion polymerization

Emulsion polymerization is a unique chemical process widely used to produce waterborne resins with various colloidal and physicochemical properties (Büttiker *et al.*, 2011). Dvorakova *et al.* (2010) synthesized nanosized MIP particles by non-aqueous emulsion polymerization. Their motivation was that the standard emulsion polymerization for MIP synthesis of using water disrupts the functional monomer-template interactions. This is owing to the strong polarity and high hydrogen bonding capability of water. Ultimately, the efficiency of the imprinting process is greatly reduced. In Pickering emulsion, dispersed liquid droplets are stabilized by solid particles instead of conventional surfactants. The stabilizing particles are located at the interface between the two immiscible liquids, thereby preventing coalescence. She *et al.* (2011) used SiO₂ as stabilizing particles.

2.8.6 Application of imprinting technology

Synthetic molecularly selective receptors such as MIPs and IIPs find a widespread application in many areas of science as depicted in Figure 2.18. A particularly promising

application of IIP is in solid phase extraction, SPE, where it is used to pre-concentrate and/or separate target species from other co-existing ions from complex matrices (Daniel *et al.*, 2005). Not much has been reported for use of these materials for environmental remediation. MIPs as sorbents with better selectivities than those of traditional SPE adsorbents have recently been introduced as novel adsorbents for the extraction and clean-up of target compounds from various matrices such as wastewater or river water samples (Ersöz *et al.*, 2004; She *et al.*, 2010).

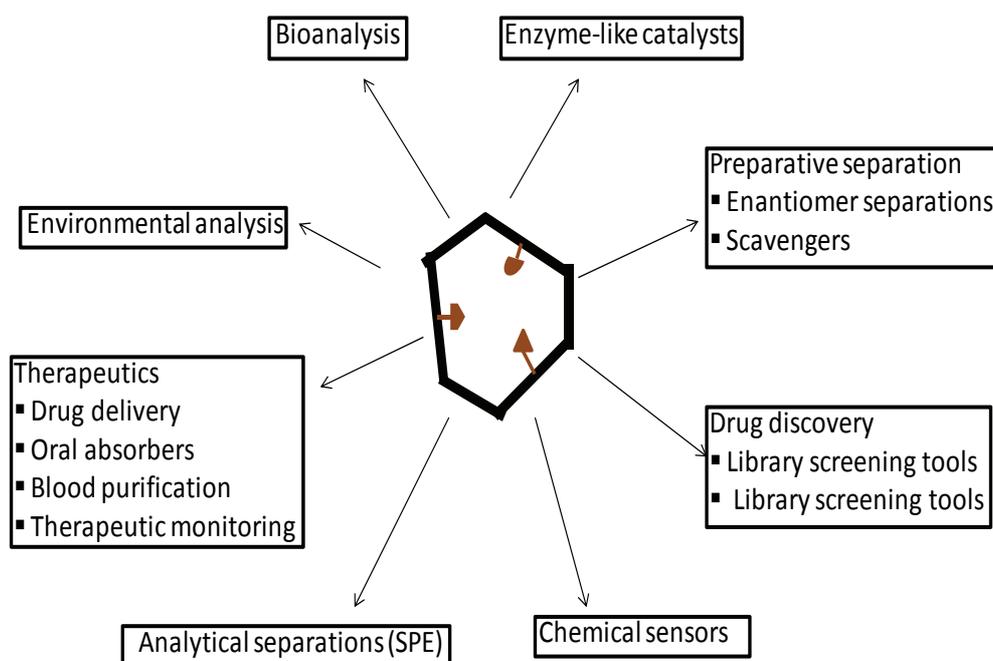


Figure 2.18: Scheme outlining the main applications envisaged for MIPs and IIPs, adapted from Sellergren and Allender, 2005.

In polymeric sorbents, the chelating functionality usually consists of some type of mono-, bi-, or polydentate moieties with donor groups contain atoms like nitrogen, oxygen and sulphur. A review of some recent synthetically-prepared polymeric sorbents obtained by immobilizing a particular type of chemical moiety on magnetic materials is presented in Tables 2.7. Some polymeric sorbents have high capacity. The higher capacity of the sorbent is very important in applications to real samples. This is because of possible competition for adsorption with other anions such as SO_4^{2-} for Cr(VI) (Pakade *et al.*, 2011). High capacity of the polymer allows the Cr(VI) to still being extracted in the presence of such competitors. The situation could be different for selectivity polymers such as ion imprinted polymers where even with low adsorption capacity is still capable of binding target metal ion (Pakade *et al.*, 2011). However, even in such selective polymers, the cavities might still be large enough to allow co-extraction of other competitors like F^- (Pakade *et al.*, 2011).

The synthetic polymeric sorbents or modified natural sorbents in theory should have high selectivity and fast mass transfers kinetics because the final functional groups of the sorbents are tailored to bind target metal ions. However, in many reported publications, selectivity

studies are often not done and this makes it difficult to compare performance on this aspect. The equilibration time seem to depend on the actual sorbent and not the type. However, on average, synthetic polymeric sorbents and modified natural sorbents seem to have low equilibration time (20-60 min), thus with fast mass transfer kinetics. Most sorbents, regardless of the type, work best in acidic pH of the sample. This is perhaps expected especially since Cr(VI) is negatively charged so a sorbent with positively charged functional groups is needed for this metal ion. Most of these functional groups are amine based and therefore work best in acidic media that favours the positive charge on the functional group (Zhao *et al.*, 2010). Duranoglu *et al.* (2010) observed the reduction of Cr(VI) to Cr(III) during the adsorption of the former onto activated carbon derived from acrylonitrile-divinylbenzene copolymer at sample pH of 2. This might not influence the overall adsorption if the formed Cr(III) is also adsorbed by the sorbent. For sorbents that are selective for Cr(VI), this reduction process could lower the amount adsorbed.

Most application of the prepared sorbents is to remediate polluted wastewaters such as acid mine drainage water where the pH of such wastewaters is generally acidic (Pakade *et al.*, 2011). Most reported polymers are therefore very suitable for application to such polluted wastewaters. The only disadvantage is that at such low pH, samples have also high concentration of Fe^{3+} and SO_4^{2-} which are the major competitors for adsorption with uranium and Cr(VI), respectively (Pakade *et al.*, 2011; 2012). Duranoglu *et al.* (2010) studied the various anionic competitors (Cl^- , NO_3^- , SO_4^{2-} , PO_4^{3-}) during the adsorption of Cr(VI) onto activated carbon derived from acrylonitrile-divinylbenzene copolymer at sample pH of 2. Factors that influence adsorption of these competitors include size, charge and hydration degree. In their study, Duranoglu *et al.* (2010) experienced a maximum fall in adsorption of Cr(VI) by the sorbent owing to PO_4^{3-} . The reason for this is that PO_4^{3-} has more negative charges and is also polyatomic with similar molecular dimensions and consequently same hydration degree (Duranoglu *et al.*, 2010). Cl^- has similar charge to Cr(VI) but has higher charge density due to the small molecular dimensions. However it has higher hydration than HCrO_4^- . Cl^- had therefore the least influence on adsorption of Cr(VI) on the sorbent. In the pH range of 1-6, chromium ions coexist in forms of $\text{Cr}_2\text{O}_7^{2-}$, HCrO_4^- , $\text{Cr}_3\text{O}_{10}^{2-}$ and $\text{Cr}_4\text{O}_{13}^{2-}$ of which HCrO_4^- is the most dominant while at higher pHs, CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ are the most dominant species (Garg *et al.*, 2007).

Table 2.7: Polymeric sorbents for the removal of U(VI) and Cr(VI) from environmental samples.

Sorbent	Target	Binding capacity (mg g ⁻¹)	Equilibrium time (min)	Initial pH	Reference
Ion-imprinted chitosan composite magnetic microspheres	U(VI)	9	30	3.5	Wang <i>et al.</i> , 2011
3-Aminopropyl triethoxysilane on silica coated Fe ₃ O ₄	U(VI)	26	30	4.0	Sadeghi and Aboobakri, 2012
Magnetic Fe ₃ O ₄ -SiO ₂ composite particles	U(VI)	52	16	6.0	Fan <i>et al.</i> , 2012
Magnetic poly-(MA-DVB) graft dendrimer microspheres	Cr(VI)	232	12	3.0	Wang <i>et al.</i> , 2012
Biofunctional magnetic beads	Cr(VI)	7	480	1.0	Li <i>et al.</i> , 2008
Magnetic poly-(GMA-EGDMA)	Cr(VI)	138	120	2.0	Bayramoglu and Arica, 2008
Ethylenediamine on Fe ₃ O ₄ magnetic polymer	Cr(VI)	137	30	2.5	Zhao <i>et al.</i> , 2010
Ethylenetriamine on Fe ₃ O ₄ magnetic polymer	Cr(VI)	150	30	2.5	Zhao <i>et al.</i> , 2010
Triethylenetetramine on Fe ₃ O ₄ magnetic polymer	Cr(VI)	204	30	2.5	Zhao <i>et al.</i> , 2009
Tetraethylenepentamine on Fe ₃ O ₄ magnetic polymer	U(VI)	370	30	2.5	Zhao <i>et al.</i> , 2010
Tetraethylenepentamine on Fe ₃ O ₄ magnetic polymer	Cr(VI)	-	60	2.0	Yao <i>et al.</i> , 2012
N, N'-bis (3-methoxysalicylidene)-1,2-phenylenediamine on Fe ₃ O ₄	U(VI)	94	360	2.0	Zhang <i>et al.</i> , 2012

2.8.7 Concluding remarks

It is clear from a review of remediation technique that current available technologies have got limitations especially for treating acid mine drainage because of extreme pH, high amounts of other anions (e.g. sulphates) and cations (e.g. Iron). Efforts are being devoted to improving the traditional techniques or developing new techniques. One area that is currently exploited is the use of large columns packed with appropriate sorbent for trapping target chemicals in acid mine drainage water. The problem with is finding new materials that can withstand harsh conditions such as extreme pH of acid mine drainage and that is selective towards the target chemicals. Traditional silica columns cannot without extreme pH conditions and are not selective. Normal linear or branched polymers that are insoluble in water are not selective but can withstand extreme pH conditions. The so called smart polymers especially based on molecularly imprinted polymers are a potential alternative because they are selective and can withstand extreme pH conditions. In order to avoid parking these sorbents as in columns that has got problems of flow blockage, alternative set-ups are required. One possible approach is holding these sorbents using a strong magnet in a flow system. For this to be feasible, one need to prepare magnet ion imprinted polymers instead of normal ion imprinted polymers. The project thus focused on preparing magnetic ion imprinted polymers for Cr(VI) and U(VI). In literature, many polymers that been prepared that can trap Cr(VI) or U(VI). However, very little has been done on preparing magnetic ion imprinted polymers for these metal ions. Further, few literature that is available never carried out a detailed study on the selectivity of such materials or application to acid mine drainage. This is very important for feasibility studies of the potential application of these materials. The reusability of such materials is also not demonstrated especially under extreme conditions of acid mine drainage. During leaching of the template from the prepared polymer, the magnetite can also be leached out and no detailed documentation of this is available including best possible leaching solutions. This project tried to fill some of the gaps in magnetic ion imprinted polymer materials mentioned above.

Chapter Three: Research Aims

3.1 Aims

The aims of the project were as follows:

- a) To prepare magnetic nano composite materials based on molecularly imprinted polymers specific for chromium(VI) and uranium(VI).
- b) To characterize the prepared magnetic nano composite beads in order to understand their morphology and functional groups.
- c) To study the binding, capacity and selectivity of the prepared magnetic nano composite beads for chromium(VI) and uranium(VI) in deionised water, acid mine drainage and wastewater treatment plants influent.
- d) To discuss of the results with relevant stakeholders such as the mining industry.
- e) To apply for provisional patent on the synthesis of magnetic nano composite beads for Cr(VI) and uranium(VI)

3.2 Key questions

1. Can the synthesized nano-magnetic IIPs be used in the remediation and recovery of U(VI) and Cr(VI) from wastewaters?
2. Is the adsorption of U(VI) and Cr(VI) onto synthesized nano-magnetic IIPs selective?

3.3 Significance of the research

Most methods of adsorption of metal ions in wastewaters are non-selective. In this study, effective and selective removal of U(VI) and Cr(VI) from acid mine drainage and wastewater using nano-magnetic IIPs was established. The preparation and use of magnetic materials for remediation of polluted wastewaters is a relatively new field. The South African mining sector has huge problems with polluted wastewaters. The potential use of selective sorbents based on magnetic materials is therefore of interest.

3.4 Hypothesis

Nanomagnetic-ion imprinted polymers can be used to selectively remove U(VI) and Cr(VI) from wastewaters and the polymers removed from the solutions by application of an external magnetic field. The performance of nano-magnetic IIPs is better than that of nano-magnetic NIPs in the uptake of uranium and chromium from wastewaters.

3.5 Novelty

Although the technology of smart polymers based on molecularly imprinted polymers is now well known, preparation of magnetic ion imprinted polymers for U(VI) and Cr(VI) is still very scarce (Wang *et al.*, 2011).

This study is therefore one of the first ones that has made attempt to prepare smart polymers for U(VI) and Cr(VI) that are magnetic. Further, this study carried out a detailed study on the selectivity of the prepared magnetic ion imprinted polymer which has rarely been done in previous studies (Li *et al.*, 2008; Bayramoglu and Arica, 2008 Zhao *et al.*, 2010; Wang *et al.*, 2011; Fan *et al.*, 2012).

3.6 Scope and limitations

The project attempted to prepare magnetic selective polymers for chromium(VI) and uranium using molecular imprinting technology in order to try and fulfil the project aims. The synthesis of the magnetic ion imprinted polymers was made by modifying some of the existing procedures from literature. The modified procedures are therefore new in the sense that there is very little literature on the magnetic ion imprinted polymers for the studied metal ion complexes. Magnetite was prepared, coated with anchoring ligands and then polymerization for the formation of ion imprinted polymers was performed in the presence of coated magnetic nano particles. The final magnetic ion imprinted polymers were characterised and optimised for the binding of these metal ions in deionised water and real samples. Objectives a, b and c were thus fulfilled. The study even went further to study the binding kinetics of the prepared magnetic ion imprinted polymers.

Chapter Four: Materials and Methods

4.1 Chemicals, stock solutions and equipment

4.1.1 Chemicals

For the synthesis of magnetite, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, of analytical grades supplied by Sigma Aldrich (Steinheim, Germany) were coprecipitated in the presence of NH_4OH from Sigma Aldrich (Steinheim, Germany). Methanol, from Sigma Aldrich (Steinheim, Germany), was used for washing magnetite.

For the synthesis of the magnetic polymers, the following chemicals were used: ethylene glycol dimethacrylate (EDGMA), methacrylic acid (MAA), 1,1'-azobis(cyclohexanecarbonitrile), salicylaldehyde (SALO), 4-vinylpyridine (4-VP), 2-methoxyethanol as well as surfactants for coating magnetite, γ -methacryloxypropyltrimethoxysilane (γ -MPS) and oleic acid (OA) all purchased from Sigma Aldrich (Steinheim, Germany). The imprint, uranyl nitrate ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was bought from BDH Chemical Ltd, (Poole, England). All other chemicals used were of the highest analytical grades and were from Sigma Aldrich (Steinheim, Germany). The leachants used for uranyl removal were HCl and NaHCO_3 all from Sigma Aldrich (Steinheim, Germany).

Deionized water was prepared from Millipore instrument (Massachusetts, USA) and was used in preparation of all aqueous solutions. Analytical grade solutions from Merck (Darmstadt, Germany) were used to prepare different buffers systems for pH optimization and adjustments: for pH 1 and 2, HCl/KCl was used, Na_2HPO_4 /citric acid was used for pH 3, $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$ was used for pH 4, 5 and 6, borax/ H_3BO_3 was used for pH 7, 8 and 9.

4.1.2 Stock solutions

A uranium(VI) stock solution was prepared by dissolving an appropriate amount of uranyl nitrate hexahydrate in one litre of deionized water with 0.05% (v:v) HNO_3 . Stock solutions of 1000 mg L^{-1} (for selectivity of Cr(VI)-magnetic ion imprinted polymers) were prepared by dissolving the following appropriate amounts of dried salts in 1 L volumetric flasks: NaF, NaNO_3 , KH_2PO_4 , Na_2SO_4 and $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$. All salts were purchased from Sigma Aldrich (Steinheim, German). A 1000 mg L^{-1} stock solution of chromium(VI) was prepared by dissolving an appropriate amount of sodium dichromate, $\text{Na}_2\text{Cr}_2\text{O}_7$ (analytical reagent grade) in deionized water. Working solutions were prepared daily from the stock solution through serial dilutions. The stock solution was stored at 4°C when not in use.

4.1.3 Equipment

All pH measurements were performed on a 766 Calimatic pH meter equipped with a Shott N61 pH electrode from Knick (Berlin, Germany). In batch adsorption studies, a Laser Photo/Contact Tachometer DT-1236L from Lutron (Taipei, Taiwan) was used to measure the rotational speed of the magnetic stirrer. A Fritsch pulveriser (Idar-Oberstein, Germany) was used to crush the synthesized bulk polymers for homogenization.

4.2 Analytical and characterization equipment

All instruments used in this study for quantification and determination of analytes (U(VI) and Cr(VI)) in solution as well as characterization of U(VI) and Cr(VI) magnetic ion imprinted polymers and other materials are briefly described below.

4.2.1 Ultraviolet visible (UV-vis) spectroscopy

A Varian Cary 50 Conc, UV-Vis spectrophotometer with a Varian Cary 1E double beam spectrophotometer (Palo Alto, CA, USA) scanning from 200 to 750 nm was used for obtaining UV-Vis absorption spectra.

4.2.2 Raman spectroscopy

Raman spectra were acquired using a Jobin-Yvon T64000 Raman spectrograph from Wirsam Scientific (Pty) Ltd (Johannesburg, South Africa) operated in single spectrograph mode and the 514.5 nm of an argon ion laser as the excitation source. An Olympus BX40 microscope attachment was used to focus the incoming light on the sample and the backscattered light was dispersed via a 600 lines mm^{-1} grating onto a liquid nitrogen cooled CCD detector for acquisition via LabSpec v 4.18 software.

4.2.3 Transmission electron microscopy (TEM)

A FEI TECNAI SPIRIT (TEM-EDS) electron microscope (Eindhoven, Netherlands) was used. Approximately 0.2 g of the powdered samples were put in eppendorf tubes where 1 mL of methanol was added. The mixtures were then sonicated for 15 minutes. After this, an aliquot was drawn and applied to a Cu grid coated with carbon film. For the excess liquid to dry, the grids were placed on the Whatman filter paper for about 5 minutes. These were then loaded into the TEM microscope where they were viewed under an electron microscope.

4.2.4 Size distribution

Because of their ultra small size, the actual diameter of each particle cannot be measured precisely, hence the use of particle size distribution. To achieve this, the size diameters for both the uncoated magnetite and the γ -MPS coated magnetite were done on the respective TEM micrographs by use of the *image j*, a public domain image processing program.

4.2.5 Powder X-ray diffraction (PXRD) analysis

A crystallographic study was performed on a synthesized iron oxide powder by a D2 Bruker Powdered X-ray Diffractometer (Karlsruhe, German), using Cu K α radiation (= 1.5418 Å). The positions and the intensities of the peaks are used for identifying the underlying structure (or phase) of the material. The particle sizes of the magnetic nanoparticles were deduced from PXRD using Scherrer equation which can be written as in equation 4.1:

$$\bar{D} = \frac{57.3k\lambda}{\beta \cos\theta} \quad (4.1)$$

Where \bar{D} is the mean size of the ordered (crystalline) domain, which may be smaller or equal to the grain size, k is shape factor, λ is the wavelength of the radiation corresponding to the Cu K α peak, β is the full-width at half maximum (FWHM) and θ is the Bragg's angle. The factor 57.3 is used for conversion of β from degree to radians. The Scherrer equation is limited to nano-scale particles. It is not applicable to grains larger than about 0.1 μm .

4.2.6 Brunauer, Emmett and Teller (BET) analysis

Surface area, pore volume and pore size were determined for both the uranyl-imprinted magnetic polymers and the control polymers. The effect of 1 mol dm⁻³ HCl and 1 mol dm⁻³ NaHCO₃ leachants on surface area formation was also investigated. An amount of 0.2 g of each of the above samples was degassed in N₂ at 150°C for 4 hours prior to analysis with the Micromeritics Flow Prep 060 instrument (Aachen, Germany). After the degassing stage, surface area, pore volume and pore size were determined at -196°C. This was achieved through N₂ adsorption and desorption using the Micromeritics Tristar surface area and porosity analyzer. BET is the commonly used gas sorption model which extends the model of gas sorption to multi-layer. It is normally solved graphically by plotting 1/[$v(p/p_o)-1$] versus p/p_o . The BET specific surface areas of the polymeric adsorbents are calculated from the corresponding isothermal adsorption of nitrogen within the partial pressure range of 5% to 35% (p/p_o) by use of the BET equation 4.2:

$$\frac{p/p_o}{v(1 - p/p_o)} = \frac{1}{v(p/p_o - 1)} = \frac{1}{v_m c} + \frac{c - 1}{v_m} \cdot \frac{p}{p_o} \quad (4.2)$$

Where p is adsorbate pressure, p_o is adsorbate vapour pressure and v is adsorbed volume v_m is monomolecular layer volume and c is a quantity related to heats of adsorption and liquefaction. These two constants can be calculated from the slope, s , and the intercept, i , through use of equations 4.3 and 4.4.

$$v_m = \frac{1}{(s + i)} \quad (4.3)$$

$$c = \frac{s}{i} + 1 \quad (4.4)$$

4.2.7 Fourier-transformed infra red (FTIR)

Fourier-transformed infra red spectra were recorded in the frequency range of 400-4000 cm^{-1} using a Bruker FTIR spectrometer, Model Tensor 27 (Ettlingen, Germany) and the spectra were recorded in the solid state. This technique is useful in the identification of functional groups in a sample.

4.2.8 Thermo-gravimetric analysis (TGA)

Thermogravimetric analysis for the prepared materials was performed with Perkin Elmer Pyris 1 TGA Thermogravimetric Analyser (Massachusetts, USA) using nitrogen as the purge gas, at a flow rate of 20 mL min^{-1} and a heating rate of 5°C per minute from 0-1000°C. This technique was used to investigate changes in a sample weight as the heating temperature was changed. These changes are usually associated with weight loss resulting from dehydration or decomposition of the sample as the temperature increases. About 0.05 g of the sample was used for the thermal gravimetric analysis.

4.2.9 Carbon, hydrogen, nitrogen and sulphur (CHNS) analysis

A LECO-932 CHNS analyser from LECO Corporation (Michigan, USA) was used to determine the amount of carbon, hydrogen and nitrogen in the organic moiety which coated the magnetite. The products of combustion in CHNS analysis are CO_2 , H_2O , N_2 and SO_x , though depends on composition. High temperature combustion was used as the means of removing the elements from material. Samples (2 mg) were weighed into tin boats, compressed and encapsulated into capsules and taken to sample loading and then dropped into the furnace. The sample was combusted in the heated oxygen rich environment. Programmable control of the direct oxygen jet injection during high-temperature combustion guaranteed complete combustion. The gaseous combustion products were purified, separated into their components by special adsorption traps, and sequentially analyzed with universally used thermoconductivity detector (TCD). Calibration was performed with corn gluten for this CHNS test.

4.2.10 Diffuse reflectance spectroscopy (DRS)

Varian Cary 500 UV-Vis-NIR spectrophotometer using a diffuse reflectance attachment from SMM Instruments (Johannesburg, South Africa) was used in the scanning range of 200 to 1000 cm^{-1} . In DRS, different types of iron oxides exhibit different colours. These differences are the basis for distinction to some extent among Fe oxides. The analysis of corresponding DRS can be used to identify and characterize different types of iron oxides.

4.2.11 Atomic force microscopy (AFM)

Atomic force microscopy was applied to study pore formation in the polymer from the study of the images of the samples before and after leaching of the uranyl ions. A Veeco/Digital Instruments Dimension 3100 Scanning Probe Microscope (Santa Barbara, USA) was used in AFM-tapping mode.

4.2.12 Ion chromatography (IC) analysis

Metrohm 762 Compact Ion Chromatograph (Leonberg, Germany) with a Metrosep A Supp 5 (6.1006.520) 150×4.0 mm analytical column was used for the determination of fluoride, nitrate, sulphate and phosphate anions. The eluent solution was of the composition of 1.0 mM NaHCO_3 and 3.2 mM Na_2CO_3 . The eluent was pumped at 0.7 mL min^{-1} . The suppressor solution was 50 mM H_2SO_4 and deionized. All the solutions, including eluents used were degassed by ultrasonication and filtered through a $0.45 \mu\text{m}$ filter paper before being used in the IC.

4.2.13 Inductively coupled plasma-optical emission spectrometer (ICP-OES)

ICP-OES from Spectro Genesis End-on-plasma Spectro Analytical Instruments (Pty) Ltd, (Johannesburg, South Africa), was used for the determination of the metals' concentration in multi-elemental solutions with parameters shown in Table 4.1.

Table 4.1: Operating conditions of the ICP-OES.

Parameter	Setting
RF Power	1400 W
Coolant Gas Flow	14.00 L min ⁻¹
Auxiliary Gas Flow	1.00 L min ⁻¹
Nebulizer Gas flow	1.00 L min ⁻¹
Sample Pump Flow	2.00 L min ⁻¹
Sample Aspiration Rate	2.00 L min ⁻¹
Replicates	3
Plasma Torch	Quartz
Spray Chamber	Single pass
Nebulizer	Crossflow
Processing Mode	Area

4.2.14 Atomic absorption spectroscopy (AAS)

AAS measurements were made on a PG-990 AAS model (Leicestershire, UK) pyrolytically coated HGA-76 graphite furnace. A uranium hollow cathode lamp was used at 358.5 nm uranium wavelength with a spectral width of 0.2 nm. Argon was used as a purge gas. A scheme diagram for the graphite furnace atomic absorption spectrophotometer is shown in Figure 4.1.

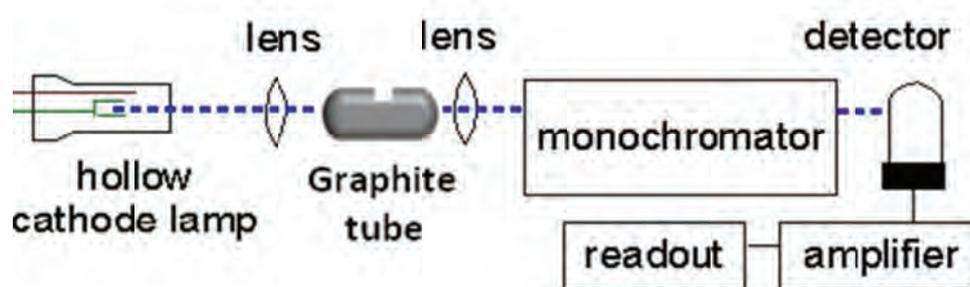


Figure 4.1: Schematic diagram of graphite furnace atomic absorption spectrophotometer.

The graphite furnace is electrically heated and undergoes a heating programme which can consist of many steps. In this work, the heating programme applied consisted of four steps, namely, drying, ashing, atomization and cleaning. The temperatures corresponding to the ramping and holding times are shown graphically in Figure 4.2.

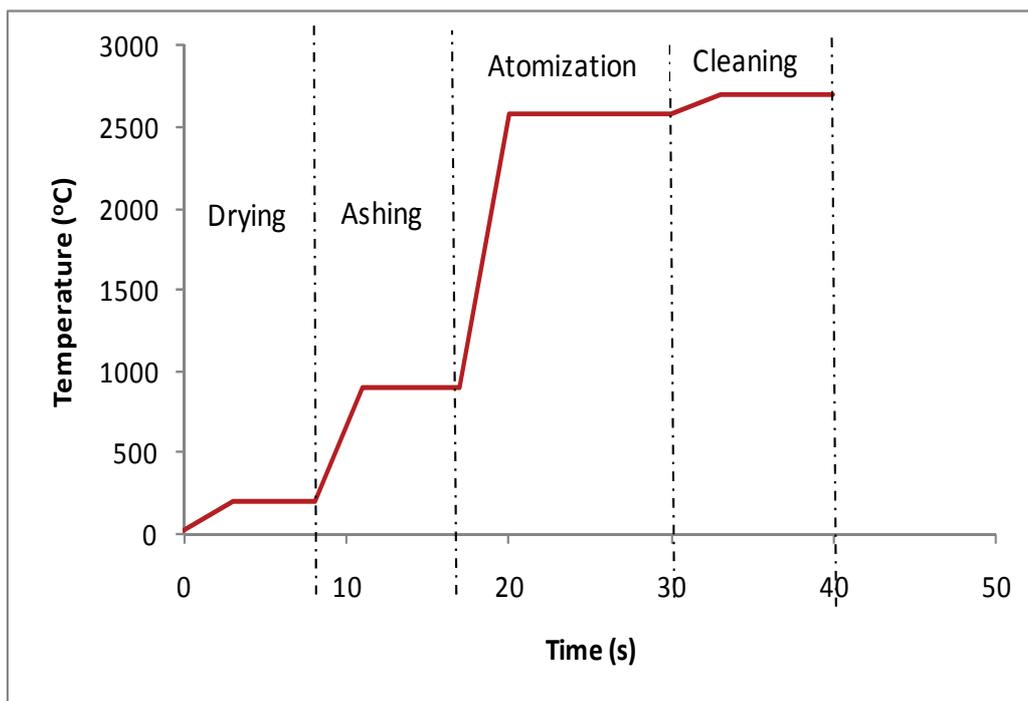


Figure 4.2: The heating programme for uranium in the graphite furnace.

4.3 Synthesis of the magnetic IIPs and NIPs

4.3.1 Synthesis of the magnetite

Synthesis *via* the co-precipitation of ferrous and ferric salts in an alkaline medium (Thorek *et al.*, 2006) was used. A volume of 180 mL of an aqueous solution containing 11.2 mmol Fe^{3+} and 5.6 mmol Fe^{2+} was heated to 50°C. After heating, 12.5 mL of ammonia was added under vigorous stirring. After 30 min, the reaction was heated and kept at 90°C for 30 min again. An inert atmosphere of N_2 was used for the whole experiment. After completion of the reaction, the black precipitate was collected by an external magnetic field, washed with water and ethanol and dried under vacuum.

4.3.1.1 Coating of magnetite with γ -MPS

In this study γ -methacryloxypropyltrimethoxysilane (γ -MPS) was used as a coating agent. This was chosen because of its physio-chemical properties. γ -MPS have the hydrophobic olefinic end which ushers a platform for polymerization.

Kan *et al.* (2010) approach was used to modify the magnetic nanoparticles with a double bond. In this method, 4 mL γ -MPS was added dropwise into the mixture of solvents of ethanol and water (1:1, *v/v*) containing dispersed Fe_3O_4 nanoparticles and the reaction was carried out for 12 h at 40°C under N_2 gas. Then the product was separated and washed by ethanol for several times and dried under vacuum. In these conditions, the methoxyl groups are firstly hydrolyzed to produce the hydrophilic silanol groups which directly covalently

bond with the hydroxyl groups around the magnetite. On the other end of the γ -MPS, there is a hydrophobic olefinic group which ushers a platform for polymerization with the monomers during polymer preparation stage.

4.3.1.2 Coating of magnetite with oleic acid

An amount of 1.0 g Fe_3O_4 particles was dispersed in 200 mL ethanol under ultrasonication, and then 5 mL oleic acid was added dropwisely into the above mixture under stirring at 80°C for 1 h. The oleic acid coated Fe_3O_4 particles were isolated by application of an external magnetic field and washed with water and ethanol to remove redundant oleic acid (Zhao *et al.*, 2010).

4.3.1.3 Bulk polymerization

The polymers were synthesized according to the method of Singh and Mishra (2009) with some modifications. Ion-imprinted polymers were prepared by thermal polymerization. The imprint ion (0.270 g) was complexed with 2 mM salicylaldoxime (SALO) and 2 mM 4-vinylpyridine (4-VP) in 10 mL of 2-methoxyethanol in which 2 g of the functionalized magnetite was suspended. The above ternary complex solutions were then mixed with 12 mmol of methacrylic acid (MAA), 36 mmol of ethylene glycol dimethacrylate (EGDMA) and 50 mg of 1,1'-azobis(cyclohexanecarbonitrile). The polymerization mixture was cooled to 0°C and purged with N_2 for 10 min, sealed and thermally polymerized in an oil bath at 80°C while stirring for 3 h. The bulk polymers were dried at 70°C to remove the solvent (porogen). The polymers were then washed with ethanol, then ethanol and water mixture with increasing amounts of water until only water was used, Table 4.2. Finally, the resulting polymer was then ground and sieved to obtain the ion-imprinted polymers in the size range of 27 and 53 μm . Magnetic NIPs were prepared likewise except that the imprint ion was not included.

Table 4.2: Volume composition of the polymer washing solution.

Wash number	1	2	3	4	5
Ethanol (mL)	10	6	5	4	0
Water (mL)	0	4	5	6	10

4.3.1.4 Precipitation polymerization

In precipitation polymerization, the same protocol for the bulk polymerization was followed except that the volume of the porogenic solvent, 2-methoxyethanol, was increased ten-fold to 100 mL.

4.3.1.5 Leaching of γ -MPS and OA based polymers

An amount of 3 g of the magnetic polymer (from bulk and precipitate) was transferred to a 250 mL volumetric flask upon which a 100 mL of 2 mol dm^{-3} HCl was added. The mixture

was stirred gently for 6 hours, after which filtration was done under vacuum. The filtrate was retained for metals analysis. A freshly prepared HCl leachant, with the same concentration and volume as above, was added to the magnetic polymer. This procedure was repeated for three more times.

A second leachant, $1 \text{ mol dm}^{-3} \text{ NaHCO}_3$ was used in the same way as HCl leachant. Leaching of the oleic acid functionalized magnetite was done in the same way as γ -MPS based polymers but only $1 \text{ mol dm}^{-3} \text{ NaHCO}_3$ was used. The magnetic NIPs were subjected to the same treatment.

4.3.2 Optimization of parameters for U(VI) uptake

Sample pH, magnetic polymer amount, contact time and initial U(VI) concentration were optimized. Optimization of was achieved by varying one parameter while keeping the others constant. All experiments were carried out in triplicates. The influence of these parameters was evaluated by calculating the extraction efficiency or recovery as shown in equation 4.5:

$$\text{Extraction efficiency (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (4.5)$$

Where: C_0 (mg L^{-1}) is the initial concentration and C_e (mg L^{-1}) represents the final equilibrium concentration after adsorption.

The adsorption capacity, q (mg g^{-1}), is defined as mass of substrate bound on a gram of adsorbent. Equation 4.6 shows the mathematical equation for the calculation of the adsorption capacity in which C_0 (mg L^{-1}) and C_e (mg L^{-1}) are as described for in equation 4.5 and V (L) is the volume of the sample solution and the mass of the adsorbent is given as W (g) (Zeinali *et al.*, 2010; Kumar and Kirthika, 2009; Maarof and Hameed, 2004).

$$q = \frac{(C_0 - C_e)V}{W} \quad (4.6)$$

4.3.2.1 Effect of sample pH

In this study, 2 mg L^{-1} of uranium solutions were prepared from a 1000 mg L^{-1} stock solution in 8 volumetric flasks. In order to investigate the effect of sample pH, the uranium solutions were adjusted between pH 2-9 and 25 mL of these were then transferred to 30 mL vials where 20 mg of an adsorbent (magnetic IIP and NIP) were added. After this, the uranyl-IIP mixture was allowed to equilibrate with stirring at 1500 rpm for 45 minutes. The loaded magnetic-IIPs were then separated from the mixture by application of an external magnetic field and the filtrate analyzed for uranium content. All adsorption experiments were carried out at room temperature.

4.3.2.2 Effect of the amount of magnetic polymer

Adsorption was carried out in a series of 30 mL vials at room temperature. Each vial was filled with 25 mL of an initial concentration of 2 mg L^{-1} solution of uranium. An optimized sample pH was used. The added magnetic polymer mass was varied between 10 to 100 mg. After stirring the solution for 45 minutes at 1500 rpm, separation of the magnetic polymers was achieved by use of a magnet. The solution was then analysed for uranium content from which the amount adsorbed on the polymer was calculated.

4.3.2.3 Effect of contact time

In order to establish the optimum contact time and adsorption kinetic behaviour of the magnetic polymers, adsorption of uranium onto the magnetic polymers was investigated at various time intervals (10-90 min).

The initial concentration of uranium was kept constant at 2 mg L^{-1} . The optimized amount of the polymer was added into 25 mL uranium solution. This mixture was then mixed at room temperature under a stirring speed of 1500 rpm. After adsorption, the polymers were separated from aqueous phase by use of an external magnetic field and the supernatant analyzed for uranium. Mass balance was then used to calculate the amount of uranium adsorbed onto the polymer. All adsorption experiments were carried out at room temperature.

4.3.2.4 Effect of initial uranium concentration

Adsorption was carried out in a series of 30 mL vials at room temperature. Each vial was filled with 25 mL of uranium solution of five varied initial concentrations ranging from $0.5\text{-}10 \text{ mg L}^{-1}$. The pH and amount of the magnetic polymer used were those optimized. After stirring the solution for the optimum period of time at 1500 rpm, separation of the magnetic polymers was achieved by use of a magnet. The solution was then analysed for uranium content from which the amount adsorbed on the magnetic polymers was calculated.

4.3.2.5 Selectivity of the magnetic polymers

Stock solutions (1000 mg L^{-1}) were prepared by weighing out an appropriate amount of the salts, namely: $\text{U}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ by dissolving them in de-ionized water. The pH adjustments were conducted using an appropriate buffer system that gave maximum adsorption capacity in section above. The working standard solution was obtained by serial dilution of the stock solution. For selectivity studies, a binary metal solution was made from 2 mg L^{-1} of U(VI) and of another metal ion. Aliquots of 25 mL of these binary metal solutions were transferred to 30 mL vials where the optimized weight (50 mg) of the magnetic IIP was added. A batch adsorption experiment was then performed at room temperature for a prescribed time of 45 minutes at 1500 rpm. Separation of the polymers was then carried by application of a magnetic field. The metals remaining in solution were then quantified with ICP-OES but uranium was quantified with GFAAS. The respective magnetic NIP was used for the control experiment.

The distribution coefficients, K_d , of UO_2^{2+} , Mg^{2+} , Fe^{3+} , Ni^{2+} and Pb^{2+} were calculated using equation 4.7:

$$K_d = \frac{(C_o - C_e)V}{C_o W} \quad (4.7)$$

Where: K_d is the distribution coefficient (L g^{-1}) and the other variables are as described for equations 4.5 and 4.6. Equation 4.8 was used to calculate the selectivity coefficients for the binding of a uranyl ion in the presence of other competing ion in a binary system:

$$K = \frac{K_d(\text{UO}_2^{2+})}{K_d(\text{B})} \quad (4.8)$$

Where: K represents the selectivity coefficient and B represents U(VI) competing ions mentioned above. The value of K gives an indication as to how selective the polymer is for U(VI) ions in the presence of other competing species in solution. If $K = 1$, it means competing ions and uranyl ions are bound equally. A large value of K is therefore preferred indicating that the magnetic polymer favours uranyl ions.

Another important parameter is the relative selectivity coefficient, K' , which represents the enhanced effect of imprinting on selectivity and adsorption affinity for the template onto the polymer. The K' of the magnetic-IIP against the magnetic-NIP was calculated using equation 4.9:

$$K' = \frac{K_{\text{IIP}}}{K_{\text{NIP}}} \quad (4.9)$$

Where: K_{IIP} and K_{NIP} are the selectivity coefficients of the IIP and NIP, respectively.

4.3.2.6 Reusability of the magnetic uranyl IIPs

In order to test the stability and reusability of the magnetic imprinted polymers, a 25 mL uranyl solution with an initial concentration of 2 mg L^{-1} was exposed to 50 mg of the magnetic polymers. After 45 min of extraction and equilibration, the aqueous solution was filtered and the magnetic polymer particles were transferred to another sample vial. After filtering the mixture, the filtrate was analyzed for U(VI) content while the magnetic polymer residues were regenerated by leaching out uranium with 25 mL of 1 M HCl solution at a stirring rate of 1500 rpm at room temperature for 45 min. These magnetic polymers were then used for the next rebinding studies.

4.3.3 Kinetic modelling

Kinetic modelling is important in order to gain insight into the mechanism and rate controlling steps affecting the kinetics of adsorption.

Adsorption data can be modelled using the Elovich equation, Intraparticle diffusion Weber-Morris kinetic model, the film diffusion model according to the Reichenberg equation, the film diffusion model according to Vermeulen's approximation, pseudo-first order or pseudo-second order models. The last two are the most widely used models for the adsorption of a solute from aqueous solution and were the ones used in this research.

4.3.3.1 Pseudo-first-order kinetic model

The pseudo-first-order kinetic model is given by:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \quad (4.10)$$

Where: q_t (mg g^{-1}) is the amount of adsorbed metal ion on the adsorbent at time t (min), q_e (mg g^{-1}) the amount adsorbed at equilibrium and k_1 (min^{-1}) is the rate constant of first-order adsorption.

After integration between boundary conditions $t = 0$ to t and $q_t = 0$ to q_e , equation 4.10 becomes:

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (4.11)$$

Where: q_e and k_1 can be determined from the intercept and slope of the plot, respectively. A plot of $\log (q_e - q_t)$ against t gives a straight line and the constants q_e and k_1 are obtained from the intercept and gradient respectively.

4.3.3.2 Pseudo-second-order kinetic model

Pseudo-second order mode is applied when the applicability of the first-order kinetics becomes unattainable. It is based on the sorption capacity of the solid phase. The equation of pseudo second-order is given in the equation below.

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (4.12)$$

Where: k_2 is the rate constant of second-order model. For boundary conditions $t = 0$ to t and $q_t = 0$ to q_e , equation 4.12 becomes:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \quad (4.13)$$

The plot of $\frac{t}{q_t}$ versus t should give a straight line if pseudo-second-order kinetic model is applicable and q_e and k_2 can be determined from the slope and intercept of the plot, respectively.

4.3.4 Adsorption isotherm models

Equilibrium relationships of how adsorbates interact with the adsorbent materials are generally described by adsorption isotherms. These adsorption isotherms are important for optimization of the adsorption mechanism pathways, expression of the surface properties and capacities of adsorbents (El-Khaiary, 2008; Thompson, 2001). In literature, there are many adsorption isotherms which include models like Langmuir, Freundlich, Dubinin-Radushkevich, Temkin and BET but the first two still remain the two most commonly used adsorption isotherm equations (Kinniburgh, 1986). The applicability of the isotherm equations is judged by the value of their correlation coefficients, R^2 and is also used in order to understand the extent and degree of favourability of adsorption (Treybal, 1981).

4.3.4.1 Freundlich isotherm model

The Freundlich model is an empirical equation which assumes that the adsorbent has a heterogeneous surface composed of adsorption sites with different adsorption potentials. The model equation is as follows:

$$q_e = K_f C_e^{\frac{1}{n}} \quad (4.14)$$

Where: q_e (mg g^{-1}) is amount adsorbed at equilibrium and C_e (mg L^{-1}) is the equilibrium concentration. K_f (L g^{-1}) and n are equilibrium constants and Freundlich coefficients which are temperature dependent and are related to adsorption capacity and intensity, respectively. The linearized form of the Freundlich sorption isotherm is:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (4.15)$$

A plot of $\ln q_e$ versus $\ln C_e$ gives a linear graph where coefficients K_f and n can be calculated from the intercept and slope respectively; $\frac{1}{n}$ is an indicator of adsorption effectiveness. The Freundlich coefficient, n , should have values in the range of $0 < n < 1$ for a favourable adsorption reaction.

4.3.4.2 Langmuir isotherm model

The Langmuir equation is based on a kinetic approach and assumes a uniform surface, a single layer of adsorbed material and constant temperature. The model is useful when there is a strong specific interaction between the surface and the adsorbate so that a single adsorbed layer forms and no multi-layer adsorption occurs. It also assumes that the surface is homogeneous. The Langmuir isotherm can be expressed by the equation:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (4.16)$$

Where: q_e (mg g^{-1}) is the substance amount of adsorbate adsorbed per gram of the adsorbent, q_m (mg g^{-1}) is the maximal substance amount of adsorbate per gram, b ($\text{mg}^{-1} \text{ dm}^3$) is the adsorption constant, C_e (mg dm^{-3}) is the equilibrium concentration of the adsorbate in solution. The linearized form of the Langmuir equation becomes:

$$\frac{1}{q_e} = \frac{1}{q_m b C_e} + \frac{1}{q_m} \quad (4.17)$$

A plot of $\frac{1}{q_e}$ versus $\frac{1}{C_e}$ gives a straight line and the constants q_m and b are obtained from the intercept and gradient respectively.

4.3.5 Sampling sites

The performance and potential future application of the magnetic U(VI) IIPs on the removal of hexavalent uranium from wastewater samples in the presence of other competing metal ions was tested on two types of waters. These were the acid mine drainage from Germiston and the treated wastewater effluent from Goudkoppies Wastewater Treatment Plant in Soweto. The sampling sites from which the real waters were sampled from are shown encircled in red in Figures 4.3 (b) and 4.4 (b). The Germiston area is located in the Central Rand area and is part of the Witwatersrand Basin where some 70 different ore minerals have been identified in the conglomerates. The most abundant ones include pyrite (FeS_2) and uranite (UO_2). This site is near an old gold mining tailings dump that underwent reprocessing. The other sampling site, Goudkoppies Wastewater Treatment Plant treats domestic and industrial wastewater from the City Centre and South-Eastern areas of Johannesburg before being discharged to a stream that eventually flows into Klip River. Raw water treatment at Goudkoppies involves several stages; among them are degritting, digestion and chlorination.

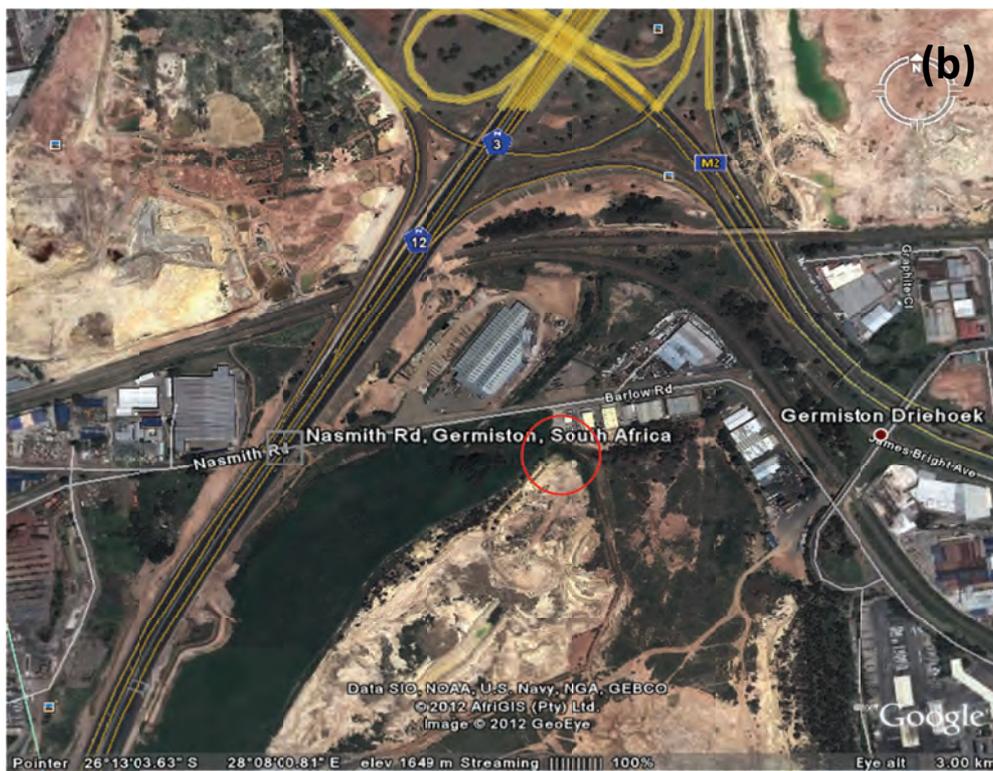


Figure 4.3: (a) Germiston site (b) Google map of the Germiston area with pointers $26^{\circ}13'07.10''$ S and $28^{\circ}08'03.79''$ E and an elevation height of 1652 m.



Figure 4.4: (a) Goudkoppies Wastewater Treatment Plant site (b) its Google map with pointers $25^{\circ}66'42.12''$ S and $27^{\circ}69'17.07''$ E and an elevation height of 1378 m.

4.3.6 Application of magnetic U(VI) IIPs to real water samples

The samples were collected, treated and stored according to published procedures (Parks *et al.*, 2004) and before the application of magnetic IIPs to real water samples, analysis of the metal content in these samples was performed with ICP-OES in triplicate. The pH and conductivity of solutions were measured in the field. The extraction of U(VI) from real water sample was then carried out in batch mode.

Mine decant sample from Germiston was buffered at pH 4 and divided into three 150 mL portions, which were spiked with 0, 5 and 10 mg L⁻¹ of uranium solution. In triplicate, 25 mL of each sample was contacted with 20 mg of magnetic IIP particles while stirring at room temperature for 45 min. The uranium adsorbed on magnetic IIP particles was then leached out with 20 mL of 3 M HCl solution at a stirring rate of 1500 rpm at room temperature for 45 min. All solutions were then filtered through a 0.45 µm filter paper and analysed for uranium content using ICP-OES.

Goudkoppies wastewater was buffered at pH 4 and divided into four 25 mL portions which were spiked with 0, 1, 5 and 10 mg L⁻¹ uranium. These solutions were then subjected to the same treatment as the AMD water sample from Germiston (described above).

4.4 Synthesis of imprinted polymers for Cr(VI) recovery

4.4.1 Synthesis of magnetic poly (4-vinylpyridine)

Prior to the synthesis of poly (4-vinylpyridine), the monomer 4-vinylpyridine was distilled at 65°C to remove the inhibitor, hydroquinone (Berkowitz *et al.*, 1958).

An amount of 2.5 mg of γ-MPS-coated magnetite was added to a volume of 28 mL of the distilled 4-vinylpyridine. This mixture was then transferred to a 50 mL volumetric flask to which 50 mg benzoyl peroxide was added with magnetic stirring. The flask was then placed into an oil bath at 85°C for 2 hours and then the temperature was elevated to 135°C where it was maintained for an hour. The whole reaction was performed under an inert atmosphere of nitrogen. The polymerization was then stopped by cooling it to 0°C. All the unreacted 4-vinylpyridine monomers were removed by washing the poly (4-vinylpyridine) with 35 mL of methanol. The free bulk poly (4-vinylpyridine) polymer was recovered by heating off the methanol solvent by use of Rotavapour II (Buchi, Switzerland).

4.4.2 Synthesis of poly (4-vinylpyridine)

The synthesis of non magnetic poly (4-vinylpyridine) followed exactly the same procedure for the synthesis of poly (4-vinylpyridine) except that γ-MPS-coated magnetite was not added.

4.4.3 Preparation of magnetic and poly (n-propyl-4 vinylpyridinium) bromide

Quaternization of magnetic and non-magnetic poly (4-vinylpyridine) was achieved by refluxing 11.34 g of magnetic and non-magnetic poly (4-vinylpyridine) in 40 mL of DMF with a slight stoichiometric excess of 1-bromopropane (10 mL). These reactions were carried out for 42 hrs at 60°C.

4.4.4 Preparation of magnetic and non-magnetic poly (n-propyl-4-vinylpyridinium) dichromate

Magnetic poly (n-propyl-4-vinylpyridinium) bromide was dissolved in 50 mL of DMF containing 0.34 g of dissolved sodium dichromate. This solution was stirred at room temperature for 2 hours. Magnetic poly (n-propyl-4-vinylpyridinium) dichromate was then obtained by driving off the excess solvent by use of a rotary vapour. The corresponding magnetic NIP was similarly synthesized except that the dichromate imprint was excluded.

4.4.5 Leaching of chromium

After polymerization has ceased, the synthesized magnetic IIPs and NIPs of chromium were ground and sieved to a particle size range of 27-53 μm range. The particles were then washed repeatedly with de-ionized water to remove all unreacted pre-polymerization reagents. The imprinted chromium was then removed by stirring 5 g of the magnetic polymers in 100 mL of 1 M HCl for 6 hours. Magnetic IIP and NIP particles were filtered through a 0.45 μm filter paper where the filtrate was analyzed for chromium content and the residue was subjected to the a fresh HCl leachant for the same period of time. This cycle was repeated several times until the chromium content detected in the filtrate was almost zero.

4.5 Optimization of parameters for Cr(VI) uptake

4.5.1 Effect of initial pH of Cr(VI) solution

The effect of pH on the adsorption of Cr(VI) onto the magnetic IIP and NIP was investigated in the pH range of 2-8. This was achieved by stirring 25 mg of the polymer particles at a stirring speed of 600 rpm in a 25 mL solution of Cr(VI) with initial concentration of 5 mg L⁻¹ for 60 min at room temperature. After 60 min, the solution was equilibrated for 10 min followed by filtration and the chromium content was then determined by FAAS.

4.5.2 Effect of the amount of the magnetic polymer

After adjusting the pH of the sample solution to pH 4, a batch adsorption was carried out in a series of 30 mL vials at room temperature. Each vial was filled with 25 mL of an initial concentration of 5 mg L⁻¹ chromium solution. The added magnetic polymer mass was varied between 5 to 120 mg. After stirring the solution for 60 minutes at a stirring speed of 600 rpm, separation of the magnetic polymers was achieved by use of a magnet. The solution was then

analysed for chromium content from which the amount adsorbed on the magnetic polymer was calculated.

4.5.3 Effect of contact time on chromium(VI) adsorption

The effect of contact time on the extraction of Cr(VI) was investigated by stirring 20 mg of magnetic IIP and NIP at room temperature in a solution containing 25 mL of 2 mg L⁻¹ of Cr(VI) at a fixed pH. The time intervals investigated were 5, 15, 45, 60 and 90 min. After each stirring time, the Cr(VI) amount was determined as described earlier.

4.5.4 Effect of initial concentration of chromium(VI) on its uptake

The effect of 25 mL of various initial Cr(VI) concentrations (2, 5, 8 and 10 mg L⁻¹) on the adsorption removal efficiency by magnetic IIP and NIP was investigated by stirring the 20 mg of the magnetic polymers at room temperature. The initial pH of the solutions was adjusted to that optimized above. After 45 min. the mixture was filtered and the filtrate was analyzed for Cr(VI) content with the FAAS.

4.5.5 Selectivity studies on the adsorption of Cr(VI) by magnetic IIP

Four point calibration standards were prepared from a mixture of four anions, namely, F⁻, NO₃⁻, SO₄²⁻ and PO₄³⁻. The concentrations used were 1, 5 and 10 and 20 mg L⁻¹. Selective adsorption of Cr(VI) onto magnetic polymers was investigated by means of binary mixtures with other anionic species which were F⁻, NO₃⁻, SO₄²⁻ and PO₄³⁻. The initial concentration of Cr(VI) and the other analyte was 2 mg L⁻¹. Twenty five millilitres of these mixtures were then equilibrated with 20 and 65 mg of magnetic IIP and NIP respectively. After adjusting the pH to 4 with NaOH and HCl, the contact time was set at 45 min and the stirring rate was 600 rpm. These experiments were performed in a batch mode and the unadsorbed concentration of each anionic species was measured using ion chromatography and AAS for the dichromate. The results obtained were used to calculate the distribution ratios, the selectivity coefficients and the relative selectivity coefficients through application of equations 4.7, 4.8 and 4.9 respectively.

4.5.6 Reusability of chromium(VI) IIP

The stability and reusability of the magnetic polymers was investigated by adding to the 50 mg of the polymer 2 mg L⁻¹ chromium(VI) solution. Other conditions used were those optimum in previous experiments. The contact was allowed for 45 min after which the mixture was filtered. The magnetic polymer residue was then stripped off the adsorbed chromium(VI) by stirring it in a 20 mL solution of 1 M NaOH for 20 min. This was followed by filtration and analysis of dichromate anions in the filtrate by FAAS. This procedure was repeated for a number of times in order to investigate the stability and reusability of these magnetic polymers.

Chapter Five: Results and Discussion

5.1 Synthesis and characterization of magnetic uranyl-imprinted polymers

5.1.1 Synthesis of the magnetite

The synthesis of magnetite by co-precipitation of the ferrous and ferric salts produced a black precipitate upon increasing of pH by addition of ammonia. The magnetic response of the magnetite towards a magnet is demonstrated in Figure 5.1.

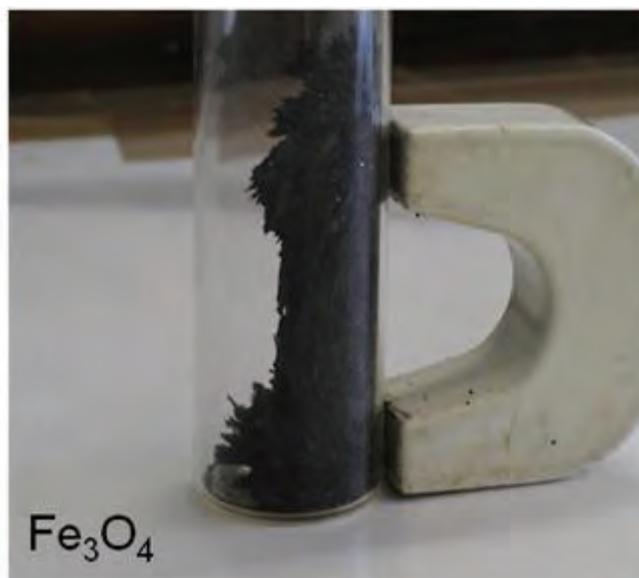


Figure 5.1: Magnetic response of magnetite.

Since this synthesis is carried out in aqueous environment, it means there is likely to be water and hydroxyl ions adsorbed on the surface of the magnetite as depicted in Figure 5.2.

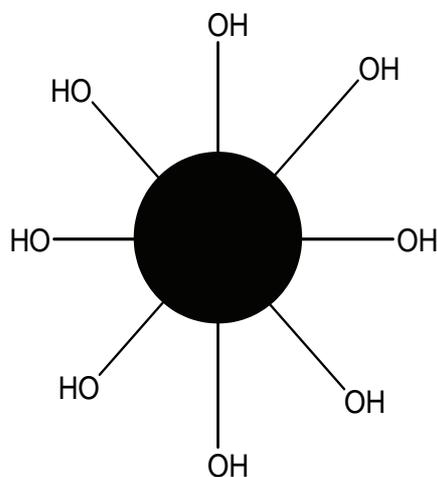


Figure 5.2: Magnetite showing the adsorbed hydroxyl ions.

5.1.1.1 Powder X-ray diffraction (PXRD) analysis

Powder X-ray diffraction was used as a diagnostic tool to check the phase of the iron oxide. In the case of magnetite, the characteristic peaks occur at $2\theta = 30.1, 35.5, 43.1, 53.4$ and 57.0° (Aguilar-Artega *et al.*, 2010). It is clear that the bulk of the particles consist mainly of Fe_3O_4 phase, Figure 5.3. It is however evident that there are some impurities in the samples as observed from peaks at $2\theta = 60^\circ$.

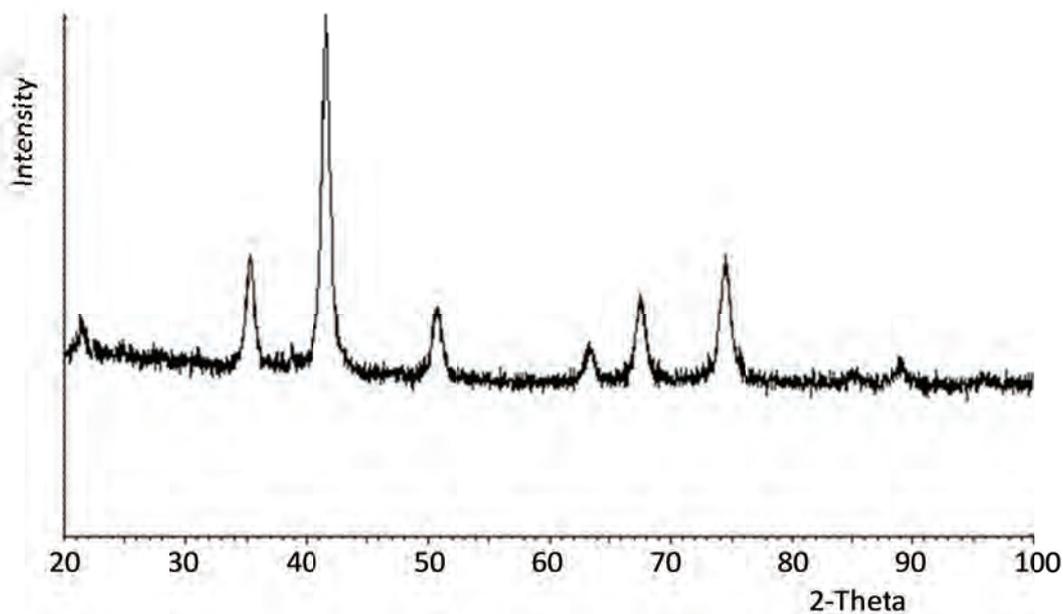


Figure 5.3: PXRD pattern for the synthesized magnetite.

The particle size of the magnetite nanoparticles, as deduced from the Scherrer equation was found to be 11.9 nm. The result is consistent and in perfect agreement with that obtained from TEM analysis (11.39 ± 2.54 nm).

The PXRD patterns of the dried sample of Fe_3O_4 from the studies of El Ghandoor *et al.* (2012) gave the crystallite size of 10 nm after application of the Scherrer formula. The other PXRD patterns of the synthesized Fe_3O_4 nanoparticles obtained by Sadeghi and Aboobakri (2012) in the 2θ region of $10\text{-}80^\circ$ displayed diffraction lines at $2\theta = 30.3, 35.4, 43.3, 57.3$ and 62.8° which were characteristic of spinel structure of Fe_3O_4 . The PXRD spectra of bare Fe_3O_4 and ethylenediamine-modified magnetic chitosan synthesized by Wang *et al.* (2011), showed six peaks at $2\theta = 30.1, 35.4, 43.0, 53.5, 57.0$ and 65.2° . After comparing the peaks to that of the database in JCPDS file (PDF No. 65-3107), the researchers concluded that the resultant magnetic iron oxide were pure Fe_3O_4 with a spinel structure.

5.1.2 γ -MPS and OA functionalization of magnetite

5.1.2.1 Functionalization of magnetite with γ -MPS

The stober-sol-gel method is the most widely used method for coating nanoparticles with silica. It relies on the use of silicon alkoxides as the source of silica matrix (Kan *et al.*, 2010).

These silica matrices are formed through hydrolysis of γ -MPS in basic alcohol/water mixtures. The silanol groups (Si-OH) will then be transformed to siloxane bonds (Si-O-Si) through condensation (Kan *et al.*, 2010). When hydrolyzed, Figure 5.4, the other end of γ -MPS with the methyl groups produced hydrophilic silanol groups that bonded covalently with the hydroxyl groups around the magnetite, Figure 5.5. The silica layer formed on the surface of the magnetite could screen the dipolar attraction between the magnetite which favours the dispersion of this magnetite in the liquid media and also protects them from leaching in acidic environments. Coating also prevented oxidation of the magnetite to maghemite in aqueous media.

Chen *et al.* (2011) used 3-methacryloxypropyltrimethoxysilane with three alkoxides which was hydrolyzed for 5 h to produce a hydrophilic end. Apart from γ -MPS, there is a wide range of coating agents that have been reported in literature. For instance, Ma *et al.* (2011) successfully encapsulated the magnetite within methacrylic acid. Qian *et al.* (2008) prepared paramagnetic magnetite/polystyrene nanocomposite by firstly modifying the magnetite nanoparticles with a Y-shaped surfactant (12-hexanoyloxy-9-octadecenoic acid).

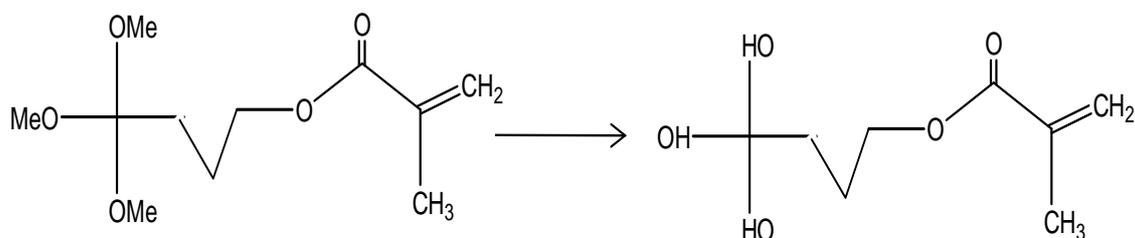


Figure 5.4: The hydrolysis of γ -MPS.

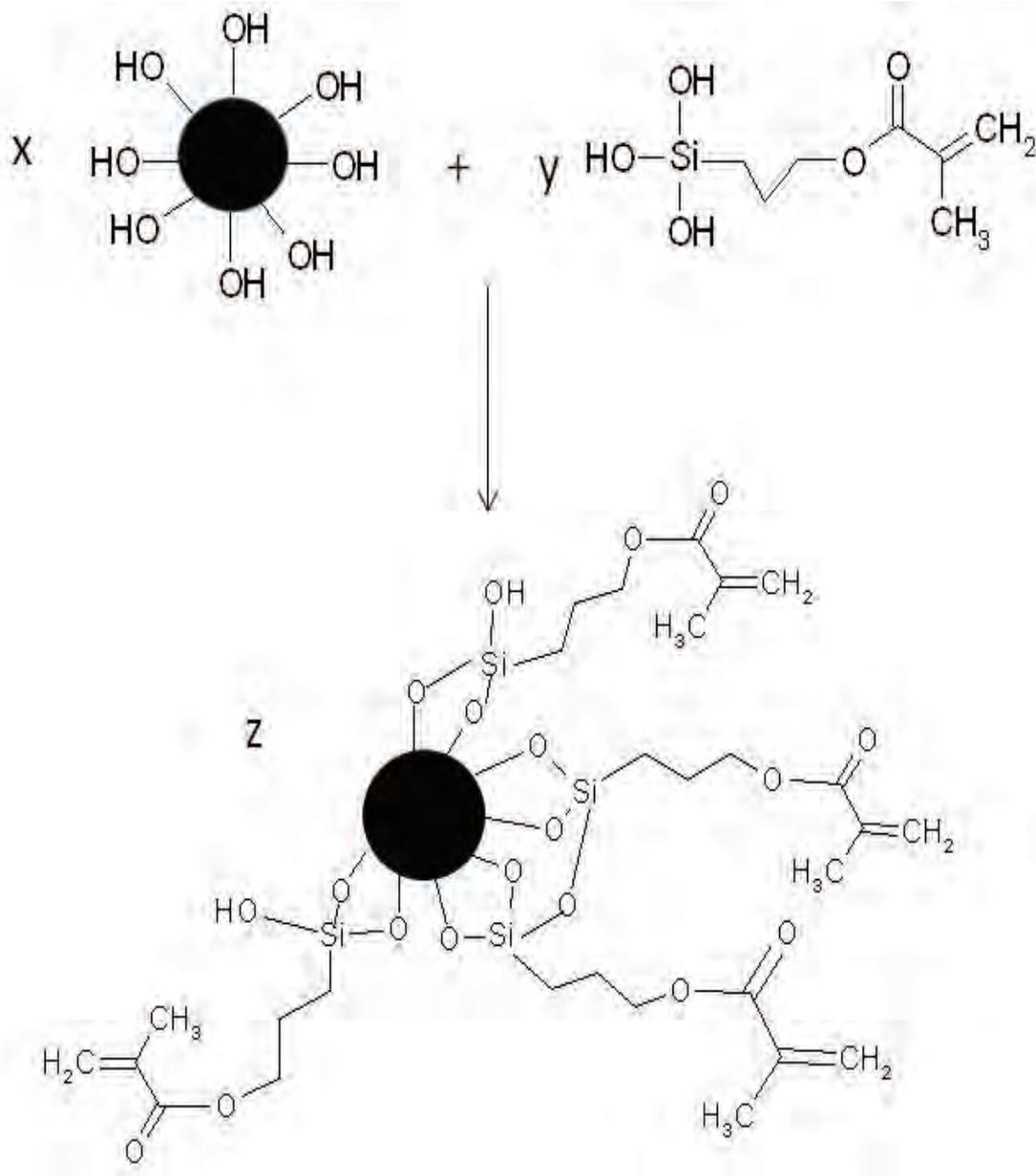


Figure 5.5: Coating of the magnetite with the hydrolysed γ -MPS.

Figure 5.6 shows a pictorial illustration of the central magnetite coated with γ -MPS.

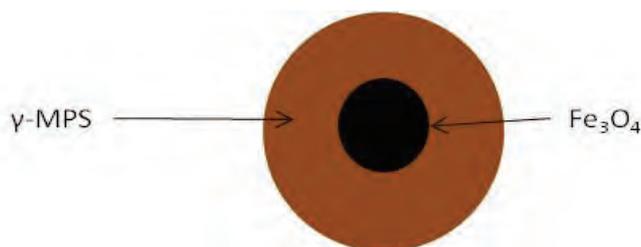


Figure 5.6: An illustration of the arrangement of γ -MPS around the magnetic core.

5.1.2.2 Functionalization of magnetite with oleic acid

Oleic acid (OA) is also another commonly used coating agent used to stabilize the magnetic nanoparticles synthesized by the traditional co-precipitation method. Some studies have proved that there is a strong chemical bond formed between the carboxylic acid and the amorphous iron and amorphous iron oxide nanoparticles (Zhang, 2006).

A structure of OA is shown in Figure 5.7. The hydrophilic carboxylate terminal will undergo charge delocalization first before it forms bidentate ligand. This ligand is shown in Figure 5.8 and its reaction with magnetite is shown in Figure 5.9.

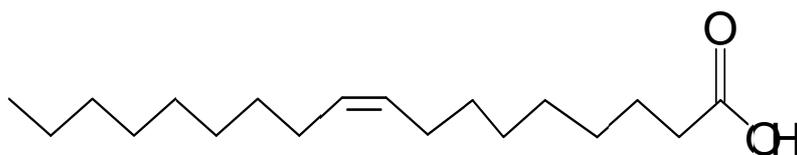


Figure 5.7: The structure of oleic acid.



Figure 5.8: Charge delocalization on the carboxylate of the oleic acid.

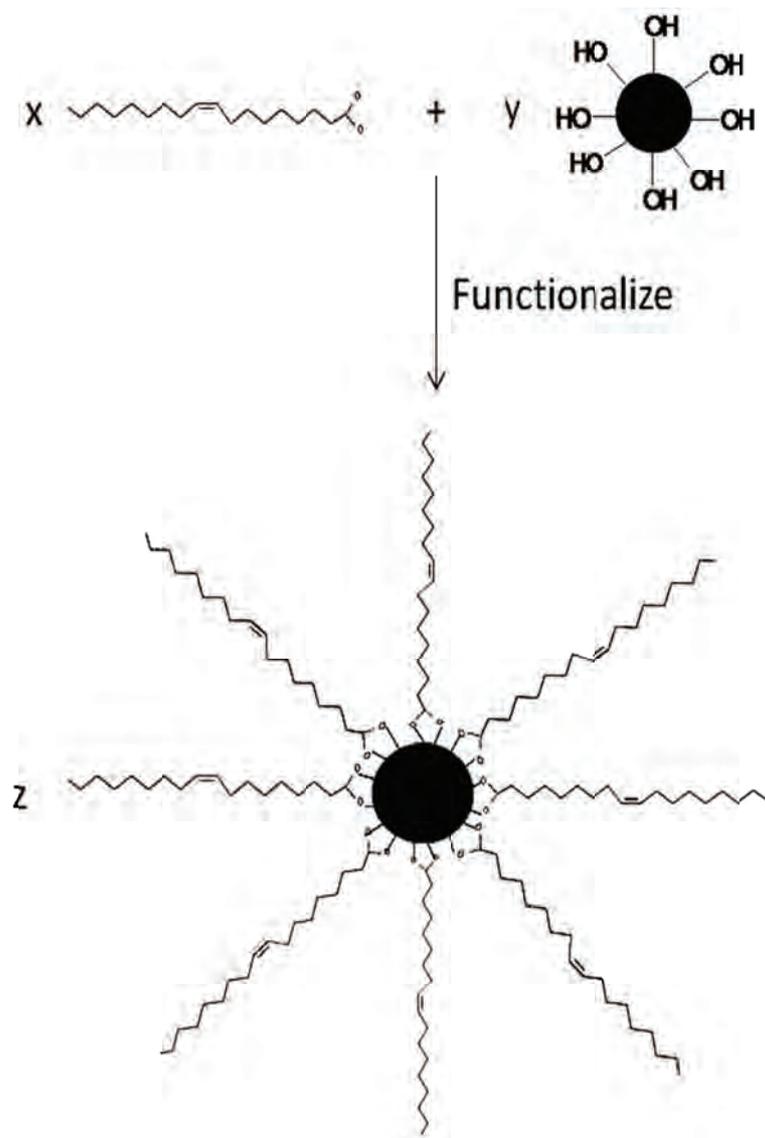


Figure 5.9: Scheme for the functionalization of magnetite with OA.

5.1.2.3 Carbon, hydrogen, nitrogen and sulphur (CHNS) analysis

Elemental analysis (CHNS) was done in order to determine the degree of coating of γ -MPS and OA on magnetite, Table 5.1. This was achieved by measuring the carbon and hydrogen content in the organic moieties.

Table 5.1: CHNS elemental analysis of coated magnetite.

γ -MPS coated				OA coated			
mass (g)	% C	% H	Ligand concentration (mmol g ⁻¹) *	mass (g)	% C	% H	Ligand concentration (mmol g ⁻¹) *
2.00	20.16	2.94	16.8		4.63	1.38	3.86
2.00	19.25	2.92	15.8	2.01	4.82	1.46	3.99
2.00	18.92	2.84	15.8	2.01	4.48	1.39	3.71

*Values for the ligand concentration were all based on the carbon content.

From values in Table 5.1 the ligand concentrations on the magnetite was found to be 16.1 and 3.82 mmol g⁻¹ for γ -MPS and OA coated magnetite respectively (The mathematical calculation is shown in the appendix section).

5.1.2.4 Diffuse reflectance spectroscopy (DRS)

Oxidation of synthesized superparamagnetic magnetite converts Fe₃O₄ to γ -Fe₂O₃ and this can be accomplished through exposure to oxygen or other oxidizing agents (Thorek *et al.*, 2006). This result in the change of the material appearance from a black-brown to a red-brown as Fe²⁺ in the magnetite lattice is oxidized (Thorek *et al.*, 2006).

From Figure 5.10, DRS peaks were observed at 443, 652 and 826 cm⁻¹. However, these peak signals were very weak due to the strong absorption of the dark magnetite samples. The colour of the iron oxide synthesized as shown in Figure 5.1, was observed to be black. This is indicative of the presence of the magnetite phase of the iron oxide.

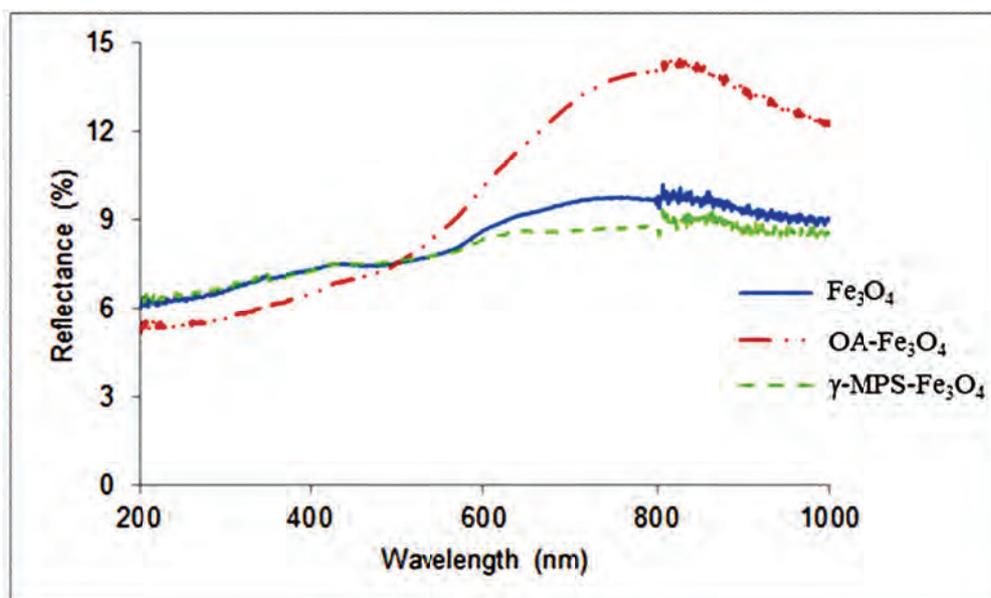


Figure 5.10: DR spectra of magnetite as well as γ -MPS and OA coated magnetite.

A few examples of different colours of iron oxides are shown in Table 5.2. However, particle size, aggregation and the presence of impurities can cause some discrepancies in the colours of the iron oxides (Torrent and Borron).

Table 5.2: Colours of different iron oxides.

Iron oxide	Colour
Magnetite	Black
Hematite	Yellowish-red
Maghemite	Dark brown

The absorption bands exhibited by the Fe oxides at UV to near IR wavelengths originate from electronic transitions within the $3d^5$ shell of the Fe^{3+} ion. Magnetite can also be identified by a unique band at 1500 nm due to Fe (II) to Fe(III) intervalence charge transfer (Scheinost *et al.*, 1998) which was however not observable in the wavelength range used in the DRS analysis.

5.1.2.5 Raman spectroscopy

Raman spectroscopy can be used to distinguish minerals like magnetite, hematite and maghemite. Both magnetite and maghemite have been used as naturally occurring magnets. Near room temperature, magnetite very slowly oxidizes to maghemite and then at higher temperatures, to hematite through a process called martitization (de Faria *et al.*, 1997). The oxidation of magnetite (Fe_3O_4) to hematite ($\alpha-Fe_2O_3$) proceeds either directly or via maghemite ($\gamma-Fe_2O_3$) (Sidhu, 1988), Figure 5.11.

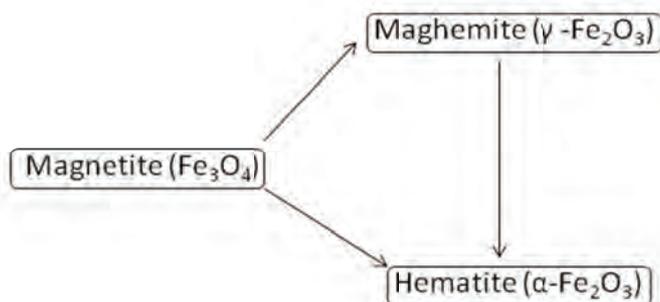


Figure 5.11: Oxidation of magnetite through two different routes.

These three phases of iron oxide (magnetite, hematite and maghemite) have very distinct bulk Raman spectra and this was used to determine the phase of the uncoated and coated iron oxide particles. The nanoparticles showed a diagnostic Raman peak at around 672 cm^{-1} which corresponds to magnetite (Tang *et al.*, 2003). Other assignments of the band positions for phase identification were compiled by Slavov *et al.* (2010) and are presented in Table 5.3. Iron oxide and γ -MPS-iron oxide under study are also included in the table together with their corresponding wavelength bands.

Table 5.3: Raman bands for magnetite, maghemite and hematite.

	Iron oxide	Wavelengths (cm^{-1})
Literature	Fe_3O_4 (magnetite)	193, 306, 538, 668
	$\gamma\text{-Fe}_2\text{O}_3$ (maghemite)	350, 500, 700
	$\alpha\text{-Fe}_2\text{O}_3$ (hematite)	225, 247, 299, 412, 497, 613
Observed	Iron oxide	667
	γ -MPS-iron oxide	670, 1400, 1600

The presence of the strong peaks around 667 cm^{-1} in Figures 5.12, 5.13 and 5.14 indicated that the phase of the iron oxide present was magnetite (Fe_3O_4).

According to Wang *et al.* (1990), all carbon systems show only a few prominent bands, no matter the final structure, and these intense bands occur between $1000\text{-}2000\text{ cm}^{-1}$. In this work, the carbon system used was from γ -MPS, which is an organic moiety, had a lot of carbon atoms. The exact peaks of the carbon peaks in the Raman spectrum for this γ -MPS were identified at 1400 cm^{-1} and 1600 cm^{-1} .

However, the same peaks, but of low intensity, were observed in the unmodified magnetite. This was unexpected and can be attributed to some organic contamination. It can be therefore concluded that the synthesized iron oxide was magnetite and it remained in this phase even in γ -MPS- Fe_3O_4 as evidenced by the presence of the 670 cm^{-1} band. This might have been a due to the use of a nitrogen protective layer purged for 10 minutes during functionalization which prevented oxidation of the magnetite.

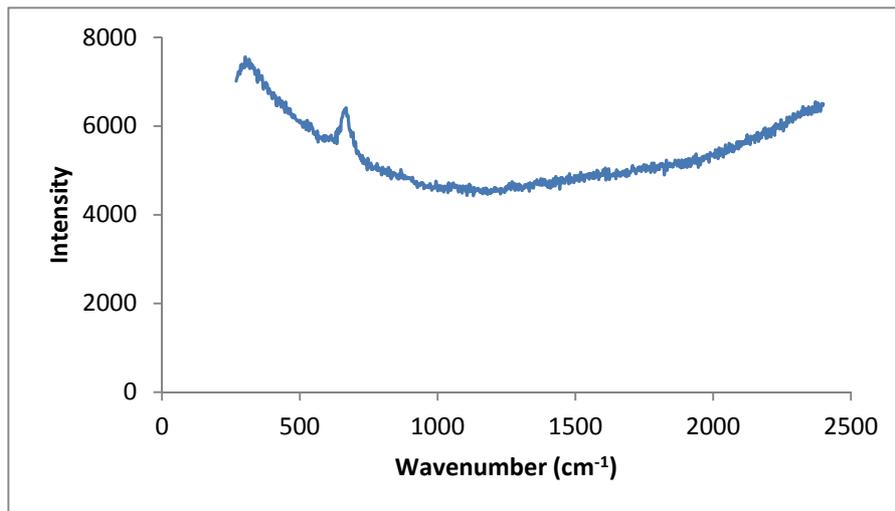


Figure 5.12: Raman spectrum of pure magnetite.

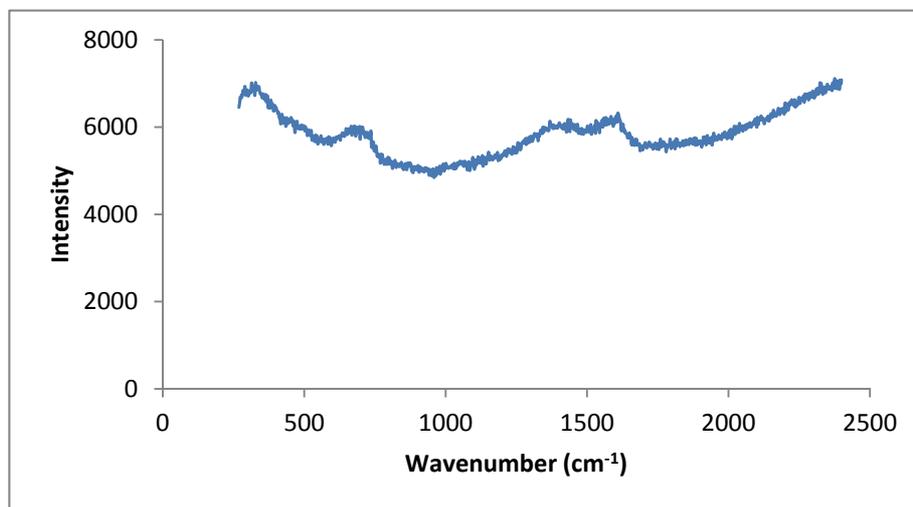


Figure 5.13: Raman spectrum of the unmodified magnetite.

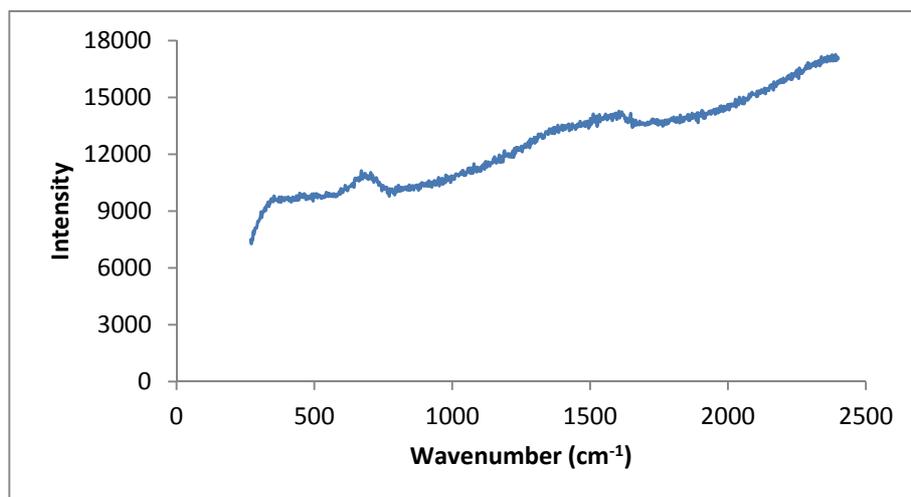


Figure 5.14: Raman spectrum of the γ -MPS modified magnetite.

5.1.2.6 Transmission electron microscopy (TEM) analysis

The prominent large black spots on the TEM image, Figure 5.15 (a), indicate that the particles have a tendency of agglomerating. This is especially so when they are synthesized in aqueous medium. One of the ways to stabilize the magnetite is by functionalizing it with a coating agents and surfactants. In Figure 5.15 (b), the coating agent was γ -MPS whose hydrophilic silanol reacted with the hydroxyl groups around the magnetite. The other end of the γ -MPS, the hydrophobic end, contained a double which made it possible for polymerization to occur. The agglomeration of the coated magnetite, after coating, was still evident though to a lesser degree. It was also observed that the synthesized particles were mostly spherical in shape. When they are coated with silica, the magnetite particles still retained their spherical shapes.

From the micrograph of Fe_3O_4 obtained by El Ghandoor *et al.* (2012), it was seen that spherically shaped particles with a narrow size distribution with mean diameter of 10.59 nm were obtained. In another study by Qian *et al.* (2008), it was revealed that the magnetic particles were dispersed very well, with an average diameter of 10 nm. Nanoparticles prepared by coprecipitation of a mixture of ferric and ferrous salt solutions, of $\text{Fe}(\text{NO}_3)_3$ and FeSO_4 added to 1M NaOH solution of ethanol and water (1:1, v/v) and gave a mean particle size of 5.0 nm with a standard deviation of 0.2 (Roca *et al.*, 2009).

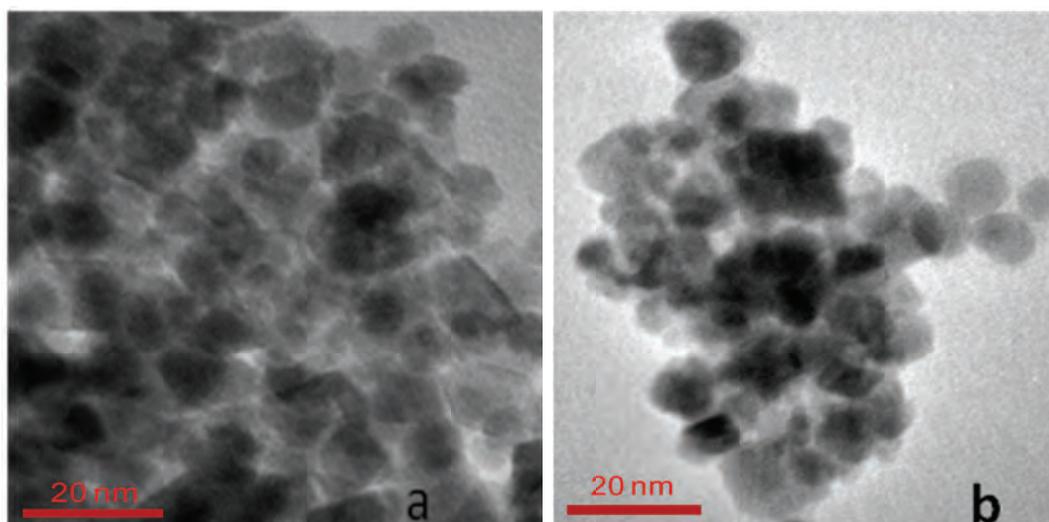


Figure 5.15: Transmission Electron Micrographs of (a) uncoated and (b) γ -MPS coated magnetite.

5.1.2.7 Size distributions

For the uncoated magnetite, a total of 237 particles were measured from four different TEM images to get the particle size distribution, Figure 5.16. It was found that the mean diameter of the uncoated magnetite was 11.39 ± 2.54 nm. This diameter was consistent with that found by Lu and Forcada (2006) who obtained a mean diameter of 10 nm after synthesizing their magnetite by co-precipitation. Pan *et al.* (2011) also obtained a mean diameter of 10 nm in

their study. The curve in Figure 5.16 is skewed to the right of the mean implying that most of the particles were having a greater diameter than the mean. This can be attributed to the agglomeration of the superparamagnetic particles.

For the γ -MPS coated magnetite, a total of 110 particles were measured from 8 TEM images for particle size distribution, Figure 5.17. The mean size diameter of the γ -MPS coated magnetite was found to be 13.35 ± 1.36 nm. The increase in diameter supports the idea that magnetite was coated with γ -MPS.

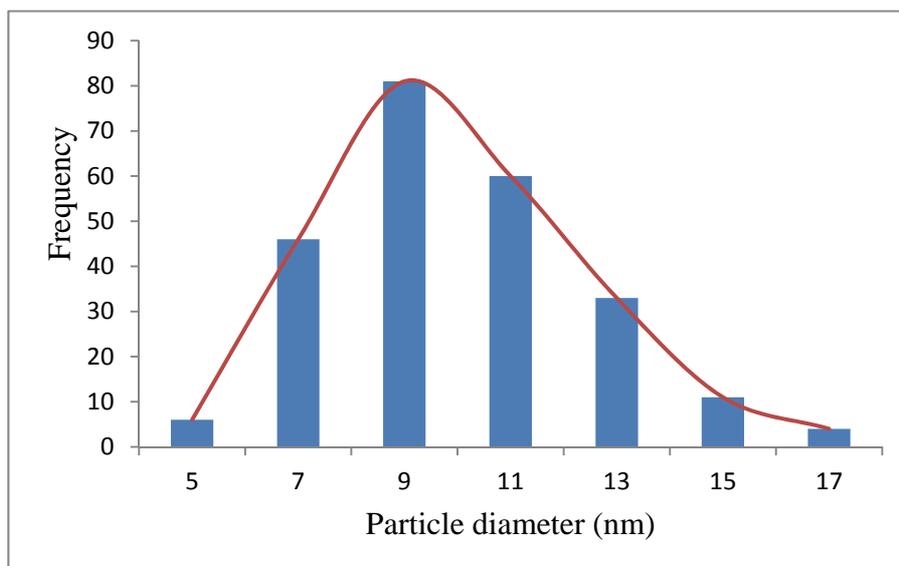


Figure 5.16: Particle size distribution of the uncoated magnetite.

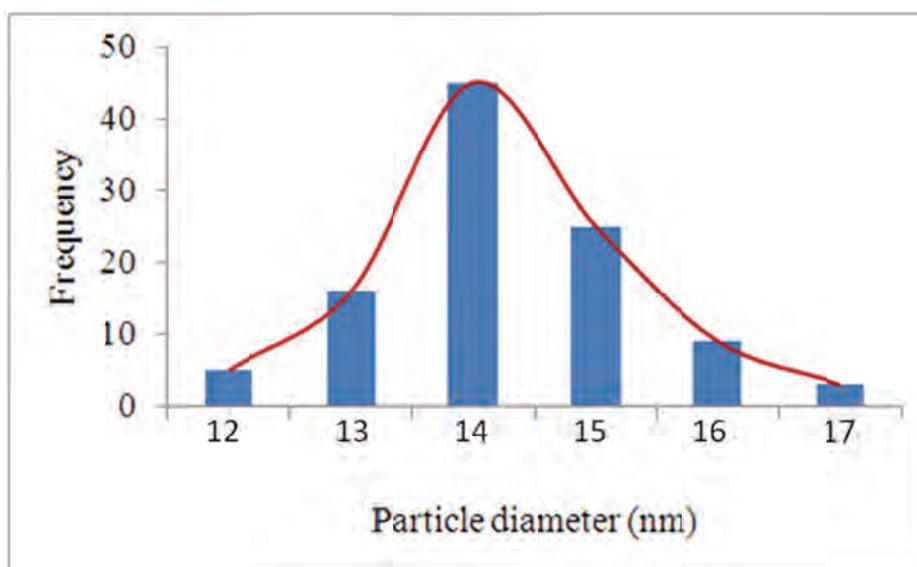


Figure 5.17: Particle size distribution of the coated magnetite.

5.1.2.8 Fourier-transformed infra red (FTIR) analysis

Fourier-transformed infra red results for both the uncoated and γ -MPS coated magnetite are shown in Figure 5.18. Figure 5.18 (a) depicts the IR spectrum of the synthesized magnetite. According to Roonasi (2007), the broad bands around 570 and 360 cm^{-1} correspond to stretching and bending vibrations of Fe-O bonds typical for the crystalline lattice of magnetite. The band at 483 cm^{-1} from Figure 4.27 (a) can be assigned to the bending vibrations of the Fe-O bonds. It is associated with the torsional vibration modes of the magnetite Fe-O bonds in octahedral sites. The lower band of 360 cm^{-1} was not able to be assigned because all the spectra obtained in this work were from 400 to 4000 cm^{-1} .

For the γ -MPS coated magnetite spectrum in Figure 5.18 (b), the shift at 1104 cm^{-1} can be attributed to the stretch of Si-O-Si, indicating the formation of silica film on the magnetite. The success of functionalization can also be observed by the presence of the C=O band at 1716 cm^{-1} , from the carboxylate of γ -MPS.

Ma *et al.* (2011) used FTIR spectroscopy for the determination of the chemical structure of Fe_3O_4 - γ -MPS. They identified that both Fe_3O_4 and Fe_3O_4 - γ -MPS had a characteristic peak of Fe-O at a stretching frequency of 586 cm^{-1} . Besides, they observed a strong stretching vibration of Si-O-Si at 1089 cm^{-1} for Fe_3O_4 - γ -MPS. Their conclusion from the two observed bands was that γ -MPS was successfully grafted onto the surface of magnetite. In another research, Qian *et al.* (2008) attributed the bands at 582 and 437 cm^{-1} to correspond to the vibration of $\text{Fe}^{2+}\text{-O}^{2-}$ and $\text{Fe}^{3+}\text{-O}^{2-}$ respectively. The same strong absorption bands appearing in all functionalized magnetic polymers were ascribed to Fe_3O_4 by Nan *et al.* (2010). These bands were observed at around 570 cm^{-1} . In the studies conducted by Sadeghi and Aboobakri (2012), the FTIR spectrum of Fe_3O_4 nanoparticles showed, among others, an absorption peak

at 577 cm^{-1} which they attributed to the Fe-O vibration frequency. In general, the bands that occur between 560 and 660 cm^{-1} are associated with the metal-O stretching vibration (Wang *et al.*, 2011).

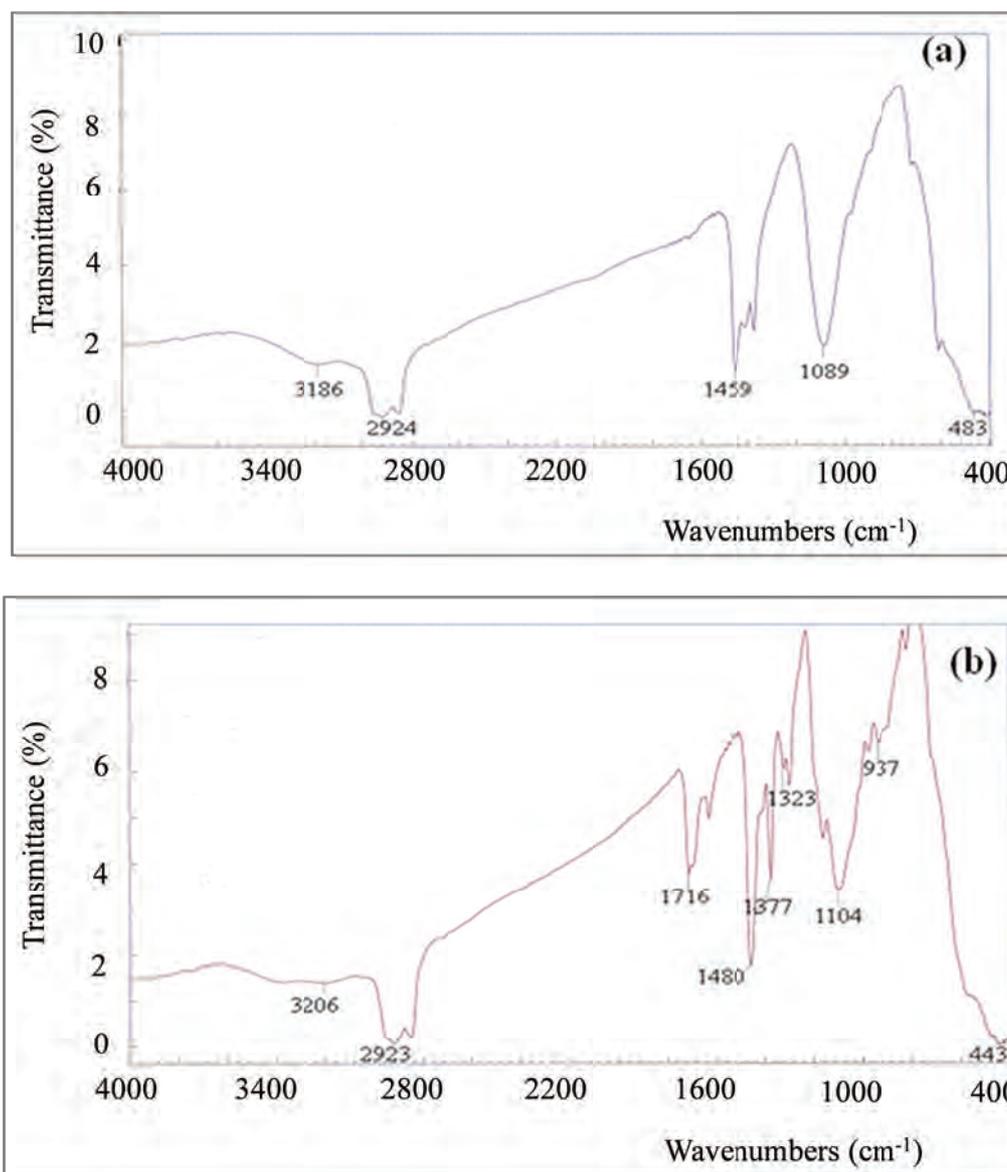


Figure 5.18: FTIR spectra of (a) uncoated magnetite and (b) γ -MPS coated magnetite.

One striking feature of the FTIR spectrum of OA- Fe_3O_4 is the absence of the C=O stretching frequency, Figure 5.19. This was expected to be present since from the structure of oleic acid, Figure 5.7, it can be seen that the carbonyl group is present. This therefore implies that there was a special type of interaction between the magnetite and the oleic acid coating agent. The magnetite, as seen from its structure in Figure 5.2, has hydroxyl groups around it and it was expected that the type of interaction of it and oleic acid be esterification. But by charge delocalization of the carboxylate, Figure 5.8, a bidentate ligand was formed and the scheme for the interaction of OA and magnetite is shown in Figure 5.9. The two bands between 2900 and 2800 cm^{-1} attributed to the asymmetric CH_2 stretch and the symmetric CH_2 stretch of the oleic acid.

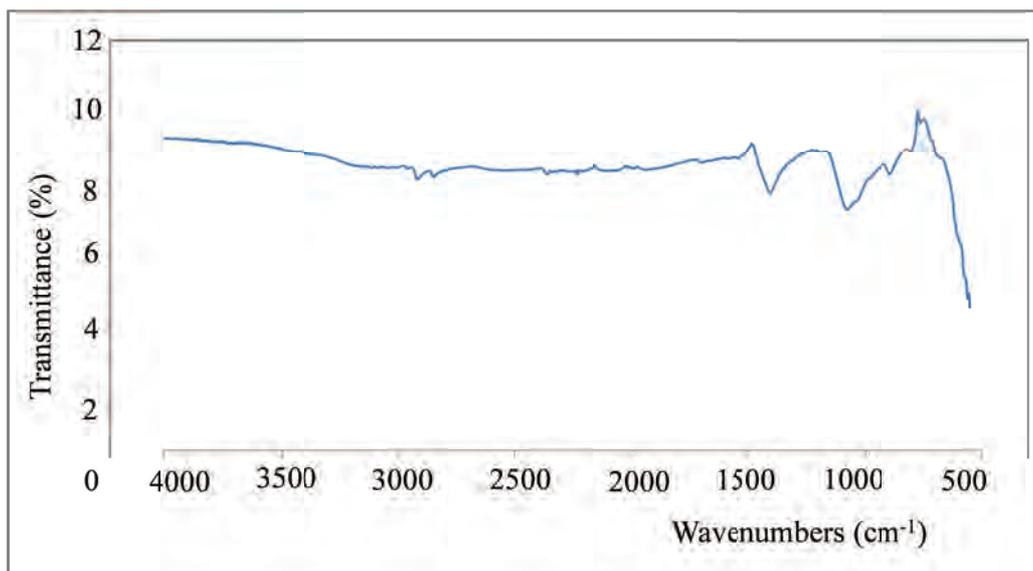


Figure 5.19: FTIR spectrum of OA-Fe₃O₄.

5.1.3 Magnetic polymer synthesis

Both the bulk and the precipitation polymerization follow the same mechanism shown in Figure 5.20. In this mechanism, 4-vinyl pyridine (4-VP) and salicylaloxime (SALO) have a direct interaction with the uranyl in the pre-polymerization step. SALO bonds to the uranyl cation through co-ordination with the lone pair of electron on the N and O atoms. 4-VP also bonds co-ordinatively through the lone pair of electrons on its N atom.

γ -MPS-Fe₃O₄ or OA-Fe₃O₄ is added to the pre-polymerization mixture before the actual polymerization is effected. Also added is the cross-linker ethylene glycol methacrylate for structural rigidity.

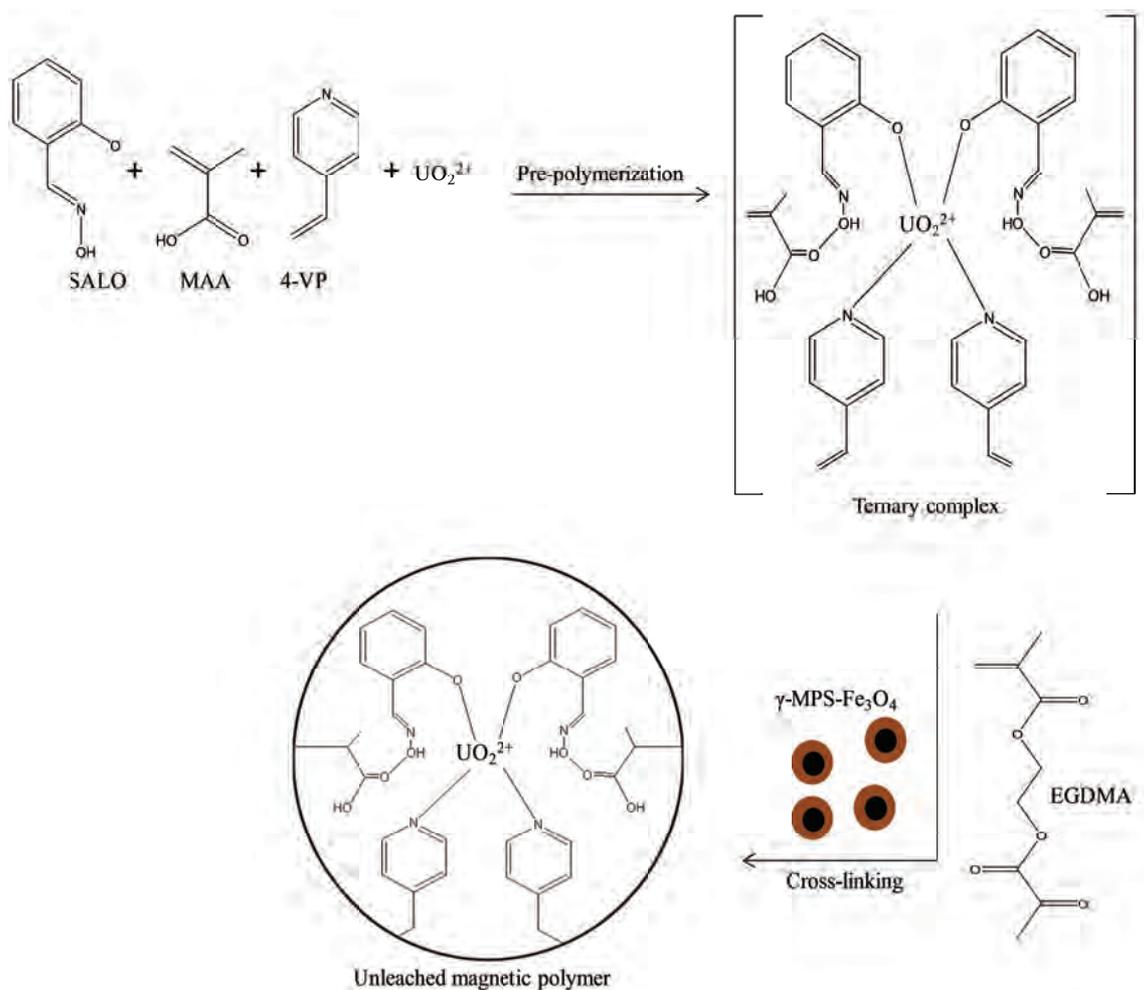


Figure 5.20: Polymerization on the γ -functionalized Fe_3O_4 particles.

The difference between bulk and precipitation polymerization was only in the amount of the porogenic solvent, 2-methoxyethanol. For precipitation polymerization 100 mL was used whilst 10 mL was used for bulk polymerization, Figure 5.21.

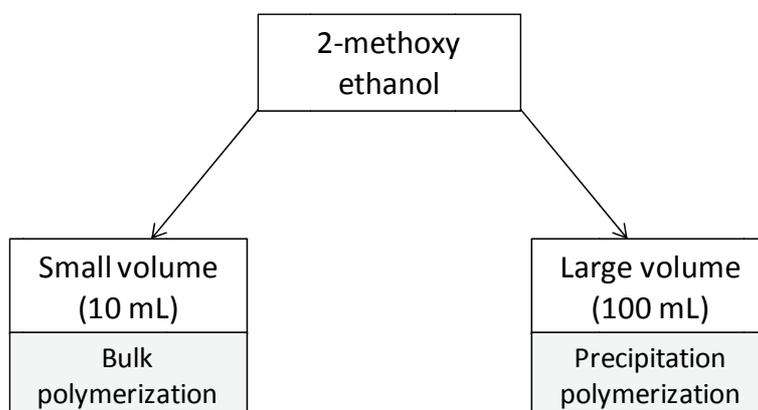


Figure 5.21: Volumes of the porogenic solvent used to effect bulk and precipitation polymerization.

5.1.4 Leaching analysis

Figure 5.22 shows the leaching of the uranyl from the magnetic polymer matrix.

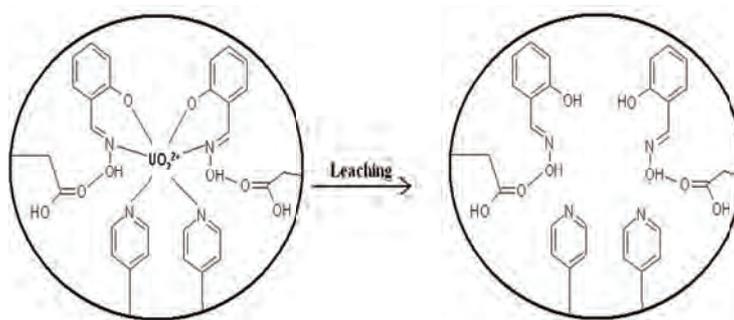


Figure 5.22: The leaching of the uranyl ion from the magnetic polymeric matrix.

The results in Figure 5.23 and 5.24 show the expected decrease of the amount of leached uranyl from some selected magnetic polymers over time. This trend was observed for both the bulk and precipitate polymers. However, there was a parallel unwanted leaching of the embedded magnetic core from the polymers. This was so pronounced for those polymers leached with 1 mol dm^{-3} HCl. In their research, Singh and Mishra (2009) had the same observation that the HCl had a greater percent removal of uranyl ion as compared to the NaHCO_3 . On the other hand, 1 mol dm^{-3} NaHCO_3 showed that it was a weak leachant towards the washing away of the magnetic core and this was desirable. However, it is also observed that the leaching of the uranyl ion was again weak with this leachant. This is undesirable as the uranyl might bleed out when the polymers are being applied to real environmental water samples.

It can also be noted that bulk polymers tended to lose more of both the uranyl as well as the magnetite than those from precipitation polymerization. This could be attributed to the crushing of the polymers in bulk polymers.

Sadeghi and Aboobakri (2012) synthesized aminopropyl triethoxysilane on functionalized silica coated Fe_3O_4 nanoparticles. This was done in the presence of a uranyl ion as a template. Finally, the uranyl was washed with 0.1 M EDTA solution for its complete removal to form an imprinted polymer selective of uranyl. Singh and Mishra (2009) used exactly the same ternary monomers as those used in this work. After crosslinking, they went further to even optimize the leachants where they used HCl, HNO_3 , NaHCO_3 , Na_2CO_3 and H_2SO_4 at various concentration.

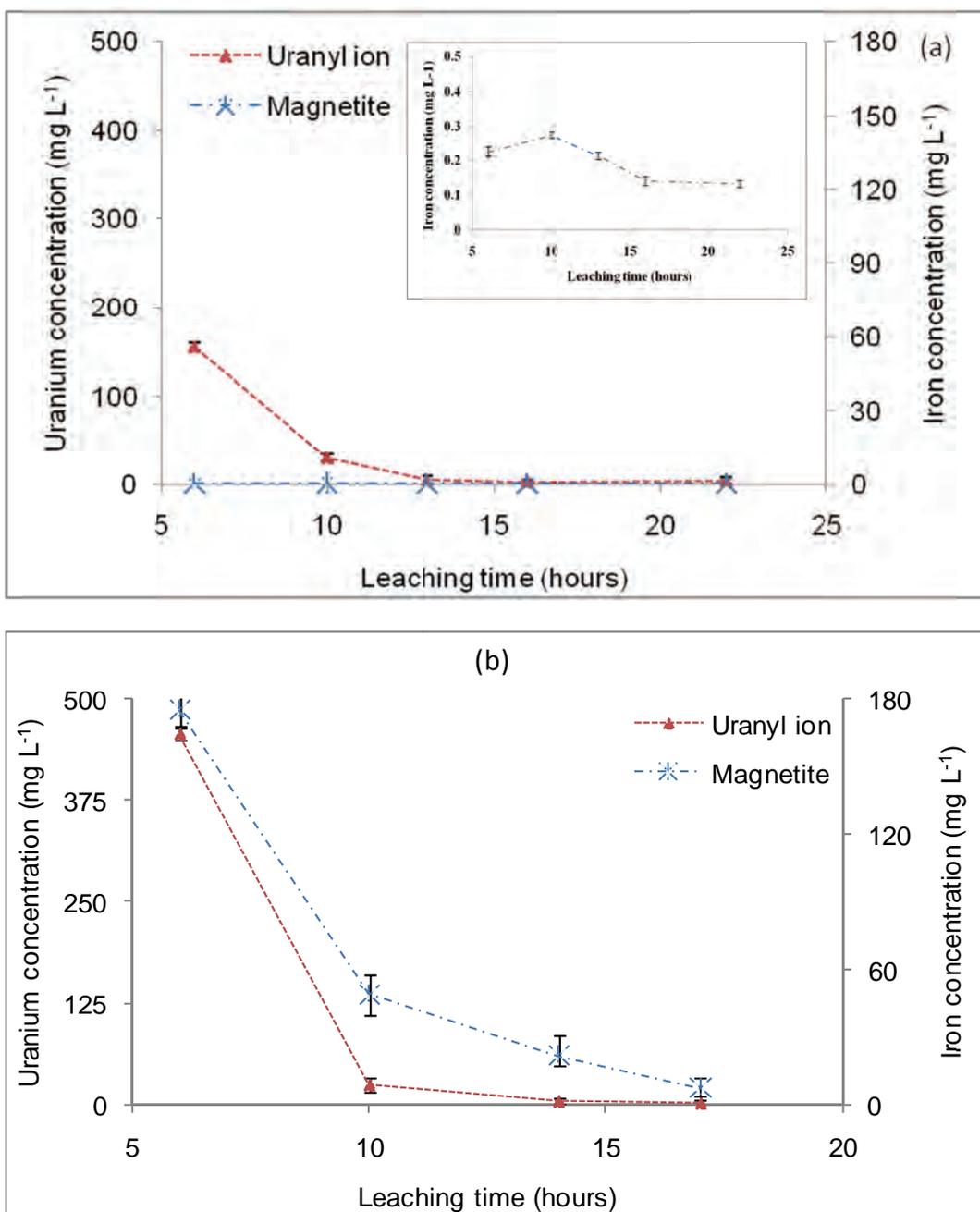


Figure 5.23: Polymers leached with 1 mol dm⁻¹ NaHCO₃: (a) bulk magnetic IIP (With the magnetite leaching expanded in the insert) (b) precipitate magnetic IIP.

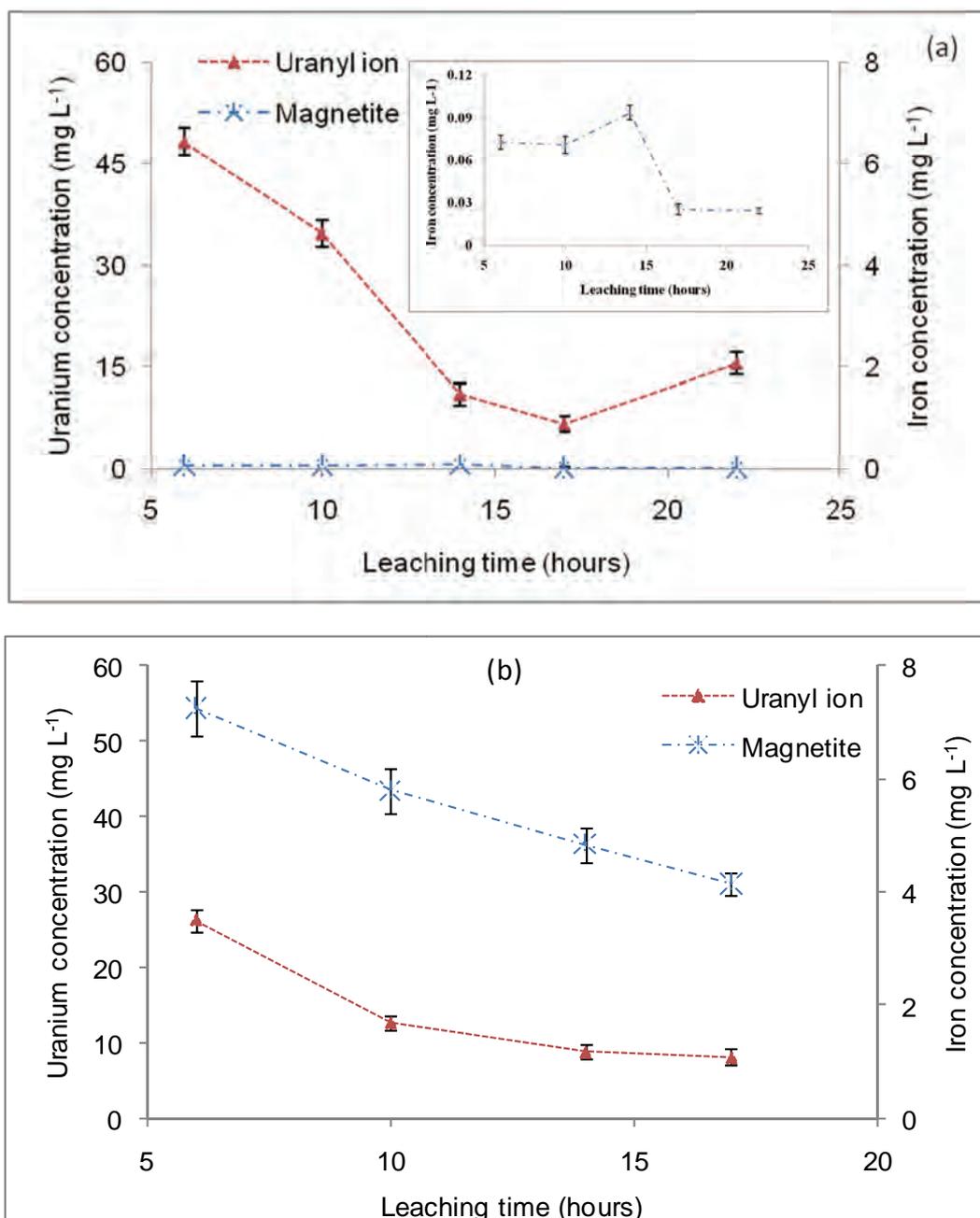


Figure 5.24: Polymers leached with 1 mol dm⁻¹ HCl: (a) bulk magnetic IIP (With the magnetite leaching expanded in the insert) (b) precipitate magnetic IIP.

Another concern was the possible problem of swelling and shrinkage of the magnetic polymers. This had a potential of causing slow bleeding of the residual templates embedded deep in the polymer matrix.

According to Sellergre (2003), the unextracted template may act as a nucleation site for template cluster formation. Also, since the solvating properties of the media are changing during polymerization, the template may again form clusters which would then be the actual species imprinted. It is therefore important to carefully determine the recovered template and to verify its identity.

5.1.4.1 Atomic force microscopy (AFM)

Imaging of unleached magnetic IIPs using tapping mode AFM proved difficult, as the tip was repelled from the surface it was supposed to image. The encircled black spots highlighted in the optical view of the magnetic IIP in Figure 5.25 are the magnetic particles responsible for this repulsion. However, imaging of the leached magnetic polymers was successful. This was made possible by the fact that some magnetite was lost during leaching hence the residual magnetite did not have sufficient power to repel the AFM probing tip.

Figures 5.26 and 5.27 are the AFM images of $20\ \mu\text{m}^2$ magnetic IIPs leached with 1M NaHCO_3 and 1M HCl solutions respectively. From the two Figures and the surface roughness data in Figure 5.29, it can be concluded that HCl was stronger leachant than NaHCO_3 . Figure 5.30 shows a three dimensional AFM image of NaHCO_3 leached polymer and it clearly shows the pores formed by the leaching of the uranyl ions from the polymer surface.

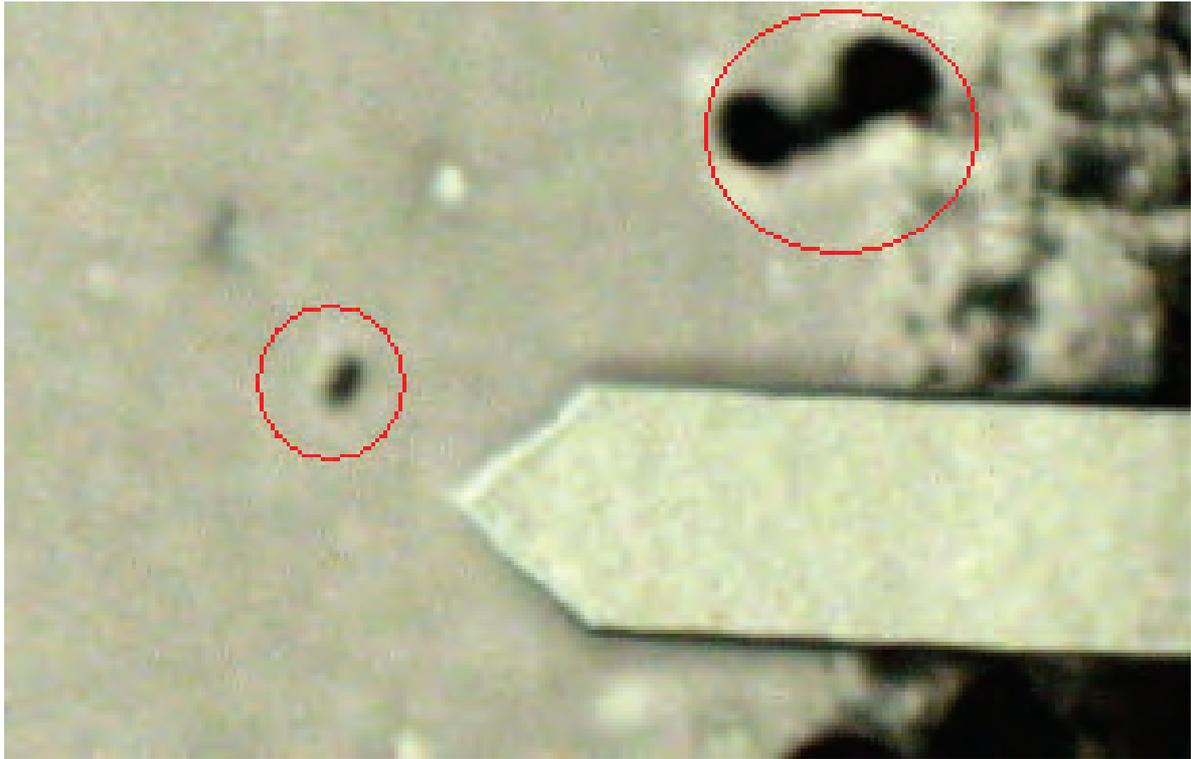


Figure 5.25: Optical view of magnetic IIP with an AFM tip of width ~25 micrometres.

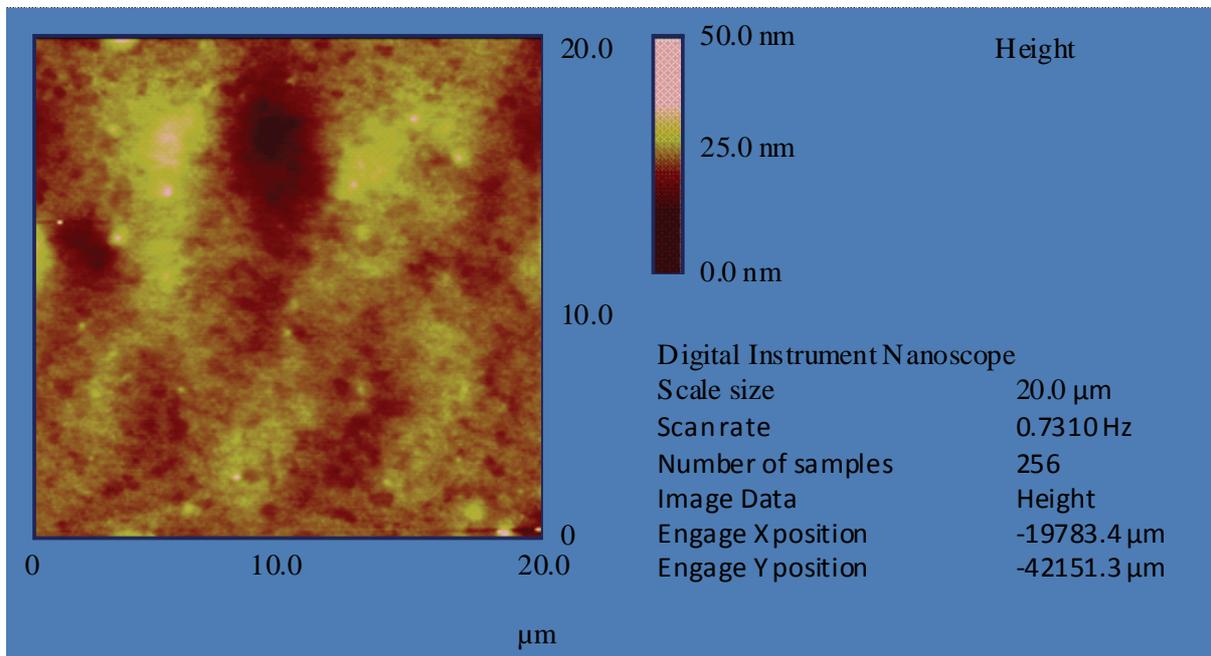


Figure 5.26: AFM image of NaHCO_3 leached magnetic IIP.

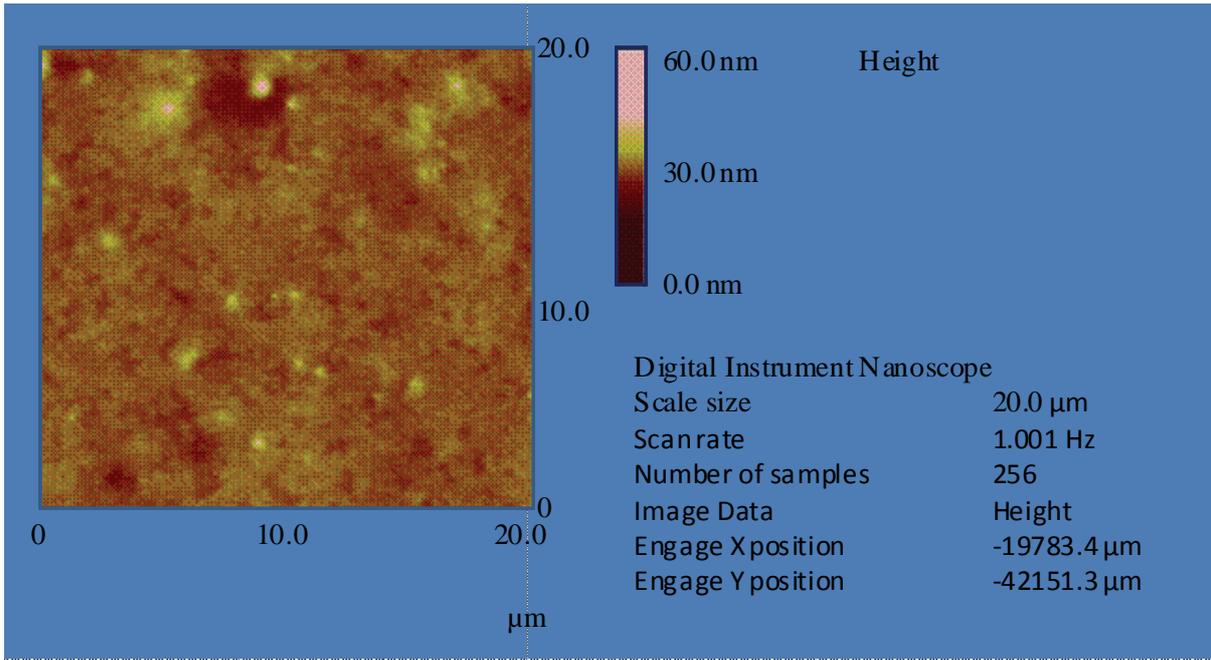


Figure 5.27: AFM image of HCl leached magnetic IIP.

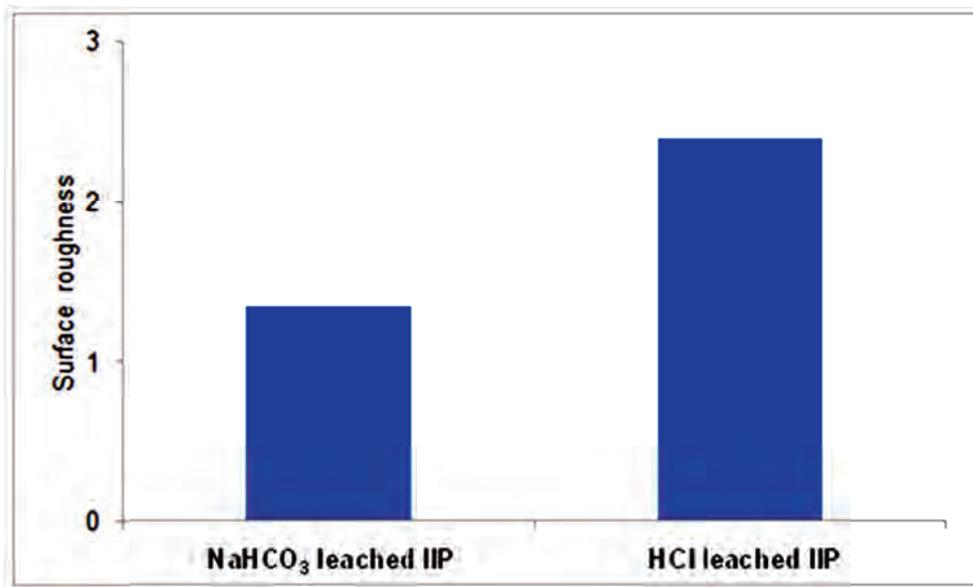


Figure 5.28: Image roughness of the NaHCO₃ and HCl leached magnetic IIPs.

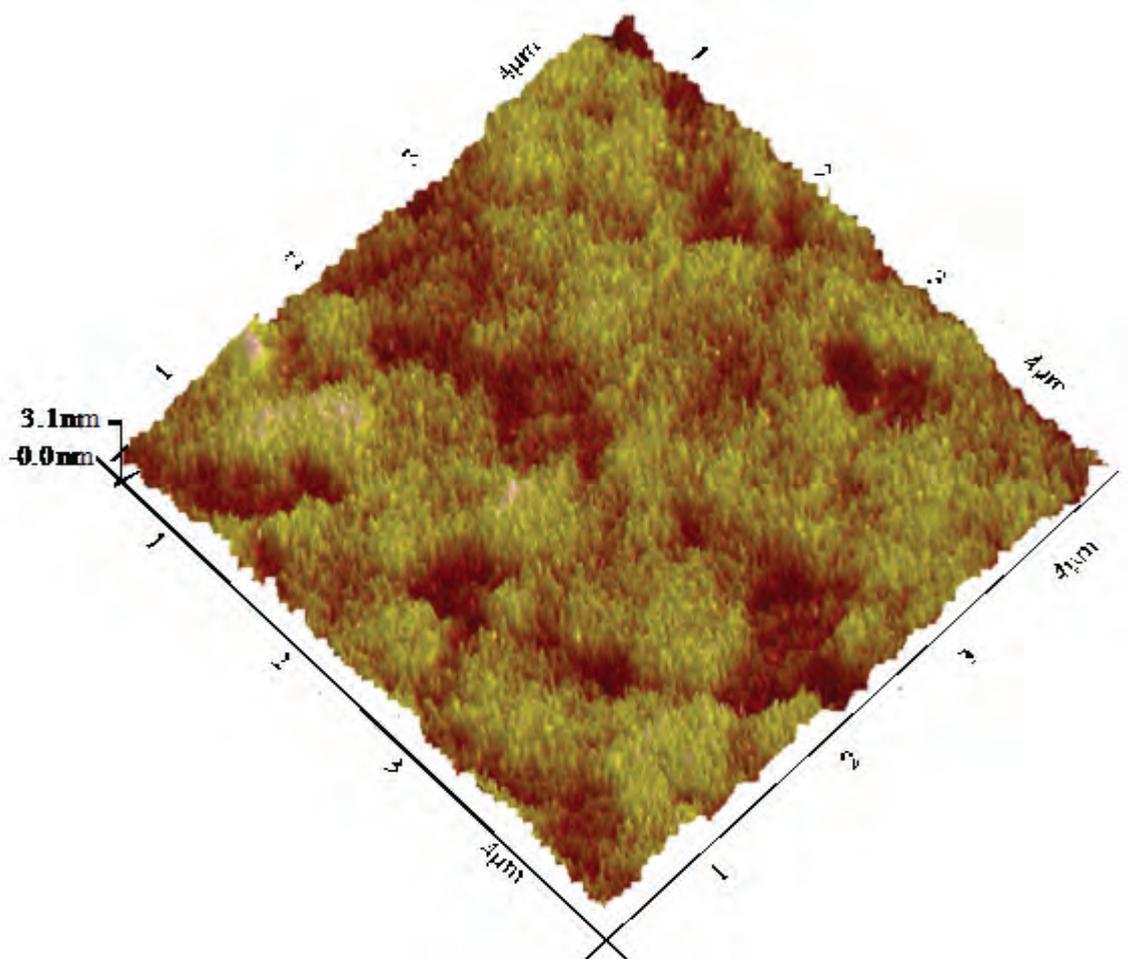


Figure 5.29: A three dimensional AFM image of NaHCO_3 leached polymer.

5.1.4.2 Brunauer, Emmett and Teller (BET) surface area analysis

Typical BET surface area measurement is given in Figures 5.30. The results demonstrated that there was an increase in the surface area of the magnetic polymers as a result of leaching action. The bulk unleached IIP had a measured surface area of $8.8 \text{ m}^2 \text{ g}^{-1}$ whilst that of the corresponding HCl and NaHCO_3 leached were increased to 88.1 and $65.2 \text{ m}^2 \text{ g}^{-1}$ respectively. These values are single point surface area measured at $p/p_o = 0.2998$. The results show consistence with the other characterization techniques, like the AFM results. These results show that the leaching with HCl resulted in magnetic polymers with a greater surface area. This is because there was a greater leaching of the uranyl from the polymer as well as the magnetic core as supported by the EDS results. The removal of these two ions left some voids which enhanced the surface area, because these pores became available for the nitrogen adsorption in the BET analysis. On the other hand, leaching with NaHCO_3 did not remove the uranyl as well as the magnetite completely. The implication of this is that the BET surface area was kept low because some of these two ions are still much present and embedded in the polymer matrix of the magnetic IIPs. The monomolecular layer volume, v_m and BET constant, c , for the bulk polymers were calculated from the slopes and intercepts of such plots such as in Figure 5.30 and the results are summarized in Table 5.4.

As a comparison, imprinted polymer nanospheres for uranium prepared by complexing uranyl ion onto quinoline-8-ol functionalized 3-aminopropyltrimethoxysilane modified silica nanoparticles by Milja *et al.* (2011), had BET surface areas of 134.69 and 188.87 $\text{m}^2 \text{g}^{-1}$ for the IIP and NIP respectively. This was evidently higher than the surface areas obtained in this research and was probably due to the strength of the monomer-template interaction and/or the strength and type of the leachants used. However, Ahmadi *et al.* (2010) found a BET surface area of 18.5 $\text{m}^2 \text{g}^{-1}$ for the unleached polymer particles. As expected, the porosity changed after the removal of uranyl ions from the IIP particle to 33.2 $\text{m}^2 \text{g}^{-1}$ which was far less than what was obtained in our studies. They prepared their adsorbent by copolymerizing of a ternary complex of uranyl ions with styrene and divinylbenzene.

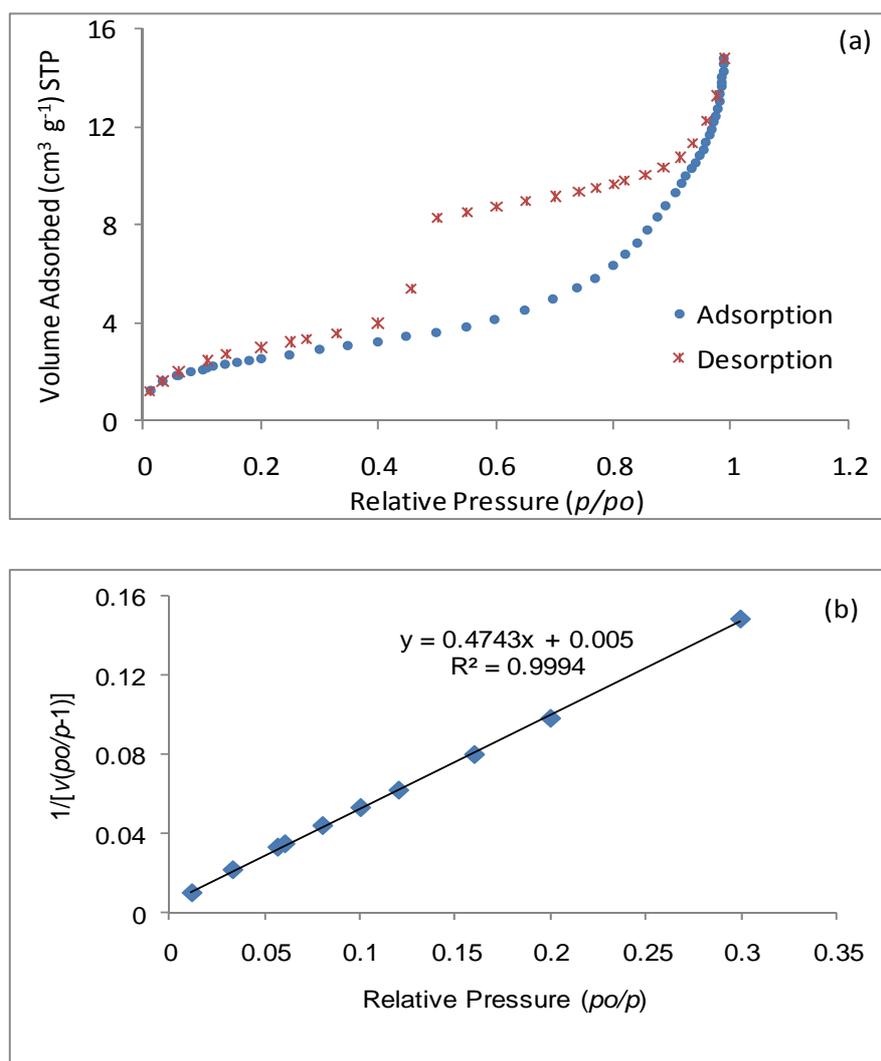


Figure 5.30: (a) The nitrogen adsorption-desorption isotherms for the unleached bulk magnetic IIP and (b) its corresponding BET plot.

Table 5.4: BET surface areas and constants for the bulk magnetic IIPs.

	BET surface area (m ² g ⁻¹)	v_m	C
Unleached magnetic IIP	8.8	2.09	94.86
HCl leached magnetic IIP	88.1	2.10	95.20
NaHCO ₃ leached magnetic IIP	65.2	15.43	129.6

5.1.4.3 Fourier-transformed infra red (FTIR) analysis

Figure 5.31 shows three spectra of the unleached IIP, leached IIP as well as the NIP of magnetic bulk polymers. The close similarities in these three spectra point to the fact that these three magnetic polymers have the same structural backbone. In all these magnetic polymers, it should be noted that EGDMA was used in excess for structural rigidity. Again, all these magnetic polymers were prepared using 2-methoxyethanol, which indicates that these magnetic polymers have similar polymeric matrices.

The absorption peaks at 1455-1470 cm⁻¹ and 1350-1493 cm⁻¹ may be assigned to C=N groups of salicylaldoxime in magnetic IIP and NIP. There was an observable change in C=N stretching frequency to higher region in the leached magnetic polymer and this proved the successful removal of uranyl ion from the magnetic polymer. Singh and Mishra (2009) synthesized similar polymers selective of uranyl though they were not magnetic. They also found similar frequency bands at 1456-1460 and 1359-1391 cm⁻¹ for the IIP (leached and unleached) and the NIP.

Salicylaldoxime (SALO) was used as one of the functional monomers but it should be borne in mind that it was not chemically bound in the magnetic polymer matrix. It is instead trapped inside the magnetic polymer during the polymerization reaction. This is the case for both the bulk and the precipitation routes. Since SALO plays a role of binding the uranyl template directly, there was need to establish whether it will be still anchored even after leaching. The N=O stretching frequency observed at 1155-950 cm⁻¹ showed that SALO was still trapped in the magnetic polymer matrix after even after leaching.

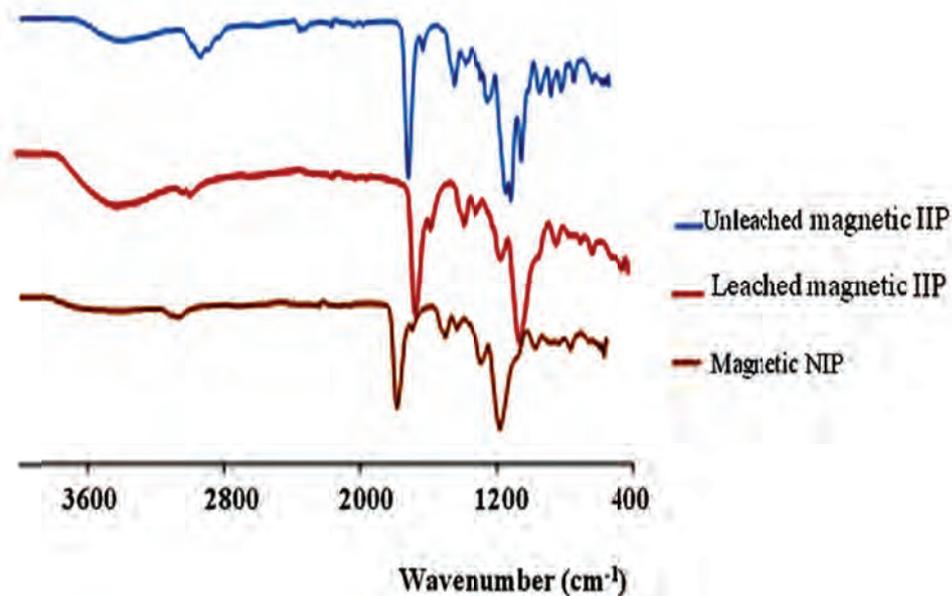


Figure 5.31: Fourier-transformed infra red spectra for γ -MPS based polymers.

5.1.4.4 Thermo-gravimetric analysis (TGA)

Thermo-gravimetric analysis was employed to quantify the amount of Fe_3O_4 encapsulated in the magnetic particles (Zhan *et al.*, 2011). The analysis was carried out in an oxygen free environment to prevent the oxidation of the Fe_3O_4 . Thermo-gravimetric analysis was also used for further structural elucidation of the γ -MPS- Fe_3O_4 .

The TGA spectra in Figures 5.32, 5.33 and 5.34 showed that the magnetite was stable under heating throughout the temperature range of 0-1000°C. From the first derivative in Figure 5.38, it was noted that the decomposition temperature at 305°C was the temperature considered to be the decomposition of the coating agent γ -MPS. The temperature of maximal decomposition was 393°C.

From Figure 5.35, it was also observed that after the analysis, at 1000°C, the residual weight of the γ -MPS- Fe_3O_4 was 69.17%. This meant that the other 30.83% was from the decomposed organic surface coating agent, γ -MPS. It was also noted that the leaching of the bulk and precipitate magnetic polymers reduced the residual weight significantly. This can be explained by the fact that the leaching of the uranyl resulted in the washing away of the magnetic core as well, Figures 5.33 and 5.34.

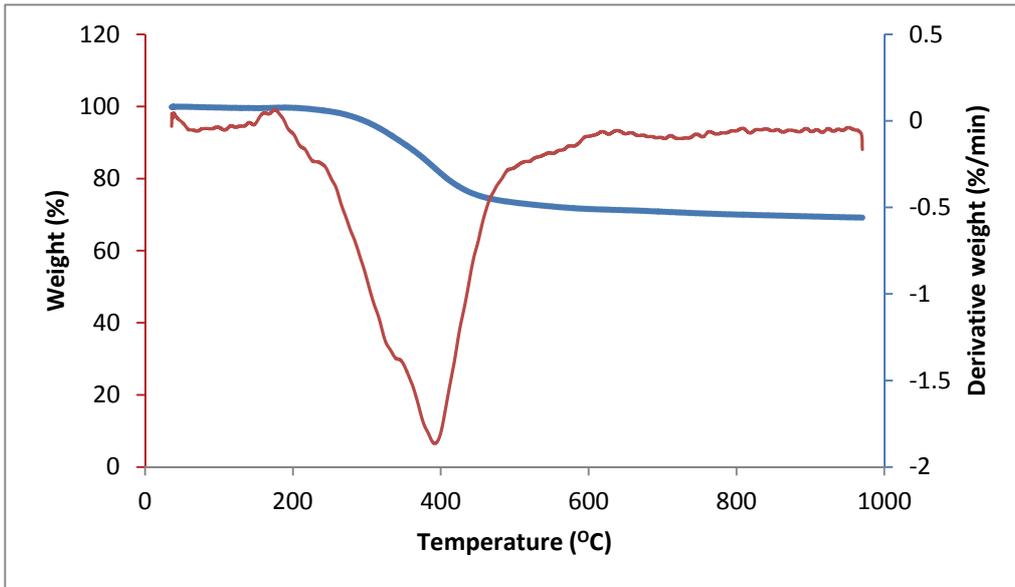


Figure 5.32: Thermo-gravimetric analysis results for γ -MPS-Fe₃O₄.

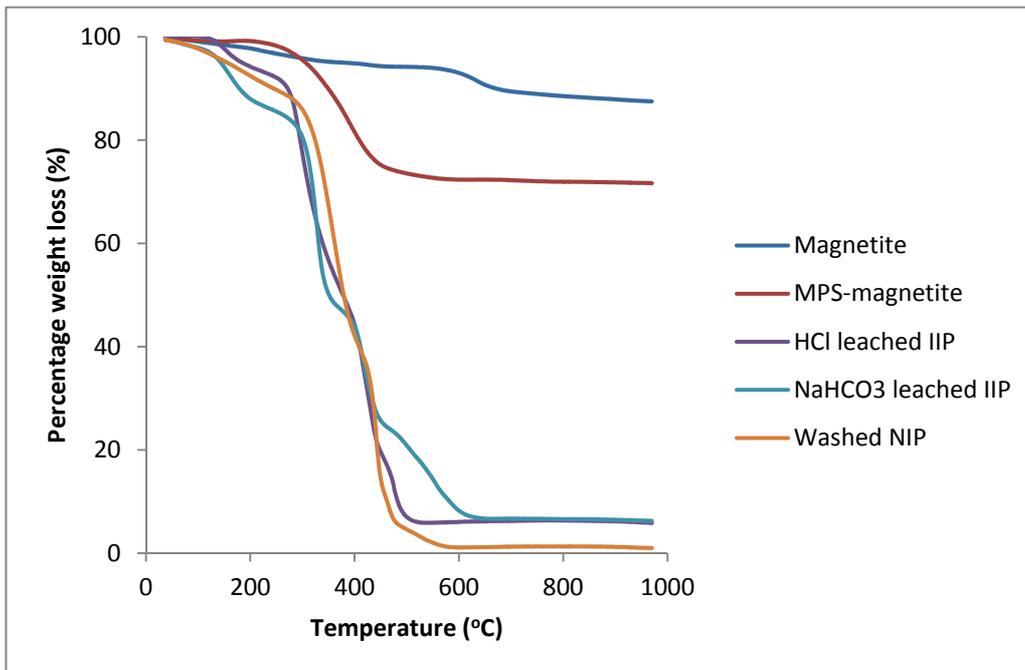


Figure 5.33: Thermo-gravimetric analysis of precipitation magnetic polymers.

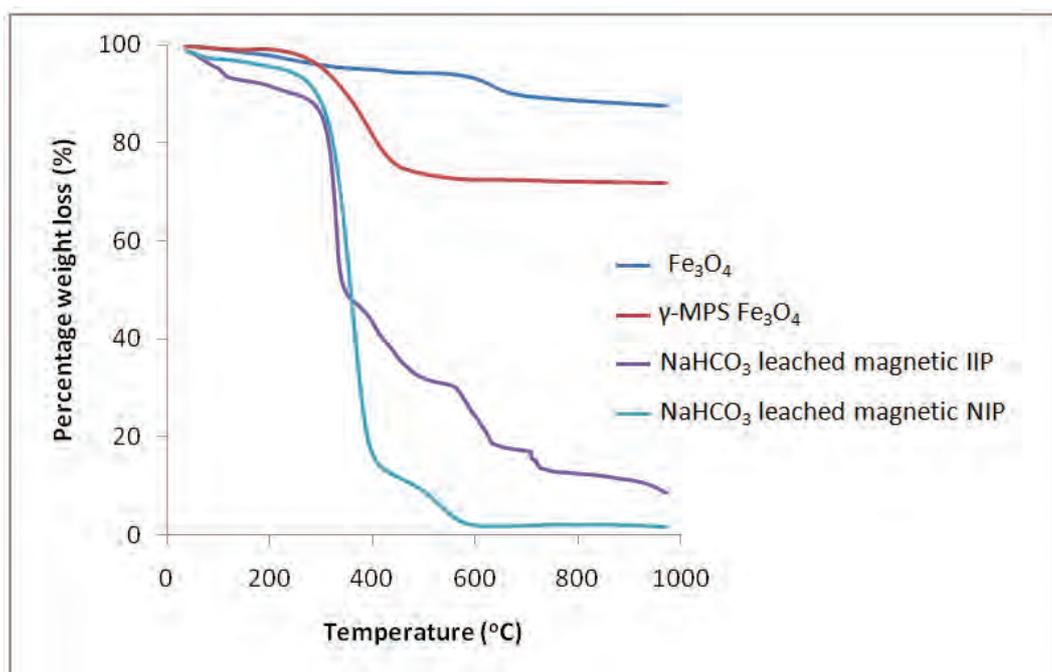


Figure 5.34: Thermo-gravimetric analysis of bulk magnetic polymers.

At temperatures above 600°C, there was a complete decomposition of γ -MPS from the metallic oxide core, Fe_3O_4 . The small initial weight loss of magnetite around 100°C was likely due to the loss of physically adsorbed water on the magnetite as well as dehydroxylation of the internal hydroxyl groups.

5.1.5 Magnetic response

The magnetic response of the Fe_3O_4 , functionalized Fe_3O_4 , unleached and leached magnetic polymer showed an expected decreasing trend with the bare magnetite (Fe_3O_4) exhibiting the strongest response and the leached magnetic polymers the least. This can be explained by the fact that the magnetic core will be embedded inside the polymer matrix of the magnetic IIPs and NIPs. They will be far inside the polymer implying that the magnetic force between it and the external magnet will be diminished (F is inversely proportional to r^2).

5.1.6 Optimization of parameters for U(VI) uptake

The prepared magnetic ion imprinted for U(VI) are summarized in Table 5.5:

Table 5.5: Summary of the prepared types of magnetic ion imprinted polymers for U(VI).

Polymer number	Type of polymerisation	Coating agent	Leaching solution
1	Bulk	Oleic acid	HCl
2	Bulk	Oleic acid	NaHCO ₃
3	Bulk	γ -MPS	HCl
4	Bulk	γ -MPS	NaHCO ₃
5	Precipitation	Oleic acid	HCl
6	Precipitation	Oleic acid	NaHCO ₃
7	Precipitation	γ -MPS	HCl
8	Precipitation	γ -MPS	NaHCO ₃

For each type of magnetic ion imprinted polymer, the corresponding non imprinted polymer was also prepared giving four non imprinted polymer types. This was used for comparison and as control.

5.1.6.1 Effect of sample pH

The adsorption efficiencies of uranyl ions by magnetic polymers at various pH values are presented in Figures 5.36-5.39.

The general trend for all magnetic polymers was as expected, i.e. the magnetic IIPs had superior extraction efficiencies compared to their corresponding magnetic NIPs. Bearing in mind that the magnetic polymers are to be used in AMD there was a need to investigate the efficiency of these magnetic IIPs and NIPs in acidic conditions as well. The variation of the adsorption percentages with the pH is clearly noticeable as they are lower in acidic medium whereas at $\text{pH} > 4$, the adsorption of uranium reached the maximum.

This result is important as it indicates that the pH plays an influential role in the adsorption of uranium. Complex formation between 4-VP, SALO, MAA and uranyl ions present in a sample is pH dependent. The low uptake of uranium at low pH values may be due to the fact that there is a higher concentration of H^+ ions which are preferentially adsorbed ahead of uranium.

Another point for the low uptake of uranium at low pH is that the amine and the hydroxyl chelating groups in the polymer matrix are protonated. This protonation means that the lone pairs for coordination with the cationic uranyl will not be present for coordination. There will be rather electrostatic repulsion of the cationic uranyl from the adsorption sites in the

magnetic polymer matrix. The optimum pH was taken to be 4 and was used in subsequent experiments.

In another study involving uranyl uptake, Wang *et al.* (2011) obtained an optimum pH of 3. However they used a different adsorbent in the form of ethylenediamine-modified magnetic chitosan which also performed poorly at lower pH and this was also as a result of protonation some functional groups within the adsorbent. Zhou *et al.* (2012) obtained an almost optimum pH (= 5) as that obtained in this work (= 4). However they experienced a decrease in the uranyl uptake after the optimum value and they attributed this to the formation of various oligomeric and monomeric hydrolyzed species of uranyl.

Figure 5.35 shows that the atoms responsible for the coordination with the uranyl cation are the nitrogens on 4-vinyl pyridine and salicylaldehyde as well as the oxygen on salicylaldehyde. Both these atoms have lone pairs of electrons which are responsible for the coordinate bonding.

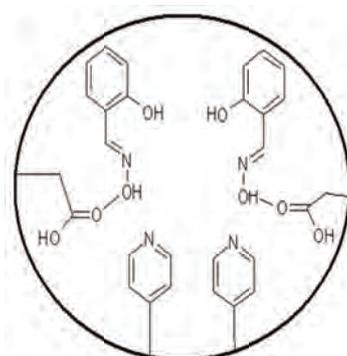


Figure 5.35: Uranium imprinted polymer showing heteroatoms responsible for the uptake of uranyl ions.

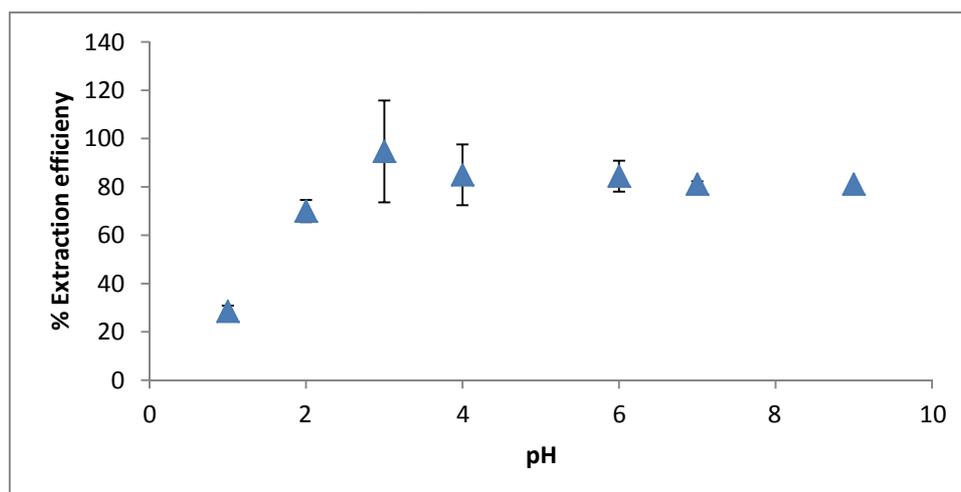


Figure 5.36: Effect of sample pH for OA IIP bulk NaHCO₃ leached. Experimental conditions: Amount of magnetic polymer, 20 mg; sample volume, 25 mL; uranium concentration, 2 mg L⁻¹; contact time, 45 minutes; stirring speed, 1500 rpm; temperature, room temperature.

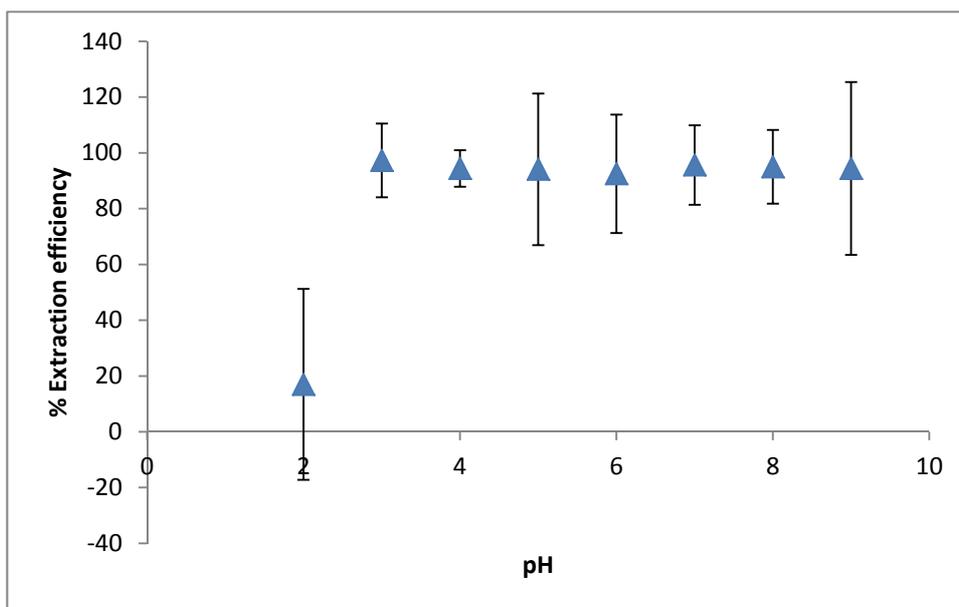


Figure 5.37: Effect of sample pH for OA NIP bulk NaHCO₃ leached (Experimental conditions: Same as those in Figure 5.36).

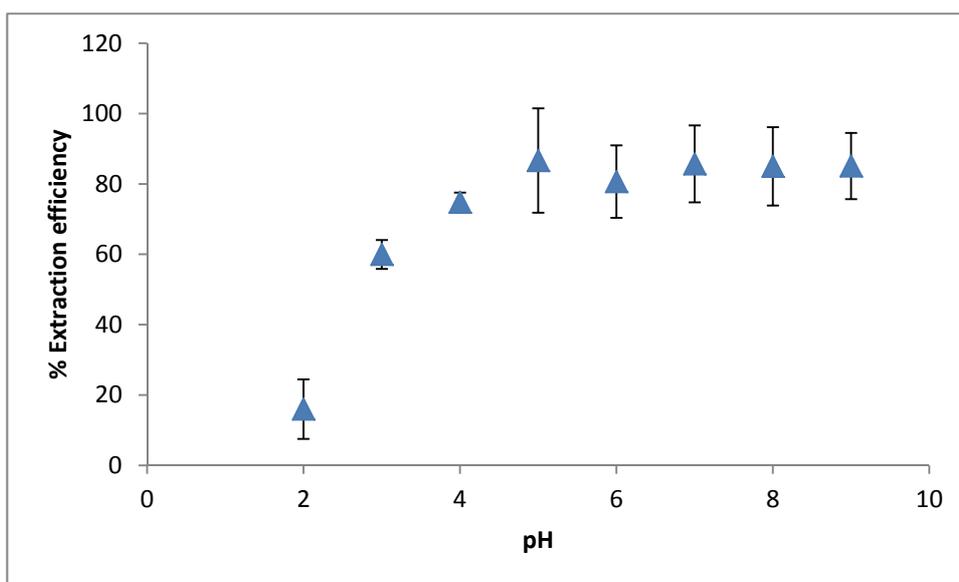


Figure 5.38: Effect of sample pH for γ -MPS IIP precipitate NaHCO₃ leached (Experimental conditions: Same as those in Figure 5.36).

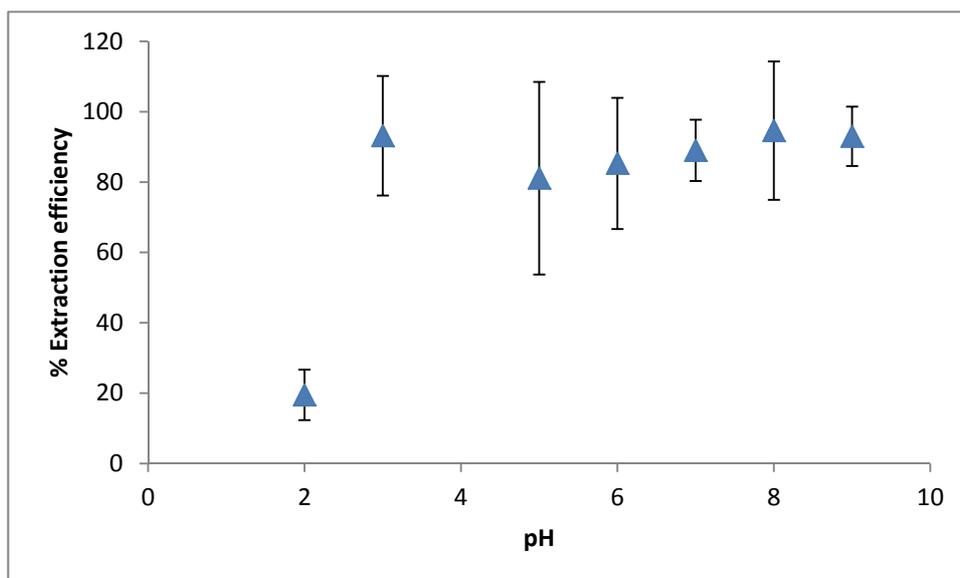


Figure 5.39: Effect of sample pH for γ -MPS IIP precipitate HCl leached (Experimental conditions: Same as those in Figure 5.36).

5.1.6.2 Effect of the amount of magnetic polymer

Figures 5.40-5.44, illustrate a clear dependency of the amount of uranium adsorbed on the quantity of the adsorbent used. It was found that with the increasing dosage of the magnetic adsorbent the amount of removal of uranium increased steadily to an almost constant value. For most magnetic polymers, the maximum uranium uptake was found when the mass of the magnetic polymer was about 50 mg which was then taken as the optimum dose.

In the work of Ahmadi *et al.* (2010), a ternary complex of UO_2^{2+} with N, N-ethylenebis (pyridoxylideneiminato) and 4-vinylpyridine was synthesized and polymerized with styrene and divinylbenzene. They found that the changes in the extraction percentage in the range of 0.05-0.5 g were very small and they took 100 mg of polymer particles to be effective for enrichment. For imprinted polymer nanospheres for uranium were prepared by complexing uranyl ion on to quinoline-8-ol functionalized 3-aminopropyltrimethoxysilane modified silica nanoparticles, the optimum amount of material required for the abstraction of uranium was found to be 20 mg (Milja *et al.*, 2011). In another research, N, N'-bis (3-methoxysalicylidene)-1,2-phenylenediamine on Fe_3O_4 by Zhang *et al.* (2012) showed that the adsorption capacity of uranium(VI) increased with the increase of adsorbent dose at $m < 20$ mg and then remains almost constant at $m > 20$ mg. Therefore, 20 mg was taken as the optimum mass of the adsorbent.

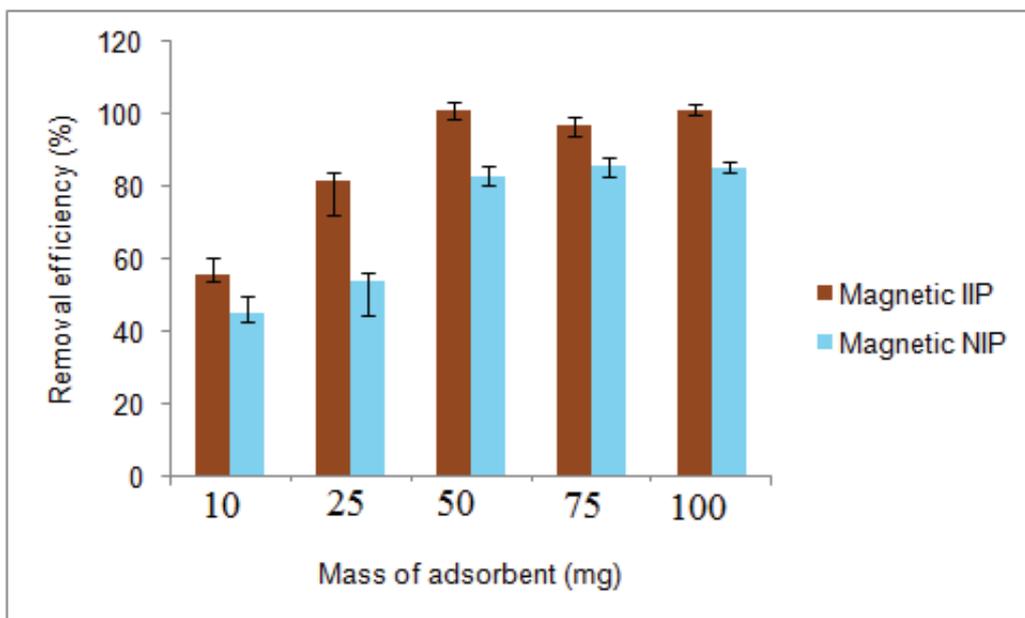


Figure 5.40: Adsorption efficiency obtained by varying the mass of (a) γ -MPS IIP ppt-HCl leached and (b) γ -MPS NIP ppt-HCl leached. Experimental conditions: Sample pH, 4; sample volume, 25 mL; uranium concentration, 2 mg L⁻¹; Contact time, 45 minutes; stirring speed, 1500 rpm; temperature, room temperature.

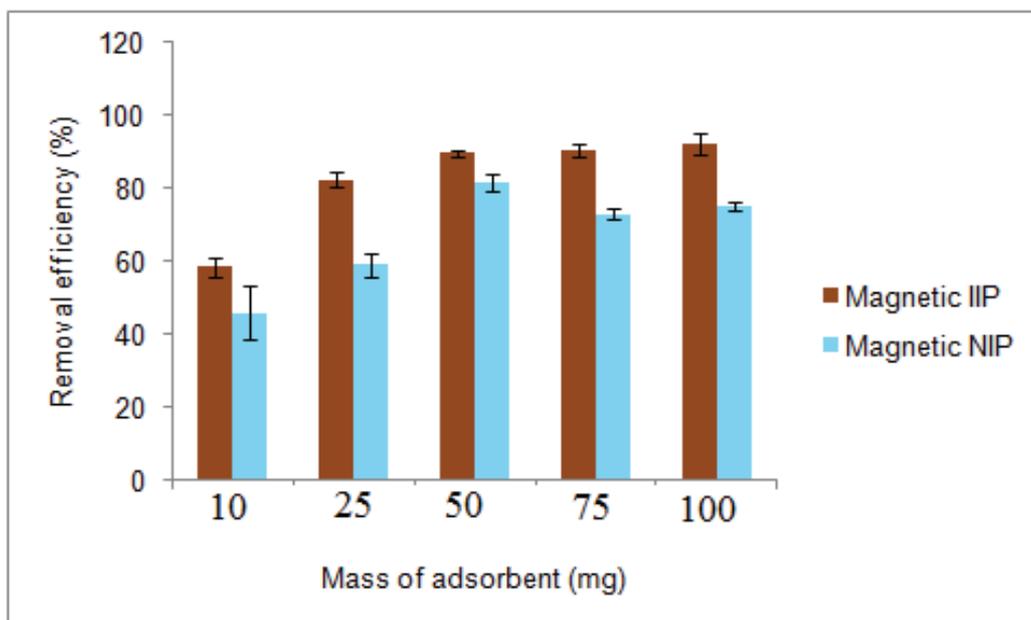


Figure 5.41: Adsorption efficiency obtained by varying the mass of (a) γ -MPS IIP bulk-NaHCO₃ leached and (b) γ -MPS NIP bulk-NaHCO₃ leached (Experimental conditions: Same as those in Figure 5.40).

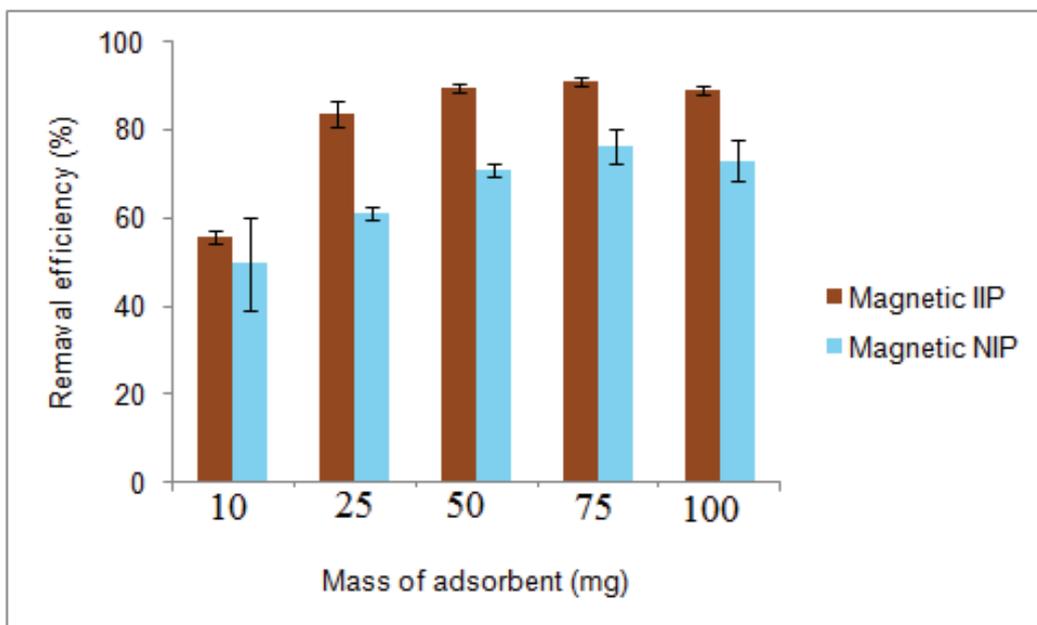


Figure 5.42: Adsorption efficiency obtained by varying the mass of (a) OA IIP bulk-NaHCO₃ leached and (b) OA NIP bulk-NaHCO₃ leached (Experimental conditions: Same as those in Figure 5.40).

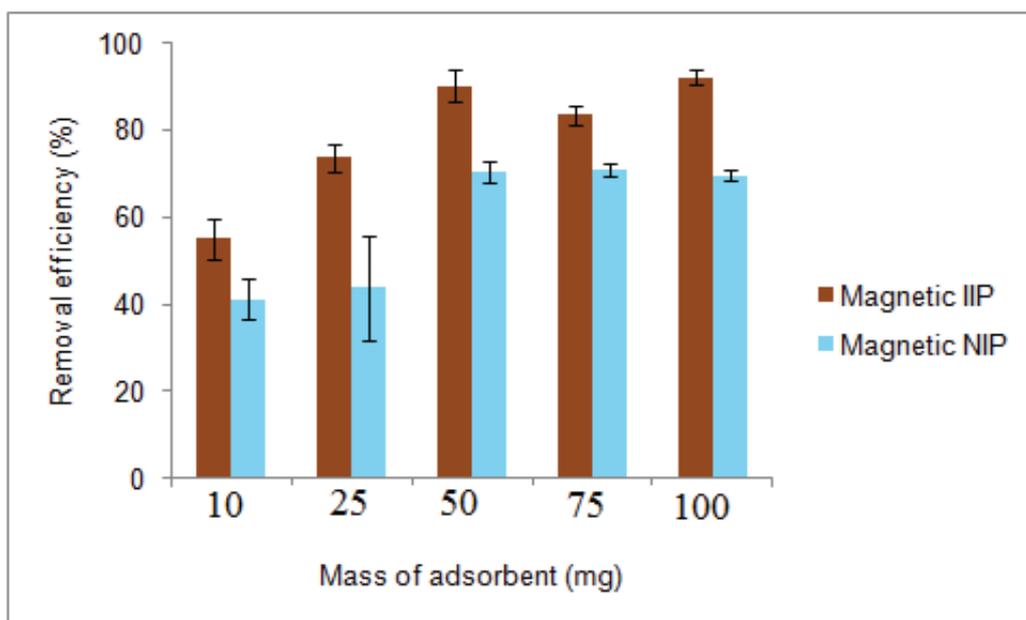


Figure 5.43: Adsorption efficiency obtained by varying the mass of (a) γ -MPS IIP ppt-NaHCO₃ leached and (b) γ -MPS NIP ppt-NaHCO₃ leached (Experimental conditions: Same as those in Figure 5.40).

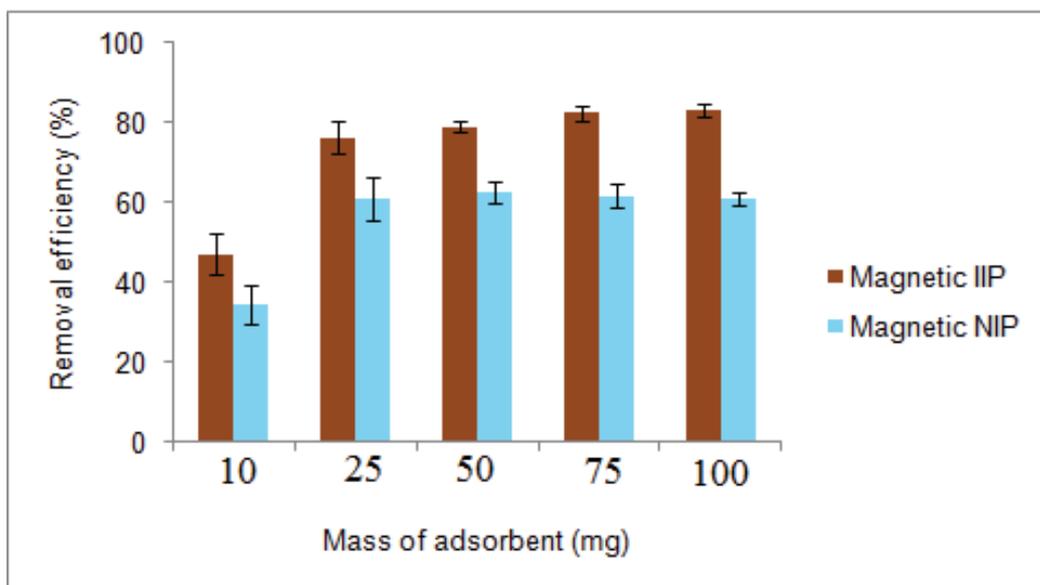


Figure 5.44: Adsorption efficiency obtained by varying the mass of (a) OA IIP ppt- NaHCO_3 leached and (b) OA NIP ppt- NaHCO_3 leached (Experimental conditions: Same as those in Figure 5.40).

5.1.6.3 Effect of contact time

The relationships between the amounts of uranium adsorbed and contact time for different magnetic polymers are shown in Figures 5.45-5.49. Under the used experimental conditions, it was observed that there was an increase in the amount of uranium adsorbed by all magnetic polymers from 0 to 45 minutes, after which equilibrium was reached. A contact time of 45 minutes was therefore selected as the optimum time as it was sufficient for the attainment of equilibrium. A further increase in time had no effect on the adsorption of uranium onto the magnetic polymers. As expected, the adsorption performances of the magnetic IIPs were all higher than of the corresponding magnetic NIPs.

Other studies for the selective uranyl uptake have demonstrated long abstraction times. For instance, from the prepared magnetic Schiff of N, N'-bis (3-methoxysalicylidene)-1, 2-phenylenediamine synthesized by Zhang *et al.* (2012) it was observed that the adsorption rate increased rapidly during the initial stages of the adsorption process. After that, uptake rate slowly declined with lapse of time and tends to be equilibrium at 6 h. This was extremely slower than our prepared magnetic IIP. On the other hand some polymeric adsorbents which were faster in the uptake of uranium(VI) were prepared by Wang *et al.* (2011); Sadeghi and Aboobakri (2012); Fan *et al.* (2012) with the first two at 30 min and the last 16 min.

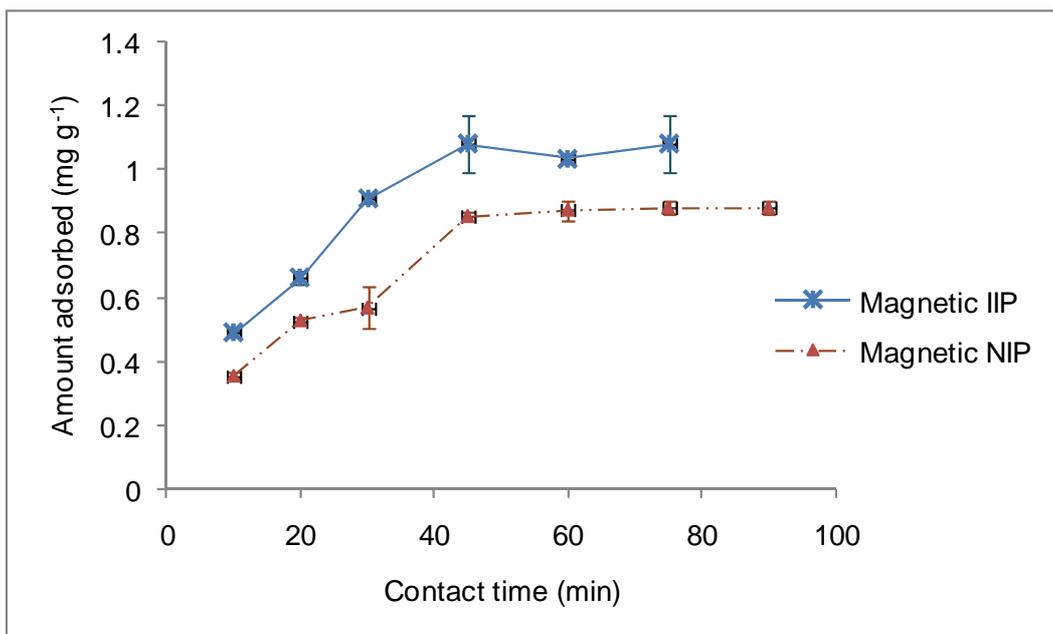


Figure 5.45: Effect of contact time on the uptake of uranium by (a) γ -MPS IIP ppt-HCl leached and (b) γ -MPS NIP ppt-HCl leached. Experimental conditions: Sample pH, 4; sample volume, 25 mL; uranium concentration, 2 mg L⁻¹; polymer weight, 50 mg; stirring speed, 1500 rpm; temperature, room temperature.

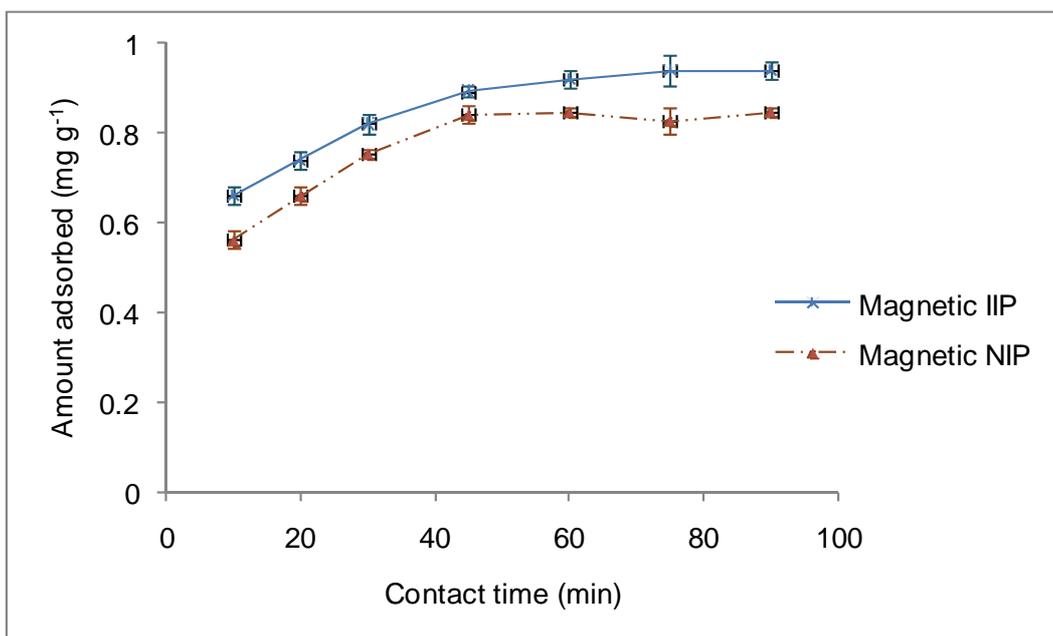


Figure 5.46: Effect of contact time on the uptake of uranium by (a) γ -MPS IIP bulk-NaHCO₃ leached and (b) γ -MPS NIP bulk-NaHCO₃ leached (Experimental conditions: Same as those in Figure 5.45).

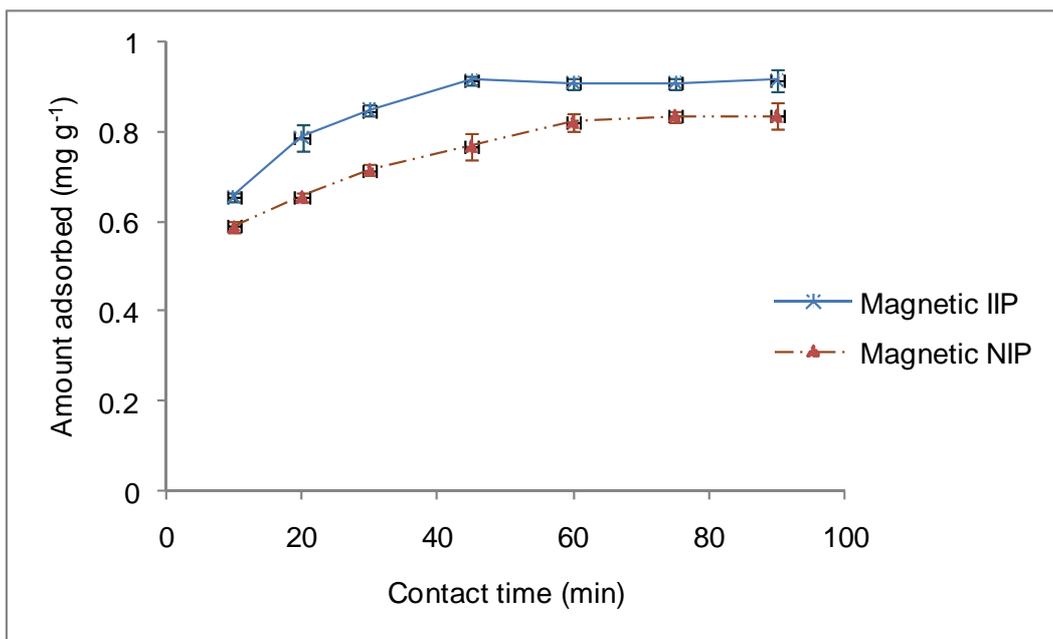


Figure 5.47: Effect of contact time on the uptake of uranium by (a) OA IIP bulk- NaHCO_3 leached and (b) OA NIP bulk- NaHCO_3 leached (Experimental conditions: Same as those in Figure 5.45).

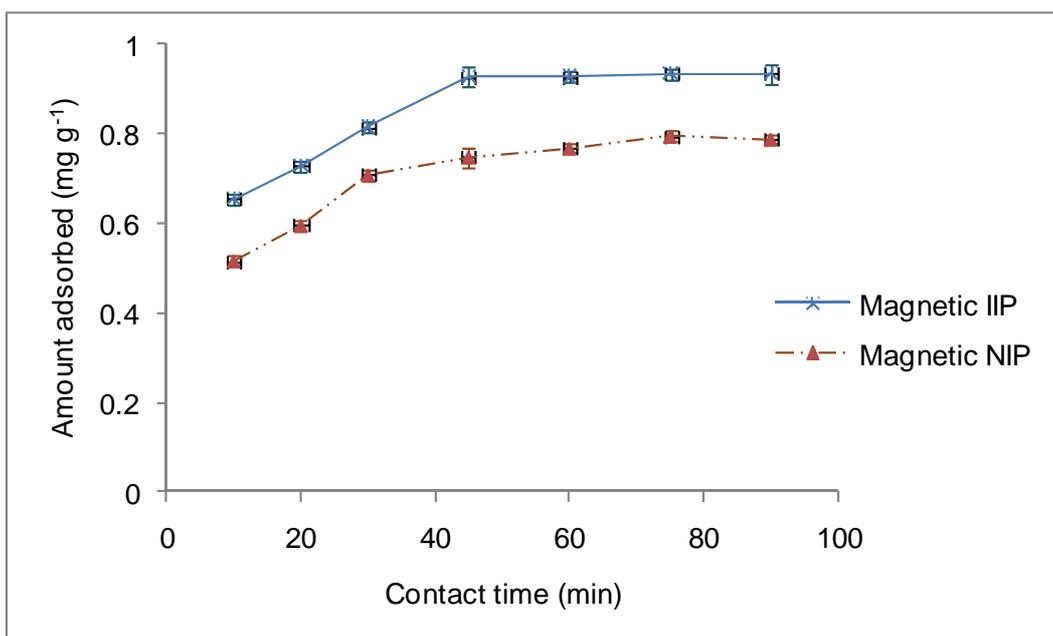


Figure 5.48: Effect of contact time on the uptake of uranium by (a) γ -MPS IIP ppt- NaHCO_3 leached and (b) γ -MPS NIP ppt- NaHCO_3 leached (Experimental conditions: Same as those in Figure 5.45).

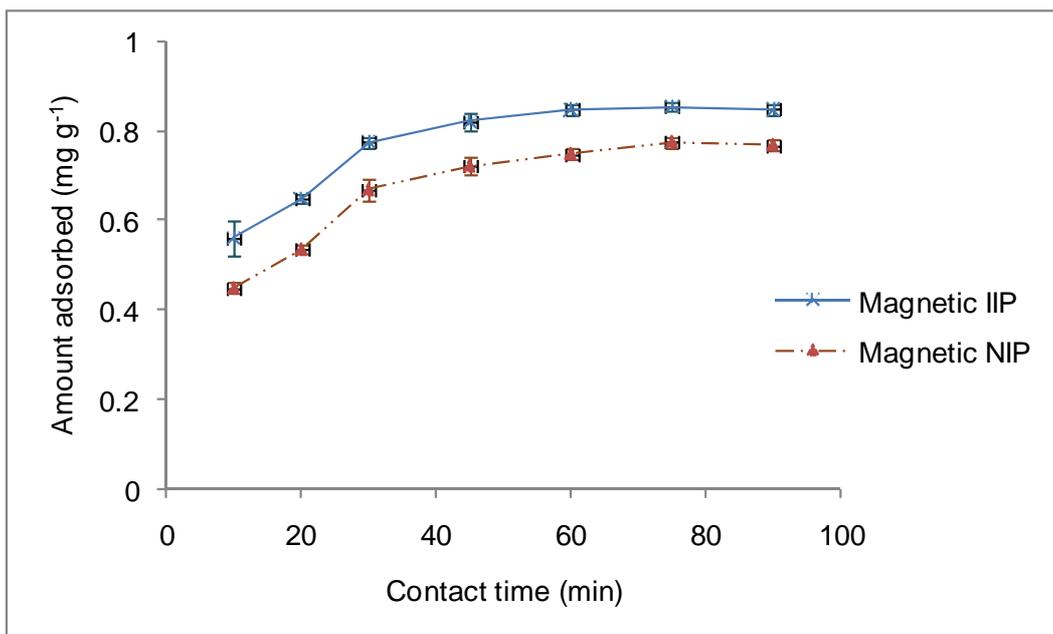


Figure 5.49: Effect of contact time on the uptake of uranium by (a) OA IIP ppt- NaHCO_3 leached and (b) OA NIP ppt- NaHCO_3 leached (Experimental conditions: Same as those in Figure 5.45).

5.1.6.4 Effect of initial uranium concentration

Figures 5.50-5.53 present the dependence of adsorption capacities of various uranium ion concentrations onto different magnetic polymers for fixed magnetic polymer dose, contact time and sample pH. A point of note is that all magnetic polymers showed similar trends. As the amount of uranium ions concentration increased so was the adsorption capacity. This can be attributed to the increasing number of U(VI) ions in solution that competed for a finite number of binding sites on the magnetic polymer surface. This equilibrium loading of uranyl ions per unit mass of the magnetic polymer increased almost linearly upon increasing the initial concentration of U(VI) ions in solution up to an adsorption capacity of between 0.8 and 1.2 mg g^{-1} for all polymers investigated. After reaching maximum adsorption, any further increase in the U(VI) concentration only saturated the binding sites, therefore there wasn't any further increase in the amount of adsorbed U(VI) ions. In all cases, adsorption performance of magnetic IIPs was always higher than their corresponding magnetic NIPs.

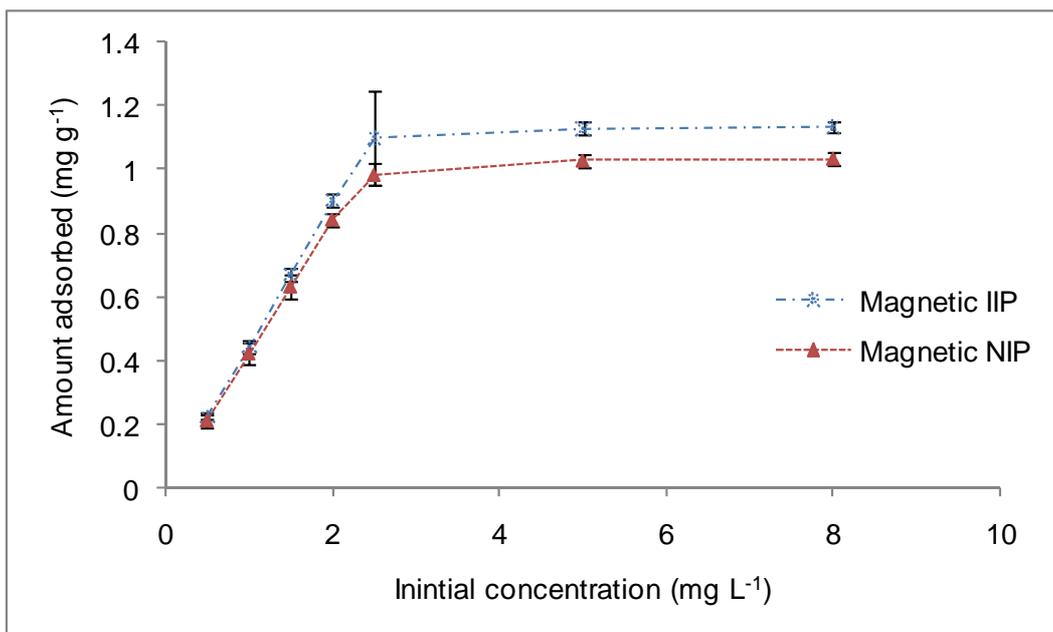


Figure 5.50: Effect of initial concentration on the uptake of uranium by (a) γ -MPS IIP bulk- NaHCO_3 leached and (b) γ -MPS NIP bulk- NaHCO_3 leached. Experimental conditions: Sample pH, 4; sample volume, 25 mL; polymer weight, 50 mg; stirring speed, 1500 rpm; temperature, room temperature.

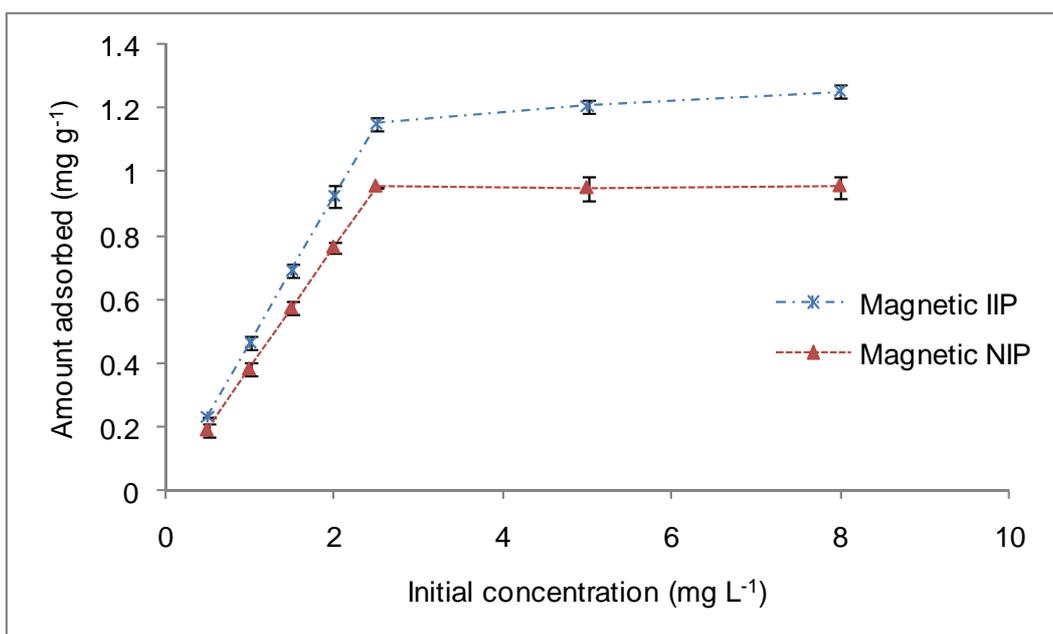


Figure 5.51: Effect of initial concentration on the uptake of uranium by (a) OA IIP bulk- NaHCO_3 leached and (b) OA NIP bulk- NaHCO_3 leached (Experimental conditions: Same as those in Figure 5.50).

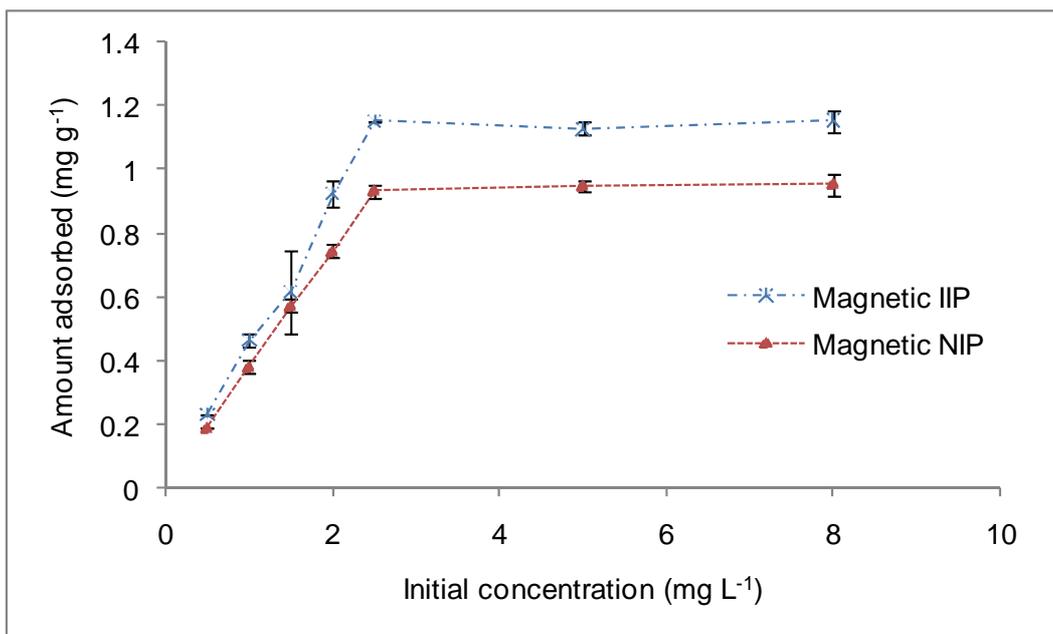


Figure 5.52: Effect of initial concentration on the uptake of uranium by (a) γ -MPS IIP ppt- NaHCO_3 leached and (b) γ -MPS NIP ppt- NaHCO_3 leached (Experimental conditions: Same as those in Figure 5.50).

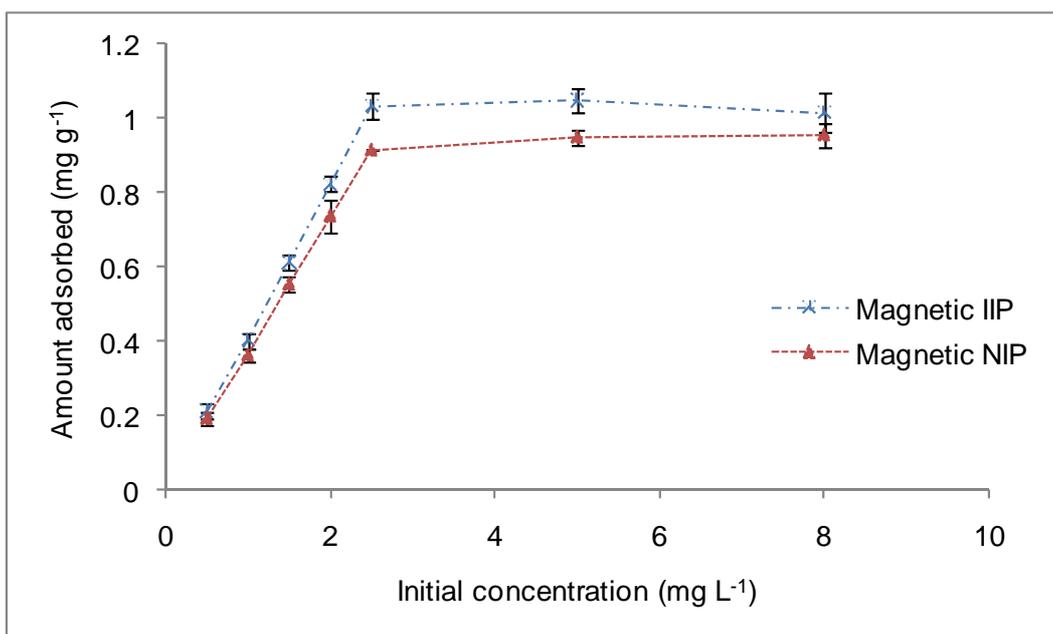


Figure 5.53: Effect of initial concentration on the uptake of uranium by (a) OA IIP ppt- NaHCO_3 leached and (b) OA NIP ppt- NaHCO_3 leached (Experimental conditions: Same as those in Figure 5.50).

5.1.6.5 Selectivity studies

Competing ions which have similar size to the uranyl ion and which are likely to coexist with uranium in environmental samples were chosen for selectivity studies and are shown in Table 5.6. Additionally, all but Fe(III) of the competing ions have the same charge as the uranyl ion.

Table 5.6: Physical properties of the uranyl ion together with those of its competitors.

Metal ion	Crystal radius (pm)	Hydrated	
		radius (pm)	Hydration energy (kJ mol ⁻¹)
UO ₂ ²⁺	95	-	-
Pb ²⁺	132	401	1480
Mg ²⁺	72	300	1828
Ni ²⁺	69	600	2106
Fe ³⁺	63	-	-

Competitive adsorption of the binary mixtures UO₂²⁺/Ni²⁺, UO₂²⁺/Fe³⁺, UO₂²⁺/Pb²⁺ and UO₂²⁺/Mg²⁺ were investigated in an equilibration-adsorption batch systems and the results are summarized in Figures 5.54-5.58. In this approach, the concentration of the un-adsorbed ions was determined by AAS. From these Figures, it was shown that the recovery of U(VI) was much higher than that of the competing ions (Ni²⁺, Fe³⁺, Pb²⁺ and Mg²⁺), demonstrating that the cavities in the magnetic uranyl IIP had higher affinity for U(VI) because of imprinting.

Tables 5.7-5.11 summarize the distribution coefficient (K_d), the selectivity coefficient (K) and the relative selectivity coefficient (K') values of the competing ions with respect to the target UO₂²⁺ ions.

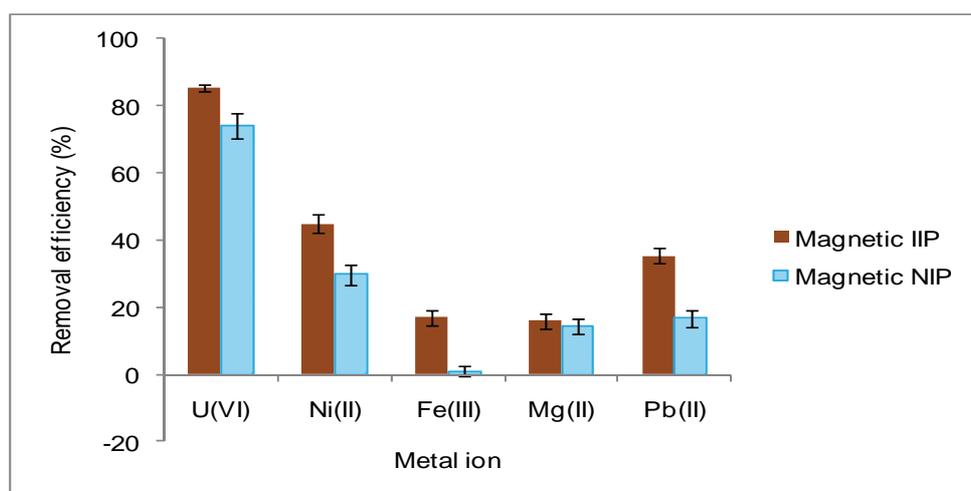


Figure 5.54: Extraction efficiencies of ions extracted by the magnetic IIP and NIP of γ -MPS bulk-NaHCO₃ leached from the spiked 2 mg L⁻¹ binary mixtures of solutions.

Table 5.7: K_d , K and K' values for the magnetic IIP and NIP of γ -MPS bulk- NaHCO_3 in binary mixtures.

UO_2^{2+} cationic competitor	K_d (L g^{-1})				K		K'
	UO_2^{2+} IIP	UO_2^{2+} NIP	Magnetic IIP	Magnetic NIP	Magnetic IIP	Magnetic NIP	
Ni^{2+}	3.07	2.83	0.18	1.33	17.06	2.13	8.01
Fe^{3+}	2.85	2.78	5.95	0.41	0.48	6.78	0.07
Mg^{2+}	3.12	3.18	0.10	0.13	31.20	24.46	1.28
Pb^{2+}	2.93	3.03	0.33	1.17	8.88	2.59	3.43

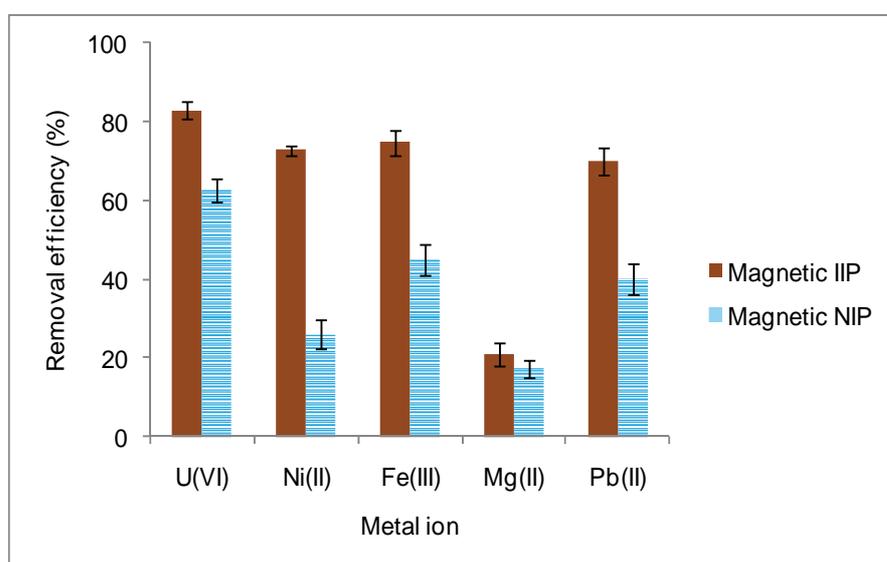


Figure 5.55: Extraction efficiencies of the ions extracted by the magnetic IIP and NIP of γ -MPS ppt- NaHCO_3 leached from the spiked 2 mg L^{-1} binary mixtures of solutions.

Table 5.8: K_d , K and K' values for the magnetic IIP and NIP of γ -MPS ppt- NaHCO_3 leached in binary mixtures.

UO_2^{2+} cationic competitor	K_d (L g^{-1})				K		K'
	UO_2^{2+} IIP	UO_2^{2+} NIP	Magnetic IIP	Magnetic NIP	Magnetic IIP	Magnetic NIP	
Ni^{2+}	2.03	0.85	0.12	0.61	16.92	1.39	12.17
Fe^{3+}	1.88	0.81	0.53	1.17	3.55	0.69	5.14
Mg^{2+}	1.79	0.89	0.19	0.50	9.42	1.78	5.29
Pb^{2+}	1.93	0.86	0.23	0.95	8.39	0.91	9.22

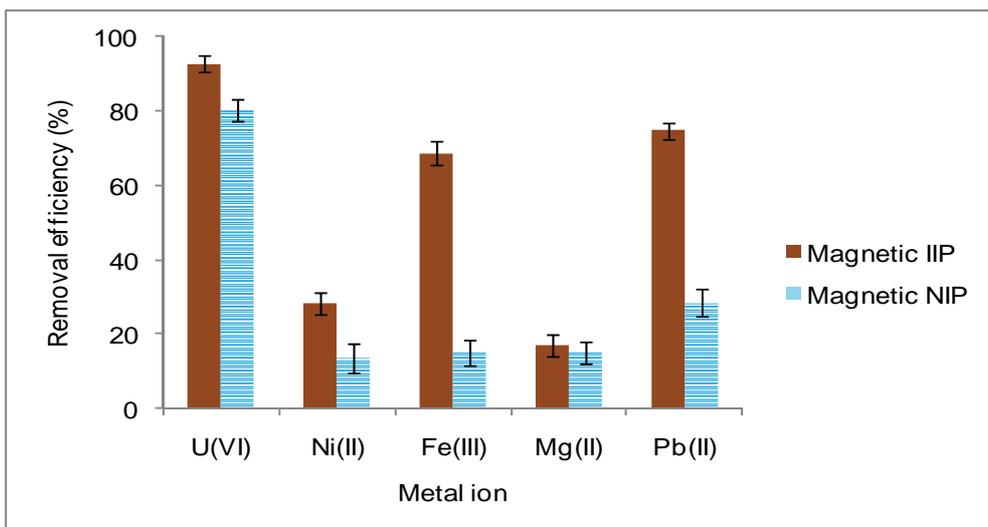


Figure 5.56: Extraction efficiencies of the ions extracted by the magnetic IIP and NIP of γ -MPS ppt-HCl leached from the spiked 2 mg L⁻¹ binary mixtures of solutions.

Table 5.9: K_d , K and K' values for the magnetic IIP and NIP of γ -MPS ppt-HCl leached in binary mixtures.

UO ₂ ²⁺ cationic competitor	K_d (L g ⁻¹)				K		K'
	UO ₂ ²⁺ IIP	UO ₂ ²⁺ NIP	Magnetic IIP	Magnetic NIP	Magnetic IIP	Magnetic NIP	
Ni ²⁺	6.64	1.42	0.21	0.41	31.62	6.76	4.68
Fe ³⁺	6.76	1.41	0.01	0.10	676.00	14.10	47.94
Mg ²⁺	6.19	1.53	0.08	0.09	77.38	17.00	4.55
Pb ²⁺	6.85	1.49	0.10	0.27	68.50	5.52	12.41

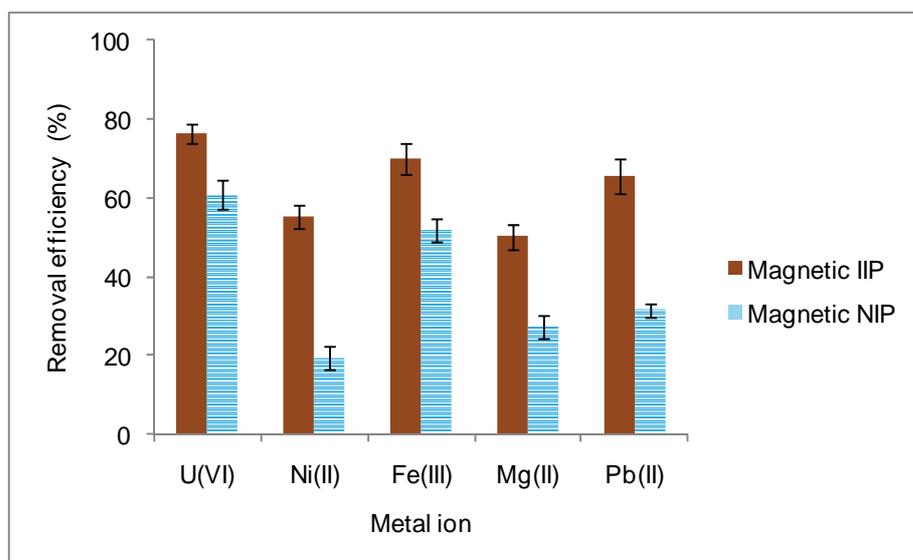


Figure 5.57: Extraction efficiencies of the ions extracted by the magnetic IIP and NIP of OA ppt-NaHCO₃ leached from the spiked 2 mg L⁻¹ binary mixtures of solutions.

Table 5.10: K_d, K and K' values for the magnetic IIP and NIP of OA ppt-NaHCO₃ leached in binary mixtures.

UO ₂ ²⁺ cationic competitor	K _d (L g ⁻¹)				K		K'
	UO ₂ ²⁺ IIP	UO ₂ ²⁺ NIP	Magnetic IIP	Magnetic NIP	Magnetic IIP	Magnetic NIP	
Ni ²⁺	1.58	0.81	0.10	0.61	15.80	1.33	11.88
Fe ³⁺	1.63	0.75	0.58	1.08	2.81	0.69	4.07
Mg ²⁺	1.19	0.82	0.09	0.49	13.22	1.67	7.92
Pb ²⁺	1.84	0.63	0.41	0.84	4.49	0.75	5.99

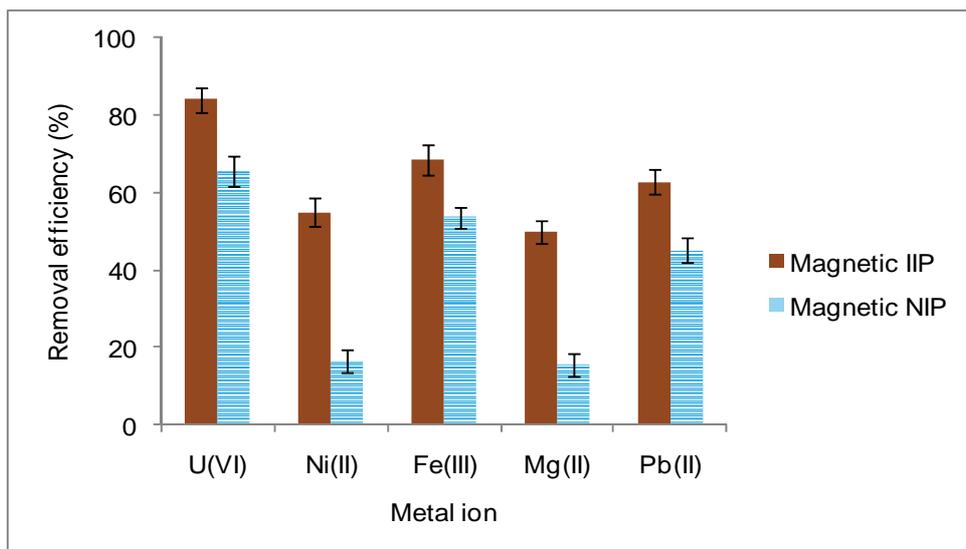


Figure 5.58: Extraction efficiencies of ions extracted by the magnetic IIP and NIP of OA bulk-NaHCO₃ leached from the spiked 2 mg L⁻¹ binary mixtures of solutions.

Table 5.11: K_d, K and K' values for the magnetic IIP and NIP of OA bulk-NaHCO₃ leached in binary mixtures.

UO ₂ ²⁺ cationic competitor	K _d (L g ⁻¹)				K		K'
	UO ₂ ²⁺ IIP	UO ₂ ²⁺ NIP	Magnetic IIP	Magnetic NIP	Magnetic IIP	Magnetic NIP	
Ni ²⁺	0.97	2.31	0.20	0.08	4.85	28.88	0.16
Fe ³⁺	1.01	2.28	1.09	0.09	0.93	25.33	0.04
Mg ²⁺	0.96	2.25	0.10	0.09	9.60	25.00	0.38
Pb ²⁺	0.96	2.24	1.48	0.20	0.65	11.20	0.06

Because Fe(III) has a smaller ionic radius of 63 pm, it had an ability to enter into the imprinting sites of the magnetic polymers freely, hence it showed highest K_d, K and K' values than its competing counterparts. It was interesting to note that although Mg(II) has a similar ionic charge and ionic radius, its adsorption performance in the imprint sites of the magnetic polymers was poor. This could probably arise from its arrangement in coordination geometry. K_d values are the ratios of how the concentration of a particular ion equilibrates between the imprinted polymer and the aqueous environment. It gives the extraction ability of a unit mass of the polymer for a particular ion in a unit volume of solution. As shown in Tables 5.7-5.11, the K_d values for all magnetic IIPs are higher for UO₂²⁺, as compared to those of competing ions. Among the competing ions, Fe(III) had the highest K_d because it occupies sizeable fractions of the imprinting sites because it perfectly fitted the fabricated recognition sites to a far greater extent than other competing ions. Another observation from Tables 5.7-5.11 is that the selectivity coefficients of magnetic IIP were higher than those of

magnetic NIPs. The functional monomers immobilized within the polymer matrix of the host magnetic IIPs had strict configurations suitable for the guest uranyl ions. Furthermore, the ionic recognition was also influenced by the nature of metal ion, its ionic radius and charge. In conclusion, for all synthesized magnetic polymers, it was generally deduced that the relative order of magnitude of metal sorption followed the order: $\text{UO}_2^{2+} > \text{Fe}^{3+} > \text{Pb}^{2+} > \text{Ni}^{2+} > \text{Mg}^{2+}$. These results were in agreement from those of Pakade *et al.* (2012) who found the selectivity order $\text{UO}_2^{2+} > \text{Fe}^{3+} > \text{Cu}^{2+} > \text{Co}^{2+} > \text{Mn}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+}$. Their IIP was not magnetic though, but was just a ternary complex of a uranyl imprint with 1-(prop-2-en-1-yl)-4-(pyrid-2-yl) piperazine and methacrylic acid which they crosslinked. Closer to this work, Singh and Mishra (2009) observed an almost similar trend of selectivity with the order of $\text{Th}^{4+} > \text{UO}_2^{2+} > \text{Fe}^{3+} > \text{Zn}^{2+} > \text{Co}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{CrO}_4^{2-} > \text{Mn}^{2+}$ as deduced from the distribution ratios they reported.

5.1.6.6 Reusability of the magnetic uranyl imprinted polymers

The repeated use of the magnetic U(VI)-imprinted polymers is a key factor that determines the applicability of these adsorbents in decontamination of wastewaters. In order to show the reusability and regeneration of the magnetic U(VI)-imprinted polymers, sorption-desorption cycles were repeated 6 times by using the same adsorbents repeatedly. These sorption-desorption cycles of the five magnetic U(VI)-imprinted polymeric sorbents with their corresponding controls are shown in Figures 5.59-5.63. The results clearly demonstrated that the magnetic U(VI) imprinted beads can be used repeatedly without significant decrease in their adsorption capacities. Similar polymers, though not magnetic, showed good reusability and stability towards uranyl ion up to the tenth cycles of repeated experiments (Singh and Mishra, 2009). For Pakade *et al.* 2012, the stability of the polymers were observed up to the eighth cycle of reuse, maintaining a 99% recovery of the uranyl from aqueous solution.

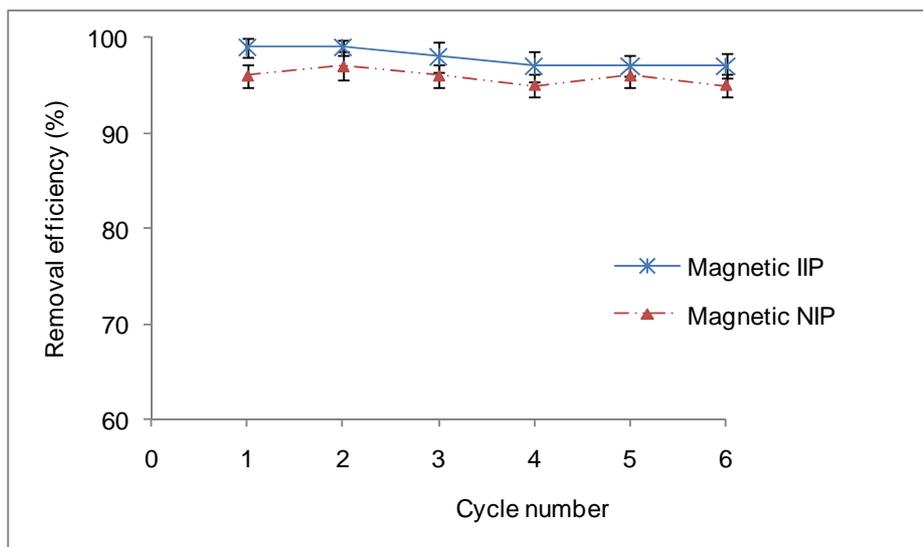


Figure 5.59: Reusability and stability of magnetic IIP and NIP of γ -MPS ppt-HCl leached. Adsorption conditions: Amount of materials, 50 mg; solution pH 4; solution volume, 25 mL; contact time, 45 min, U(VI) concentration, 2 mg L⁻¹, Desorption conditions: Solution volume, 25 mL; contact time, 45 min, [HCl] leachant, 1 M.

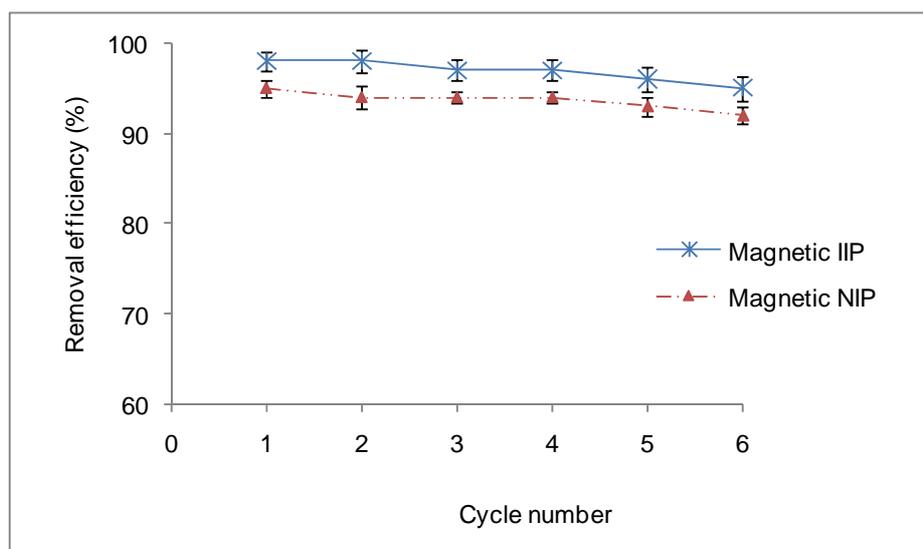


Figure 5.60: Reusability and stability of magnetic IIP and NIP of γ -MPS bulk-NaHCO₃ leached. Adsorption conditions: Amount of materials, 50 mg; solution pH 4; solution volume, 25 mL; contact time, 45 min, U(VI) concentration, 2 mg L⁻¹, Desorption conditions: Solution volume, 25 mL; contact time, 45 min, [HCl] leachant, 1 M.

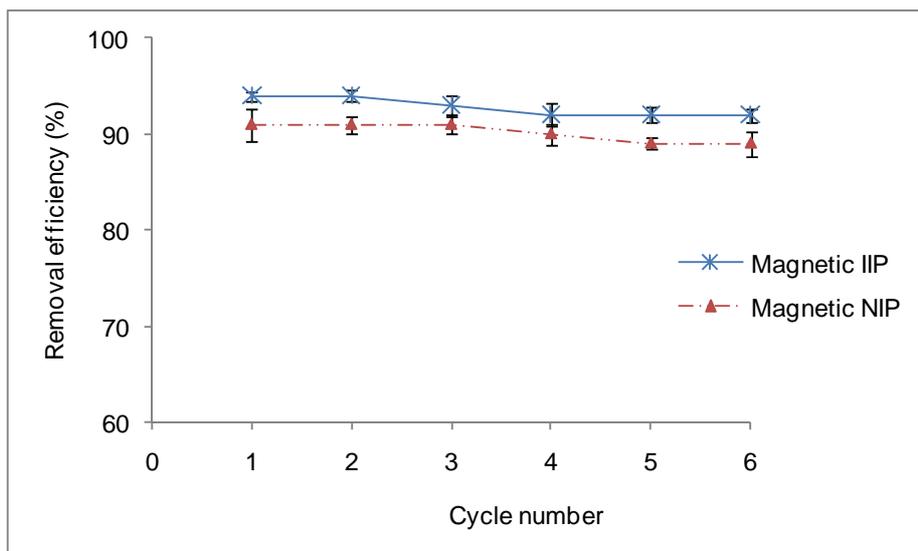


Figure 5.61: Reusability and stability magnetic IIP and NIP of OA bulk-NaHCO₃ leached. Adsorption conditions: Amount of materials, 50 mg; solution pH 4; solution volume, 25 mL; contact time, 45 min, U(VI) concentration, 2 mg L⁻¹, Desorption conditions: Solution volume, 25 mL; contact time, 45 min, [HCl] leachant, 1 M.

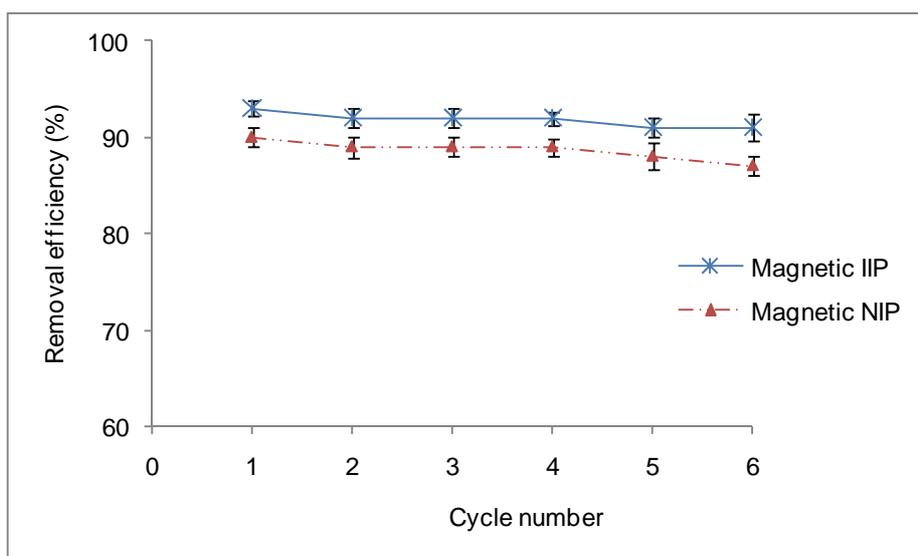


Figure 5.62: Reusability and stability magnetic IIP and NIP of γ -MPS ppt-NaHCO₃ leached. Adsorption conditions: Amount of materials, 50 mg; solution pH 4; solution volume, 25 mL; contact time, 45 min, U(VI) concentration, 2 mg L⁻¹, Desorption conditions: Solution volume, 25 mL; contact time, 45 min, [HCl] leachant, 1 M.

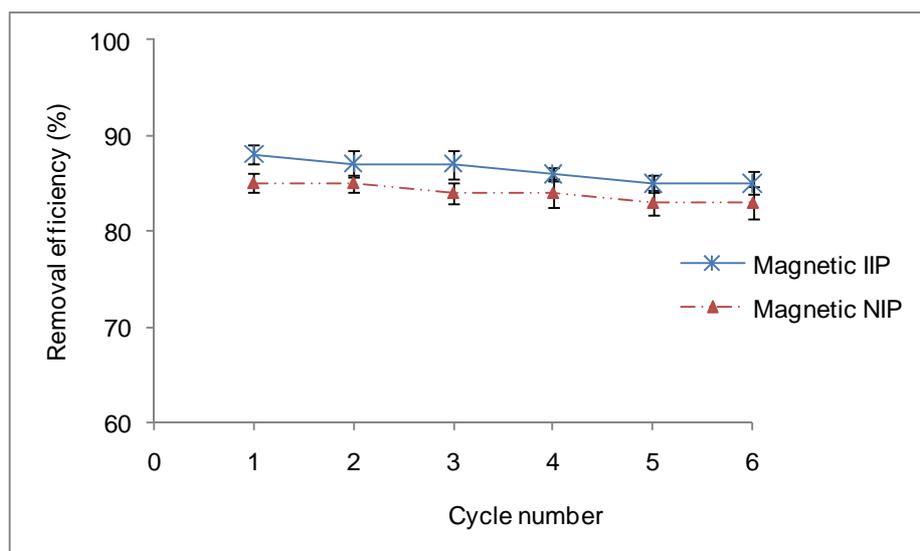


Figure 5.63: Reusability and stability magnetic IIP and NIP of OA ppt-NaHCO₃ leached. Adsorption conditions: Amount of materials, 50 mg; solution pH 4; solution volume, 25 mL; contact time, 45 min, U(VI) concentration, 2 mg L⁻¹, Desorption conditions: Solution volume, 25 mL; contact time, 45 min, [HCl] leachant, 1 M.

5.1.7 Kinetic modelling

Table 5.12 gives the calculated results of the pseudo first and second-order rate equation. When the two modelling approaches are compared, the pseudo-second-order model showed better correlation because of the high values of correlation coefficients based on the linear regression, $R^2 > 0.97$.

Table 5.12: Summary of results of calculated kinetic parameters of pseudo-first order and pseudo-second order for U(VI) adsorption with an initial concentration of 5 mg L⁻¹.

Polymer*	Pseudo first-order			Pseudo second-order		
	R ²	k ₁ (L min ⁻¹)	q _e (mg g ⁻¹)	R ²	k ₂ (g mg ⁻¹ min ⁻¹)	q _e (mg g ⁻¹)
1	0.982	0.052	1.005	0.9811	0.042	1.354
2	0.928	0.093	2.163	0.9721	0.039	1.142
3	0.915	-0.026	11.32	0.9940	0.157	1.012
4	0.602	0.048	3,035	0.9976	0.183	0.910
5	0.962	0.061	0.419	0.9992	0.261	0.961
6	0.928	0.056	0.542	0.9988	0.163	0.901
7	0.885	0.088	1.100	0.9979	0.163	1.008
8	0.986	0.054	0.478	0.9988	0.163	0.859
9	0.979	0.071	0.659	0.9982	0.163	0.923
10	0.991	0.057	0.612	0.9977	0.163	0.864

Polymer*: 1. γ -MPS IIP ppt-HCl leached, 2. γ -MPS NIP ppt-HCl leached, 3. γ -MPS IIP bulk-NaHCO₃ leached, 4. γ -MPS NIP bulk-NaHCO₃ leached, 5. OA IIP bulk-NaHCO₃ leached, 6. OA NIP bulk-NaHCO₃ leached, 7. γ -MPS IIP ppt- NaHCO₃ leached, 8. γ -MPS NIP ppt- NaHCO₃ leached, 9. OA IIP ppt- NaHCO₃ leached, 10. OA NIP ppt-NaHCO₃ leached.

The correlation coefficients values of all pseudo first orders were generally lower than those of the pseudo second orders` thereby showing bad quality of linearization. Again, the q_e values obtained (0.478-11.32 mg g⁻¹) from pseudo first orders differed greatly with the experimental values which means reaction cannot be safely be considered as pseudo first-order.

Generally, the pseudo second-order gave the best fits and it could therefore be used to predict the kinetics of adsorption of uranium onto the magnetic polymers. Riva *et al.* (2008) attached different functional groups to the backbone of synthetic polymers in order to improve the effectiveness of uranyl-binding properties. The polymers obtained after modifications were poly (N-(3-dimethylamino) propylmethacrylamide), poly ((3-dimethylamino) propylacrylate), poly (4-acryloylmorpholine-co-acrylic acid), poly (N-(3-dimethylamino) propylmethacrylamide-co-4-vinyl pyridine), poly ((3-dimethylamino,) propylacrylate-co-acrylic acid) and poly (N-(3-dimethylamino) propylmethacrylamide-co-acrylic acid) which gave the adsorption capacities of 2.80, 2.85, 2.40, 3.25, 2.95 and 3.25 mg g⁻¹ respectively. As can be noted, these polymers are endowed with multi ligands and have expectedly higher adsorption capacities as compared to the polymer synthesized in this work.

5.1.8 Adsorption isotherm modelling

The profiles obtained from the study of the effect of initial uranium concentration, Figures 5.50-5.53, were used to obtain Langmuir and Freundlich adsorption isotherms.

5.1.8.1 Langmuir model

The Langmuir constant, b , can be used to determine the type of interaction between the adsorbate and adsorbent using the dimensionless separation factor, R_L . This factor is defined quantitatively by equation 5.1, (Hall *et al.*, 1966):

$$R_L = \frac{1}{(1+bC_0)} \quad 5.1$$

Where C_0 is the initial metal concentration (mg L⁻¹) and b is the Langmuir constant (L g⁻¹). Based on the quantity of R_L values, the affinity of adsorption of the analyte of interest unto the adsorbent can be classified into categories shown in Table 5.13. The Langmuir constant, b , as well as q_m , can be deduced from the slopes and intercepts of the Langmuir plots.

Table 5.13: Types of adsorption with respect to Langmuir isotherms.

R_L	Adsorption type
$R_L = 0$	Irreversible
$0 < R_L < 1$	Favourable
$R_L = 1$	Linear
$R_L > 1$	Unfavourable

All R_L values obtained for U(VI) adsorption onto magnetic polymers (IIPs and NIPs) were in the range of 0.13-0.93 and are summarized in Table 5.14. These values showed that favourable adsorption occurred in all magnetic polymers used.

Table 5.14: The Langmuir constants and the R_L values for adsorption of U(VI) on magnetic polymers.

Magnetic polymer	b (L g ⁻¹)	q_m (mg g ⁻¹)	R_L	R^2
γ -MPS IIP bulk-NaHCO ₃ leached	3.34	1.94	0.13	0.965
γ -MPS NIP bulk-NaHCO ₃ leached	0.16	16.6	0.76	0.999
OA IIP bulk-NaHCO ₃ leached	0.09	67.1	0.85	1.000
OA NIP bulk-NaHCO ₃ leached	0.04	45.5	0.93	1.000
γ -MPS IIP ppt-NaHCO ₃ leached	0.09	67.1	0.85	1.000
γ -MPS NIP ppt-NaHCO ₃ leached	0.22	7.4	0.69	0.999
OA IIP ppt-NaHCO ₃ leached	0.95	2.9	0.34	0.982
OA NIP ppt-NaHCO ₃ leached	0.66	2.6	0.43	0.992

5.1.8.2 Freundlich model

The constants K_f and n are calculated from the intercept and slope of the Freundlich plots and are presented in Table 5.25. These values were found to be in the range of 1.0-6.0 and 1.0-1.3 respectively. According to Treyball (1980), the values of n between 1 and 10 are considered as good adsorbent and this implies that all magnetic polymers synthesized were effective in the uptake of uranium adsorption.

Table 5.15: Freundlich constants of different uranium magnetic polymers.

Magnetic polymer	n	K_f (L g ⁻¹)	R^2
γ -MPS IIP bulk-NaHCO ₃ leached	1.21	3.09	0.966
γ -MPS NIP bulk-NaHCO ₃ leached	1.05	2.39	0.996
OA IIP bulk-NaHCO ₃ leached	1.00	5.77	1.000
OA NIP bulk-NaHCO ₃ leached	1.00	1.59	1.000
γ -MPS IIP ppt-NaHCO ₃ leached	1.00	5.77	1.000
γ -MPS NIP ppt-NaHCO ₃ leached	1.07	1.43	0.997
OA IIP ppt-NaHCO ₃ leached	1.07	2.07	0.980
OA NIP ppt-NaHCO ₃ leached	1.11	1.24	0.993

5.1.9 Application of magnetic U(VI) IIPs to real water samples

Germiston water had a pH of 2.6, oxidation reduction potential of 436 mV and conductivity of 680 μScm^{-1} . The pH of the water sample was 2.6 which is very acidic and this was expected because of the effect of AMD. In the vicinity of the water source, there are disused

mines (as can be seen in the background of Figure 4.3 (a), which were previously engaged in open cast and deep mining. These activities led to the exposure of the pyrite rock, FeS₂, to air and water which further led to the formation of H₂SO₄ which decanted into the water body where the samples were collected. A reduction oxidation potential of 436 mV showed oxidative conditions. This meant that most metals in the AMD water were subjected to oxidative environments. A high conductivity value of 680 $\mu\text{S cm}^{-1}$ indicated that most metals which constituted the sample, some of which are shown in Table 5.16, were in their ionic form. This resulted from the action of the highly acidic water which leached out metallic ions as it flowed down to water bodies. When the method was applied to real water samples, high extraction efficiencies of over 81% and 64% were obtained for the magnetic IIP and NIP respectively, Table 5.17-5.21. This was a demonstration of the suitability of the magnetic sorbent to selectively remove uranium from complex aqueous matrix. The developed method proved to be suitable for quantitative removal of uranium in wastewaters.

Table 5.16: Metal composition in real water samples.

Metal	Mine wastewater		Wastewater from treatment works	
	Mean (mg L ⁻¹)	SD	Mean (mg L ⁻¹)	SD
Al	648	0.014	0.104	0.012
Au	0.273	0.005	0.007	0.001
Ca	0.123	0.054	23.88	0.003
Co	22.950	0.003	0.044	0.001
Cr	0.836	0.027	-	-
Cu	11.250	0.002	0.029	0.001
Fe	1.800	0.001	-	-
Hg	0.675	0.032	0.030	0.005
Mg	541	0.016	11.85	0.001
Mn	72.05	0.005	0.165	0.001
Ni	48.3	0.004	0.108	0.001
Pb	0.428	0.049	-	-
U	8.500	0.015	-	-
Zn	54.750	0.004	0.023	0.002

Table 5.17: Application of magnetic γ -MPS IIP bulk- NaHCO_3 leached and the corresponding NIP on unspiked and spiked real water samples. Sample pH = 4; solution volume = 25 mL; sorbent mass = 20 and 65 mg for the magnetic IIP and NIP respectively.

Sample	Uranium concentration (mg L^{-1})			% Recovery	
	Spiked	Determined		Magnetic IIP	Magnetic NIP
		Magnetic IIP	Magnetic NIP		
AMD	-	8.50 (0.02)	8.50 (0.02)	-	-
	5.00	13.23 (0.01)	11.34 (0.03)	78	67
	10.0	17.58 (0.05)	15.17 (0.04)	76	66
WWTP	-	< DL	< DL	-	-
	1.00	0.97 (0.08)	0.81 (0.02)	78	65
	5.00	4.75 (0.05)	4.20 (0.01)	76	67
	10.0	9.80 (0.03)	8.30 (0.07)	78	66

< DL : Below detection limit and SD values in parenthesis.

Table 5.18: Application of magnetic OA IIP bulk- NaHCO_3 leached and the corresponding NIP on unspiked and spiked real water samples. Sample pH = 4; solution volume = 25 mL; sorbent mass = 20 and 65 mg for the magnetic IIP and NIP respectively.

Sample	Uranium concentration (mg L^{-1})			% Recovery	
	Spiked	Determined		Magnetic IIP	Magnetic NIP
		Magnetic IIP	Magnetic NIP		
AMD	-	8.50 (0.02)	8.50 (0.02)	-	-
	5.00	12.29 (0.03)	10.87 (0.06)	73	63
	10.0	17.21 (0.07)	14.99 (0.08)	74	65
WWTP	-	< DL	< DL	-	-
	1.00	0.92 (0.03)	0.77 (0.02)	74	62
	5.00	4.50 (0.06)	3.80 (0.07)	72	61
	10.0	9.30 (0.02)	7.80 (0.01)	74	64

< DL: Below detection limit and SD values in parenthesis.

Table 5.19: Application of magnetic γ -MPS IIP ppt- NaHCO_3 leached and the corresponding NIP on unspiked and spiked real water samples. Sample pH = 4; solution volume = 25 mL; sorbent mass = 20 and 65 mg for the magnetic IIP and NIP respectively.

Sample	Uranium concentration (mg L^{-1})			% Recovery	
	Spiked	Determined		Magnetic IIP	Magnetic NIP
		Magnetic IIP	Magnetic NIP		
AMD	-	8.50 (0.02)	8.50 (0.02)	-	-
	5.00	12.15 (0.08)	9.59 (0.07)	72	57
	10.0	16.47 (0.06)	13.32 (0.03)	71	57
WWTP	-	< DL	< DL	-	-
	1.00	0.88 (0.04)	0.72 (0.02)	70	56
	5.00	4.45 (0.06)	3.75 (0.02)	71	60
	10.0	9.10 (0.02)	7.60 (0.02)	73	61

< DL: Below detection limit and SD values in parenthesis.

Table 5.20: Application of magnetic OA IIP bulk- NaHCO_3 leached and the corresponding NIP on unspiked and spiked real water samples. Sample pH = 4; solution volume = 25 mL; sorbent mass = 20 and 65 mg for the magnetic IIP and NIP respectively.

Sample	Uranium concentration (mg L^{-1})			% Recovery	
	Spiked	Determined		Magnetic IIP	Magnetic NIP
		Magnetic IIP	Magnetic NIP		
AMD	-	8.50 (0.02)	8.50 (0.02)	-	-
	5.00	11.75 (0.04)	9.18 (0.05)	70	54
	10.0	15.73 (0.04)	12.40 (0.03)	68	54
WWTP	-	< DL	< DL	-	-
	1.00	0.87 (0.05)	0.66 (0.04)	70	53
	5.00	4.30 (0.07)	3.40 (0.06)	69	54
	10.0	8.70 (0.03)	6.80 (0.02)	70	54

< DL: Below detection limit and SD values in parenthesis.

Table 5.21: Application of magnetic γ -MPS IIP ppt- NaHCO_3 leached and the corresponding NIP on unspiked and spiked real water samples. Sample pH = 4; solution volume = 25 mL; sorbent mass = 20 and 65 mg for the magnetic IIP and NIP respectively.

Sample	Uranium concentration (mg L^{-1})			% Recovery	
	Spiked	Determined		Magnetic IIP	Magnetic NIP
		Magnetic IIP	Magnetic NIP		
AMD	-	8.50 (0.02)	8.50 (0.02)	-	-
	5.00	10.94 (0.03)	8.75 (0.07)	65	52
	10.0	15.36 (0.06)	11.47 (0.01)	66	50
WWTP	-	< DL	< DL	-	-
	1.00	0.82 (0.06)	0.63 (0.04)	66	50
	5.00	4.15 (0.01)	3.25 (0.02)	66	52
	10.0	8.10 (0.08)	6.40 (0.09)	65	51

< DL: Below detection limit and SD values in parenthesis.

5.2 Synthesis and characterization of magnetic Cr(VI) polymers

5.2.1 Synthesis of magnetic poly (4-vinylpyridine)

4-vinylpyridine was homopolymerized and copolymerized with functionalized magnetite as shown in the schemes in Figure 5.64. The expanded structure of the magnetic poly (4-vinylpyridine) is shown in Figure 5.65.

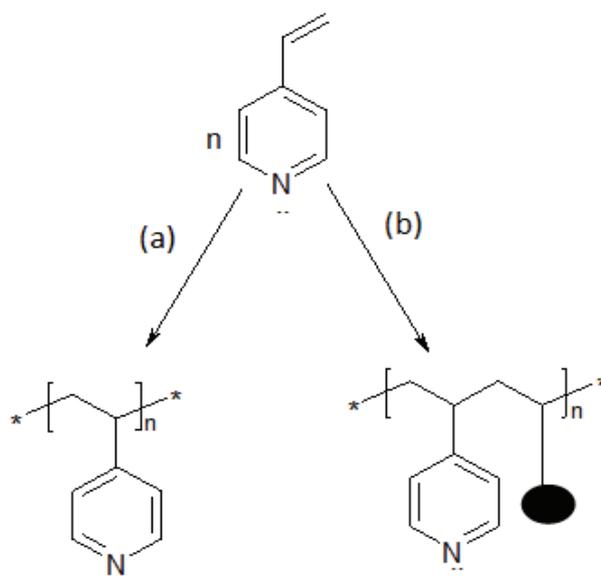


Figure 5.64: Synthetic routes of (a) homopolymer and (b) magnetic polymer of poly (4-vinylpyridine) where the black dot indicates γ -MPS coated magnetite.

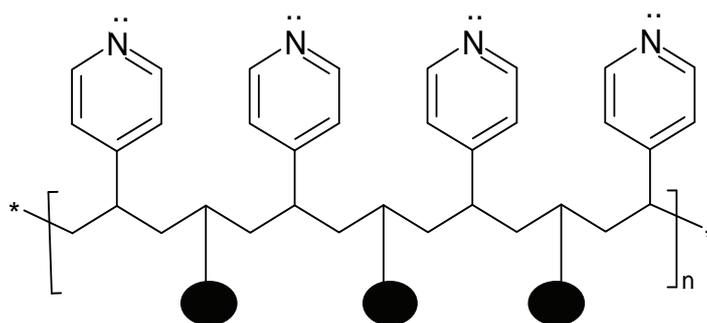


Figure 5.65: Structure of magnetic poly (4-vinylpyridine).

5.2.2 Quaternization of magnetic poly (4-vinylpyridine)

In order to remove metallic oxy-anions in aqueous environments, a positive charge has to be introduced by contacting poly (4-vinylpyridine) particles with acids such as hydrochloric acid (Barakat and Sahiner, 2008). However, in order to introduce a permanent positive charge in the polyelectrolyte, an alkyl group was chosen in this study. N-propyl reacted with the pyridine nitrogen to give quaternized magnetic poly (4-vinylpyridine). In order to have a high positive charge building up in the polymer, a solvent of high dielectric constant should be used (Masamoto *et al.*, 1960). In this work, DMF was used as a solvent and the bromide ions formed diffused away from the pyridinium ions of the cationic polyelectrolyte. The proposed reaction of the n-propyl bromide with magnetic poly (4-vinylpyridine) is shown in Figure 5.66.

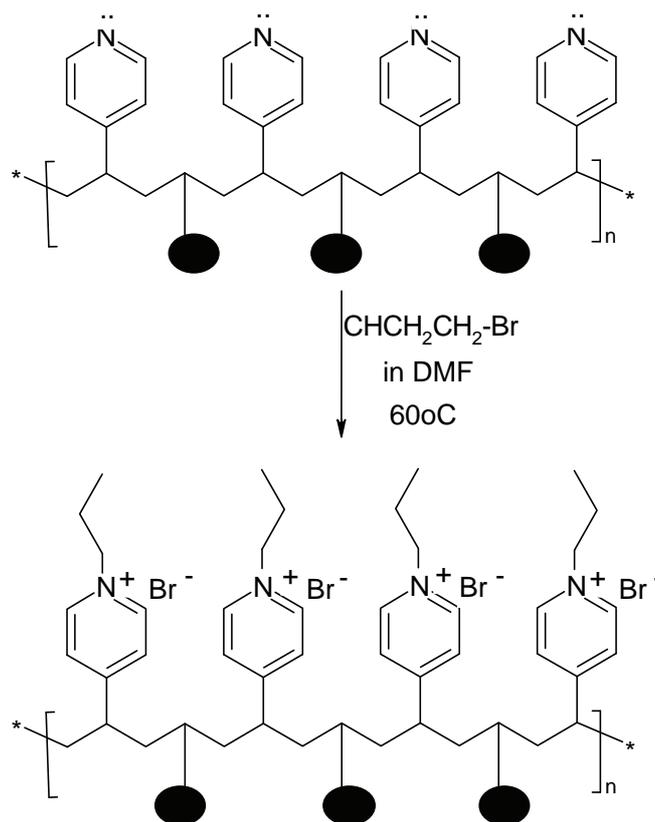


Figure 5.66: Reaction for the quaternization of magnetic poly (4-vinylpyridinium) bromide.

Due to the neighbouring group effect, quaternization of the poly (4-vinylpyridine) does not occur with quantitative conversions and typically, 65-70% quaternization are most common with most alkyl halides (Dautzenberg *et al.*, 1994). However, in their research, Bicak and Gazi (2003) found out that methyl iodide is likely to give high quaternization yields of up to 95%.

Another reason of not achieving 100% quaternization was discussed by Sonmez and Bicak (2002). They pointed out that some small percentages of pyridine groups remain embedded deep in the polymer matrix and may remain unreacted. Hence the reaction to introduce a charge on the polyelectrolyte only represents quantitative quaternization of the pyridine rings in accessible positions of the crosslinked matrix.

5.2.2.1 Quaternization study using Fourier-transformed infra red

Fourier-transformed infra red analysis was carried out to estimate the degree of quaternization. During alkylation of magnetic and non magnetic poly (4-vinylpyridine) with N-propyl bromide, aliquots of the solutions were withdrawn at 14 hrs intervals and purged with nitrogen to form a viscous solution. This was then FTIR analyzed to check the shift of the band at 1600 cm^{-1} .

In quaternization of magnetic and non magnetic poly (4-vinylpyridine), a C=N band in pyridine, usually at 1600 cm^{-1} , was displaced to higher wavenumbers to 1636 cm^{-1} and 1636 cm^{-1} respectively, Figure 5.79. These results were consistent with those obtained by Li *et al.* (2005) who obtained a shifted value of 1636 cm^{-1} .

This was also in agreement with reports of the quaternization reaction by the introduction of a positive charge to form a pyridinium ring in the polymer structure (Landfester, 2001; Caruso *et al.*, 2002). Additionally, the intensity of the band at about 1560 cm^{-1} , as shown in Figure 5.67, corresponds to positively charged nitrogen atoms.

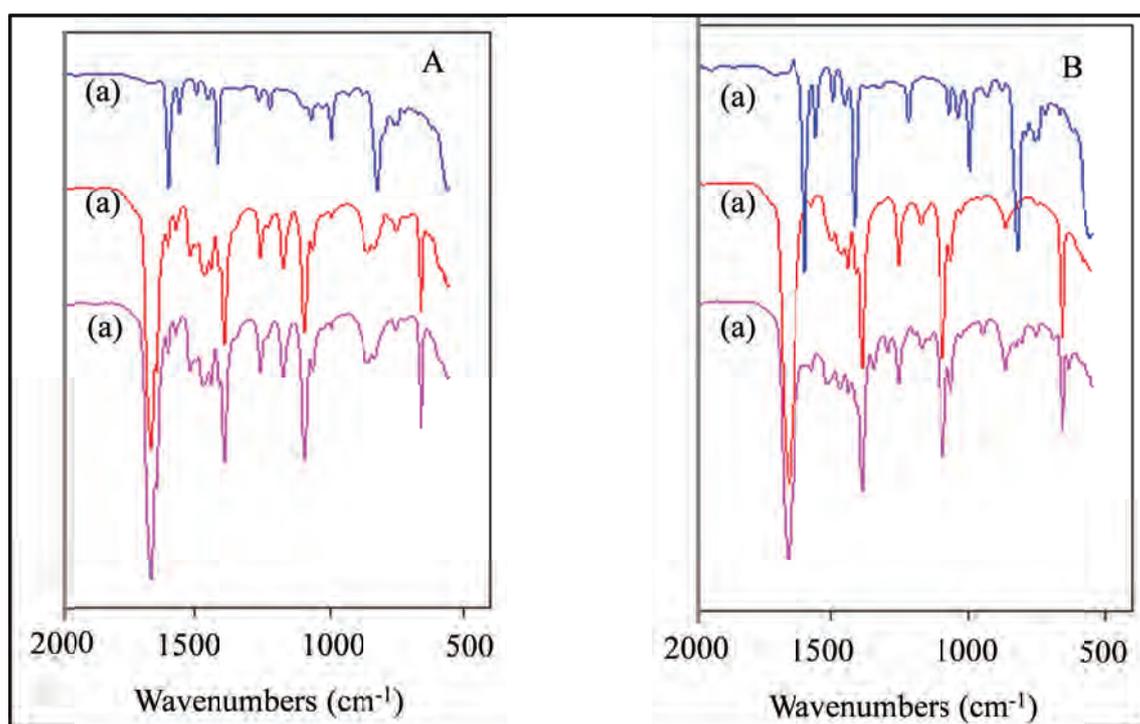


Figure 5.67: FTIR spectra of quaternized of (A) non and (B) magnetic poly (4-vinylpyridine) after (a) 0 hrs, (b) 14 hrs and (c) 42 hrs.

5.2.3 Addition of the dichromate imprint to the magnetic poly (4 vinylpyridine)

The dichromate displaced the smaller bromide anion from the magnetic polymer backbone and that was the start of the formation of micro cavities that were specific for the dichromate

ion. The addition of sodium dichromate to magnetic poly (4-vinylpyridinium) bromide is demonstrated in Figure 5.68.

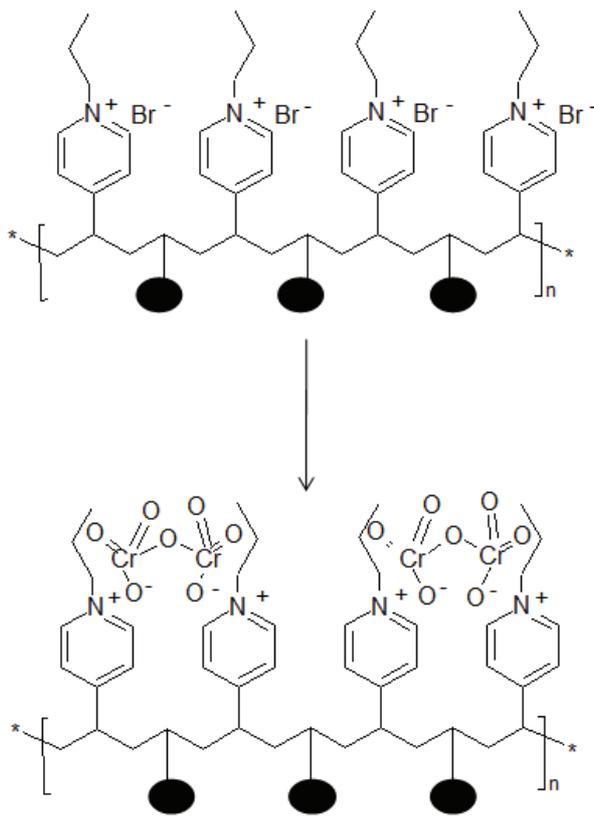


Figure 5.68: Substitution reaction of the bromide ions from magnetic poly (4-vinylpyridinium) bromide by dichromate ions.

5.2.3.1 Fourier-transformed infra red (FTIR) analysis

Evidence of the embedment of dichromate into the magnetic polymer is shown by the resonance peak of the Cr-O and Cr=O bonds at 943 cm^{-1} in the spectra in Figures 5.69. In two separate studies by Arslan *et al.* (2006) and Ortiz-Palacios (2008), these resonance peaks were assigned to 943 and 934 cm^{-1} respectively.

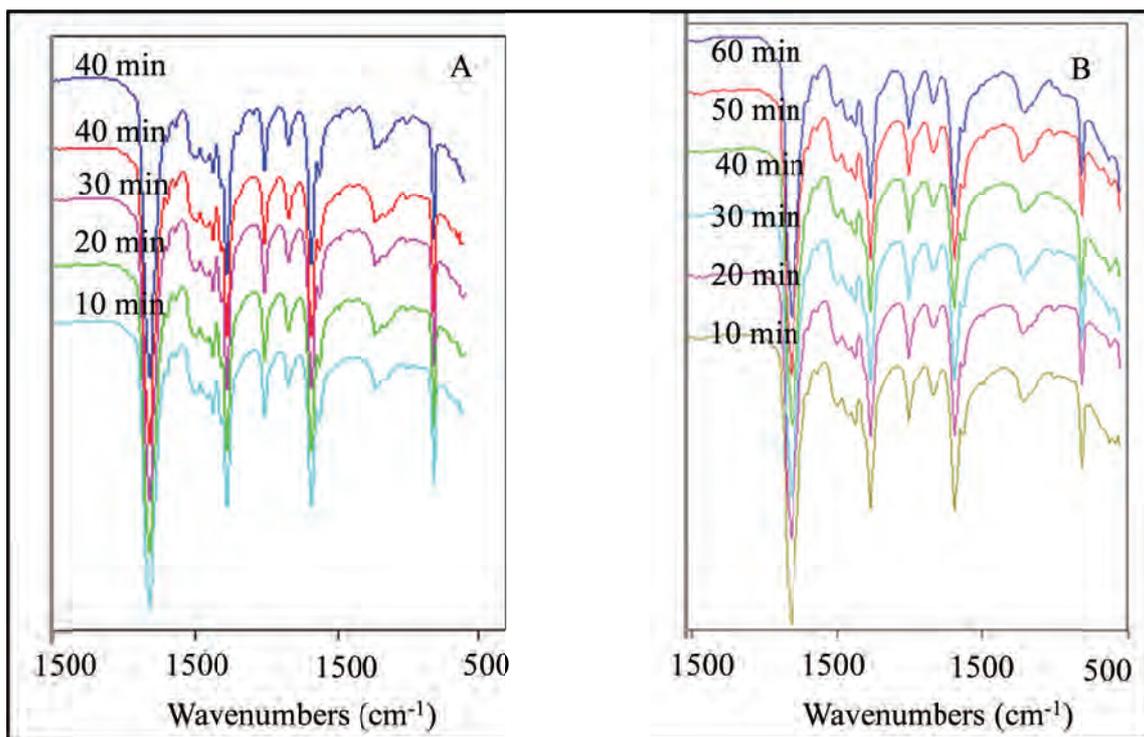


Figure 5.69: FTIR spectra of quaternized of (A) non and (B) magnetic poly(4-vinylpyridine) after addition of $\text{Na}_2\text{Cr}_2\text{O}_7$.

5.2.4 Cross-linking and leaching of dichromate from the magnetic polymers

Cross-linking

For structural rigidity, EGDMA crosslinking monomer was used, Figure 5.70. This ensured that the magnetic polymers could not dissolve in solution during their applications in adsorption studies.

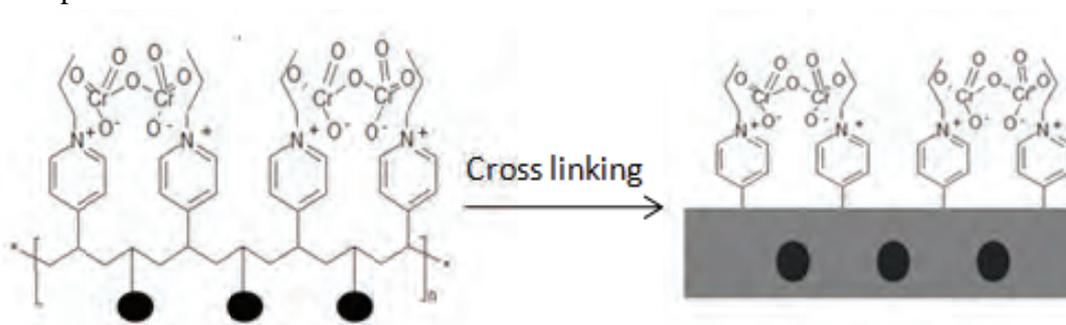


Figure 5.70: Cross-linking of the magnetic polymer.

Leaching of dichromate from the magnetic polymers

After crosslinking, the magnetic polymers were leached for many cycles, Figure 5.71. Figure 5.72 shows the first seven solutions collected after washing the magnetic polymers with 1M HCl. These solutions were analyzed for chromium content with the FAAS. Leaching was only stopped after the chromium content was zero or close to zero. The magnetic polymers were then conditioned with deionized water in order to remove all the excess chloride ions from HCl leachant and dried in the oven at 50°C for 12 hours.

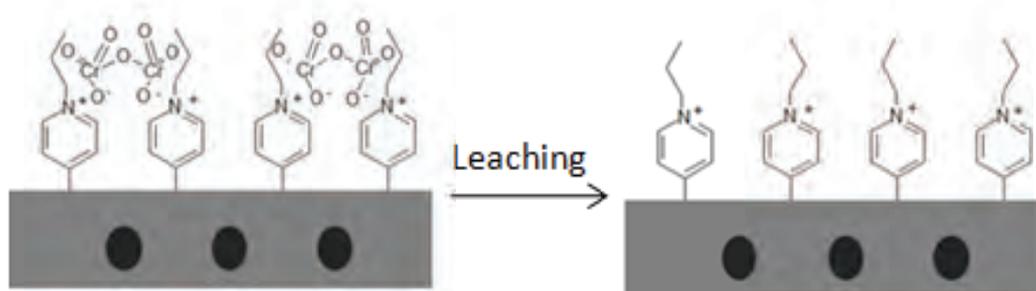


Figure 5.71: Leaching of the dichromate with 1 M HCl.

Leaching studies

The magnetite was observed washing away from the polymeric matrix. This was in parallel with the leaching of the chromium to form pores within the magnetic polymer matrix. However, an important note was that the magnetite was not totally washed away otherwise it was going to defeat the whole purpose of the project (making the polymers magnetic). The last washing of the magnetic IIP detected 0.3 mg L⁻¹ and 8.6 mg L⁻¹ for the chromium and iron respectively, Figure 5.73. Figure 5.74 shows the decrease of the magnetite when the magnetic NIP was washed and the last washing had an iron content of 11.7 mg L⁻¹.

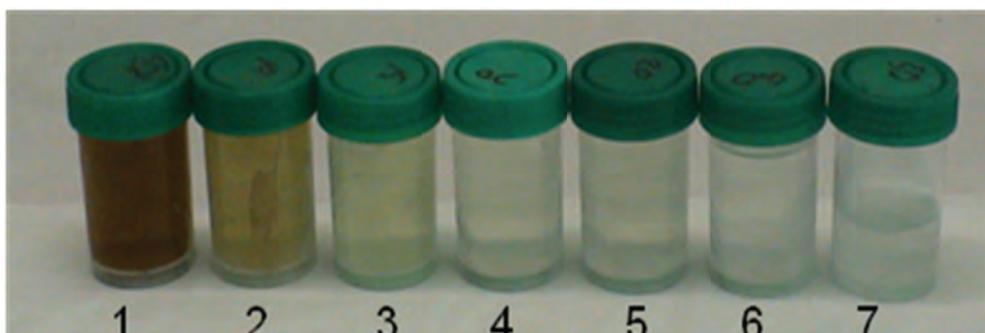


Figure 5.72: Aliquots collected after different leaching times.

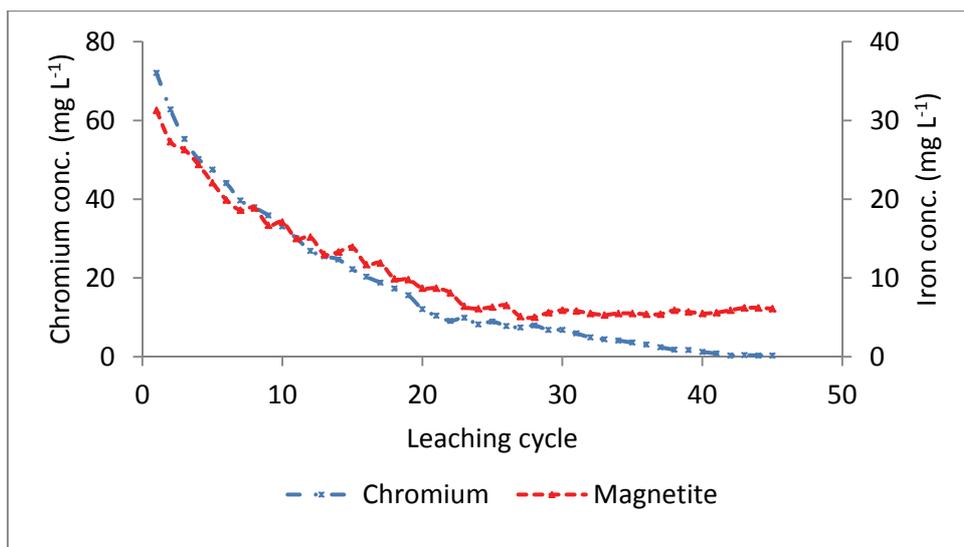


Figure 5.73: Leaching of chromium and iron from the magnetic IIP.

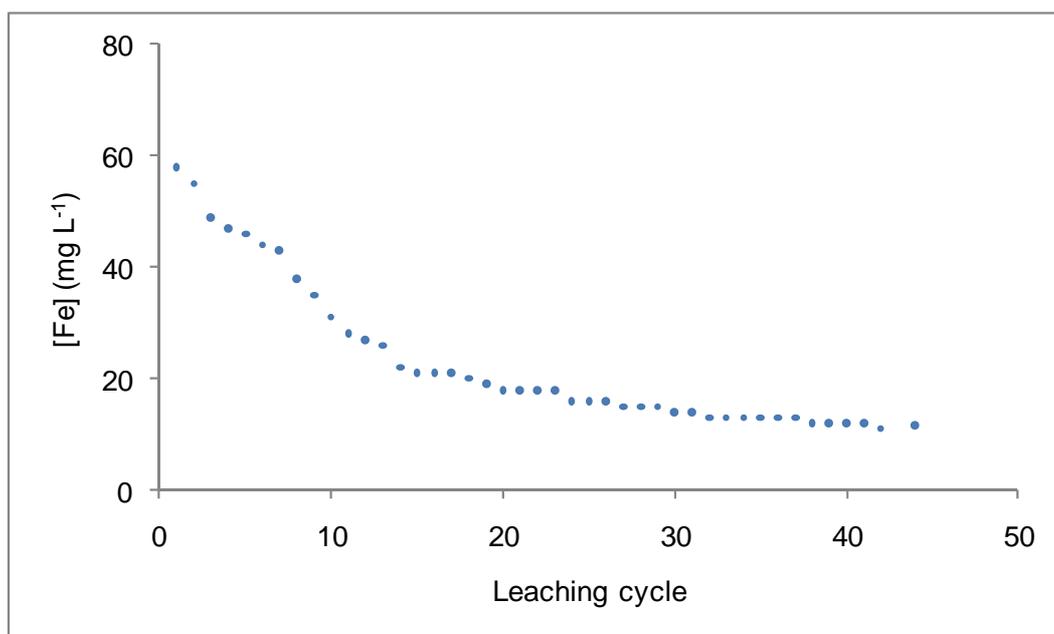


Figure 5.74: Washing of magnetite from magnetic NIP.

5.2.4.1 Brunauer, Emmett and Teller surface analysis

The BET surface area calculations gave good straight line data fits, as shown in Figures 5.75 (b) used as an example for a partial pressure range of 5% to 35%. Similar plots were obtained for other polymers shown in Table 5.22. By application of BET equations, the BET constant, c , was found to be 64.81 and the monomolecular layer volume, v_m , was 5.54 for the unleached non-magnetic poly (n-propyl-4-vinylpyridinium) dichromate polymer. As for the unleached magnetic poly (n-propyl-4-vinylpyridinium) dichromate polymer, c was 8.71 and v_m was 0.23. The surface areas for the unleached magnetic and unleached non-magnetic poly

(n-propyl-4-vinylpyridinium) dichromate polymer were found to be $1.00 \pm 0.02 \text{ m}^2 \text{ g}^{-1}$ and $25.4 \pm 0.3 \text{ m}^2 \text{ g}^{-1}$ respectively.

After leaching of the chromium from the magnetic IIP, there was an increase in the surface area to $132 \pm 1 \text{ m}^2 \text{ g}^{-1}$ which corresponded to 132% increase. However, even though there was an increase in the surface area of the magnetic NIP (16.8%), it was not as significant as that obtained from the magnetic IIP. The BET constants, c , for the leached magnetic IIP and NIP were found to be 163 and 124 respectively. The monomolecular layer volumes, v_m , were 30.5 and 6.7 respectively. All the BET surface areas and constants for the magnetic polymers are summarized in Table 5.22. Bayramoglu and Arica (2008), found that the specific surface area of the IIP and the corresponding NIP particles to be $34.5 \text{ m}^2 \text{ g}^{-1}$ and $21.7 \text{ m}^2 \text{ g}^{-1}$ respectively which indicated the presence of microporous on the surface of the Cr(VI)-imprinted particles.

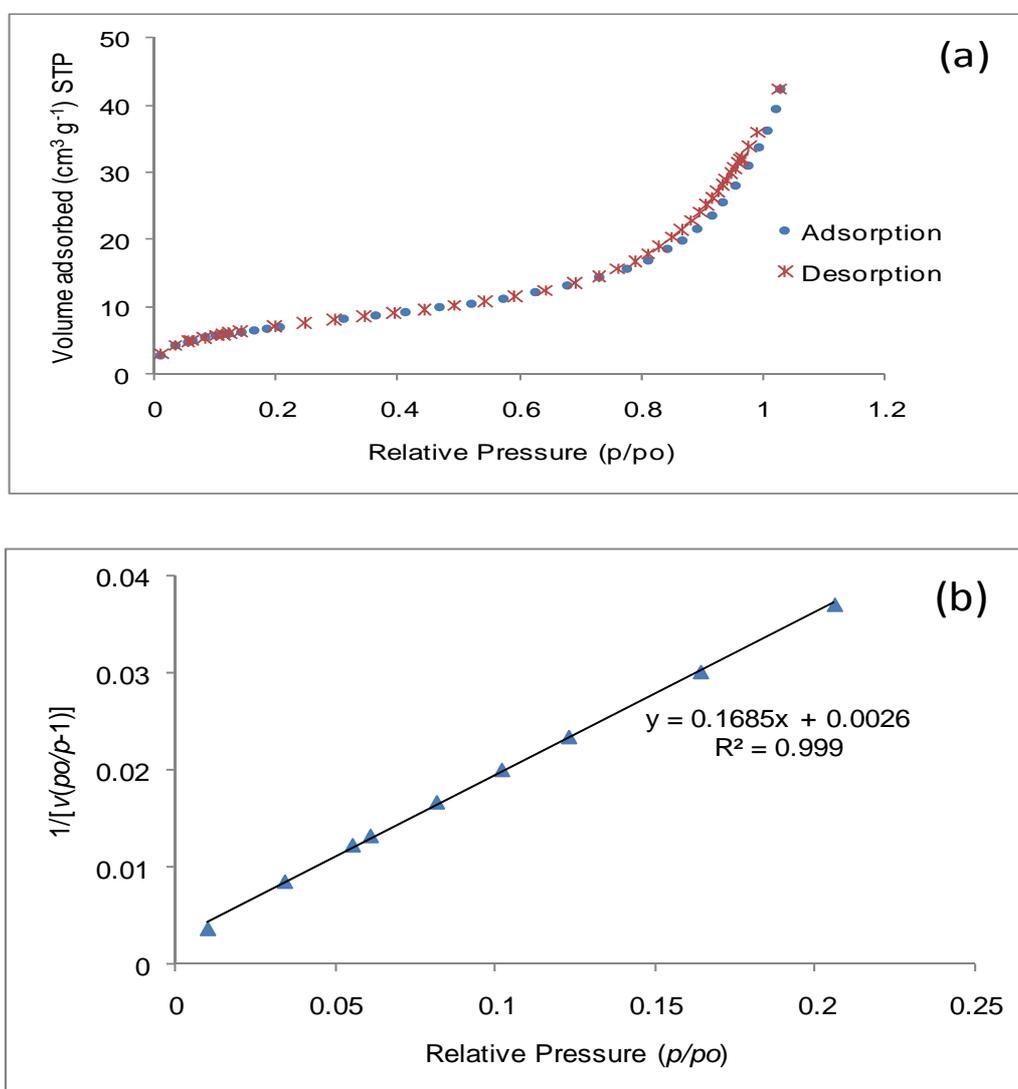


Figure 5.75: (a) The nitrogen adsorption-desorption isotherms for the unleached non-magnetic poly (n-propyl-4-vinylpyridinium) dichromate polymer and (b) its corresponding BET plot.

Table 5.22: BET surface areas and constants for the magnetic polymers.

	BET surface area (m ² g ⁻¹)	v_m	c
Unleached non-magnetic	25.4	5.54	64.81
Unleached magnetic	1.0	0.23	8.71
Leached non-magnetic	132	30.5	163
Leached magnetic	16.8	7.7	124

5.2.4.2 Thermo-gravimetric analysis (TGA) analysis

In order to gain insight into the thermal changes in the magnetic polymers, the thermal stability was probed with TGA. Thermal degradation profiles of leached and unleached Cr(VI) magnetic polymers are shown in Figure 5.76. The maximum weight loss occurred at 425°C, corresponding to degradation of the polymer backbone, and a small peak that occurred at around 220°C can be attributed to the loss of moisture from the magnetic polymers. It can also be observed from the TGA spectrum of the Cr(VI) loaded magnetic polymer that the maximum weight loss due to the decomposition of the backbone occurred at a slightly lower temperature. This indicated that the unleached magnetic polymer was slightly more stable than the leached one. It was also observed that the leached and unleached Cr(VI) magnetic polymers had total weight losses of 82.5 and 59.2%. The remaining mass corresponds to the presence of Cr(VI) and magnetite in the unleached magnetic polymer and magnetite in the leached magnetic polymer.

In almost similar studies by Toral *et al.* (2009), where they quaternized the polymer with an octyl moiety, the stability of the Cr(VI) loaded polymer was also stable as compared to the leached one. The decomposition of the two polymers occurred at around 500 and 400°C respectively. However, in terms of the residual weight of the leached polymer, they found it to be close to 100%. In our work it was observed to be 59.2% because of the embedded magnetite in the polymer matrix.

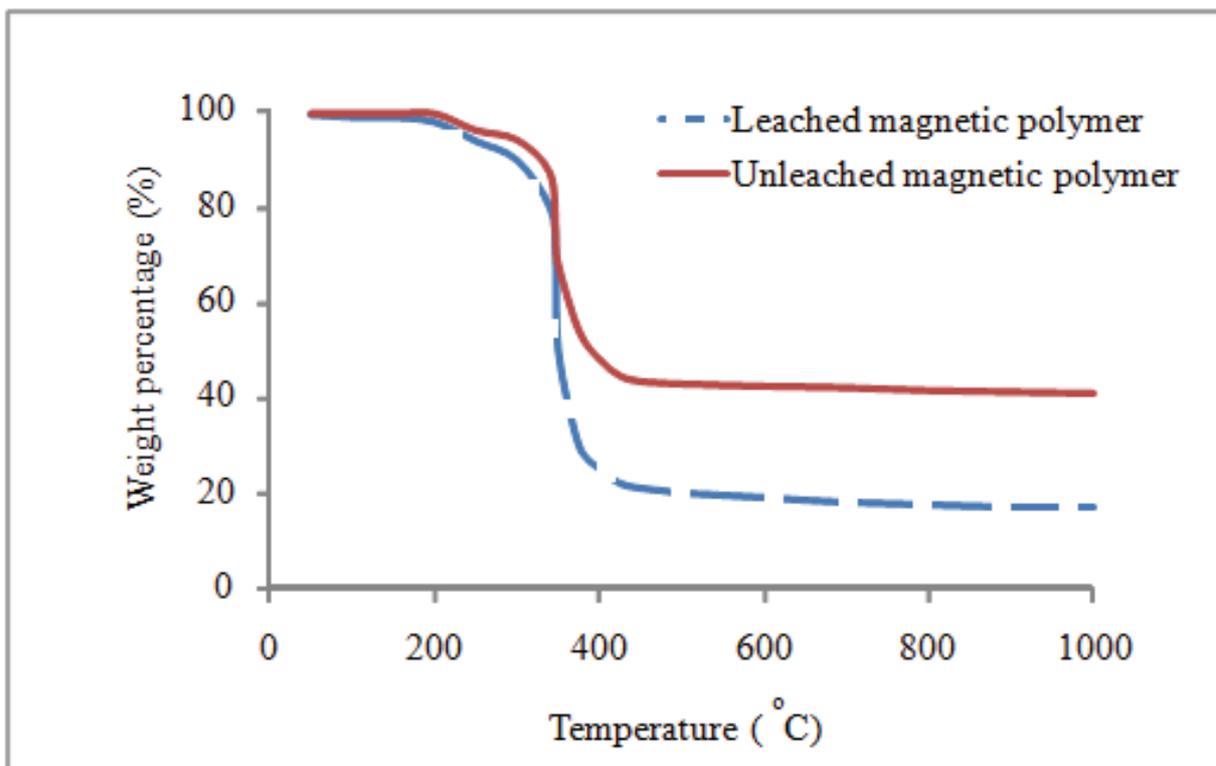


Figure 5.76: Thermogravimetric analysis of chromium magnetic polymer.

5.2.5 Optimization of parameters for Cr(VI) uptake

5.2.5.1 Effect of sample pH

Sample pH dictates the speciation of metals in solution and also the form of protonation on the active sites within the adsorbent. The positive charge on the quaternized nitrogen is responsible for the $\text{Cr}_2\text{O}_7^{2-}$ uptake and other anions. Since the hydroxyl ions are possible competitors for dichromate sorption, it therefore becomes apparent that sample pH affects this adsorption. This effect is demonstrated in Figure 5.77.

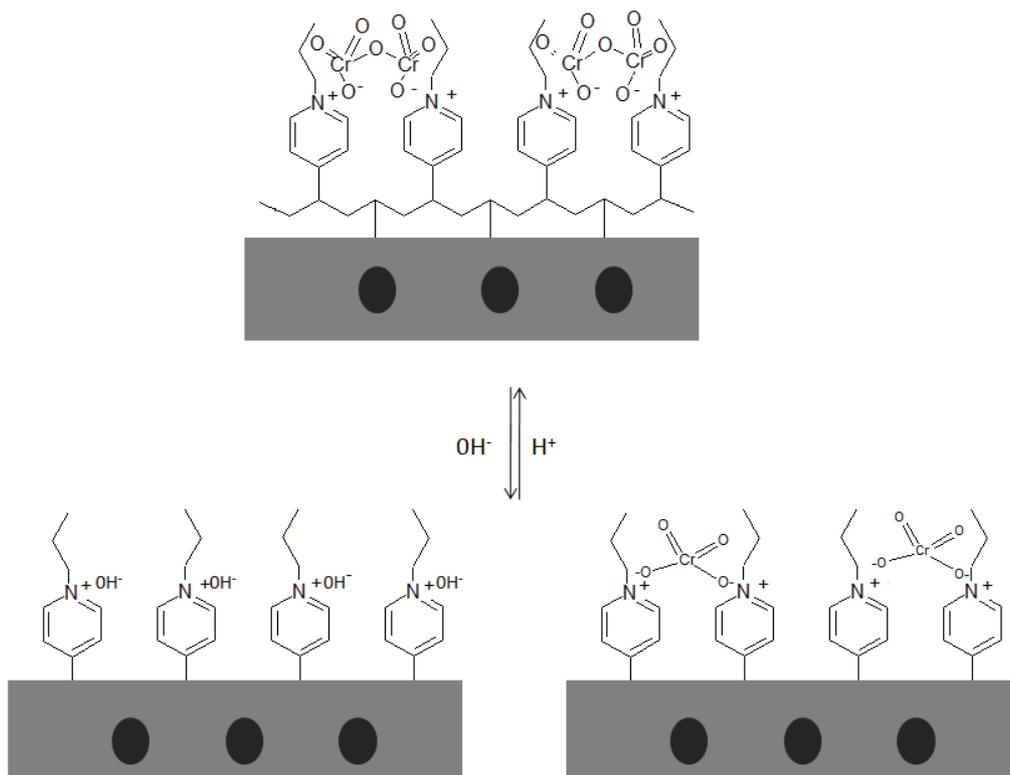


Figure 5.77: The effect of pH and also the demonstration of the chromate/ hydroxyl competition.

The effect of pH on the removal of Cr(VI) was investigated in the pH range of 1-10 at room temperature. The experimental results are presented in Figure 5.78 where it was observed that the maximum adsorption occurred at pH 2-6. The optimum pH for the uptake of Cr(VI) was then chosen to be 4 which corresponded to 90 and 73% Cr(VI) removal for the magnetic IIP and NIP respectively. The Cr(VI) removal efficiency decreased at pH values greater than 6 for both the magnetic IIP and its control polymer. Beyond this pH, there is an anticipated strong competition between hydroxyl ions and the dichromate ions in solution. These two anions compete for the fabricated active adsorption sites on the magnetic polymers. Similar results were obtained by Bayramoglu and Arica (2008) who showed that at high acidic pH of 2-4, adsorption was very high and decreased rapidly after pH 5. However, they did not quaternize their polymers but rather they used 4-VP as a functional monomer. Their Cr(VI)-ion imprinted poly (4-vinyl pyridine-co-2-hydroxyethyl methacrylate) particles were prepared by bulk polymerization. On poly (4-vinylpyridine) coating onto a granular activated carbon Fang *et al.* (2007) observed a 90% Cr(VI) removal at a pH of 2 which was almost maintained but decreased sharply at pH 6 to 8 and no apparent sorption was observed when pH was above 9. After firstly forming a linear copolymer from 4-VP and styrene, Pakade *et al.* (2011) prepared an IIP selective of Cr(VI) by quaternizing the linear copolymer with 1,4 dichlorobutane. The pH trend they got did not show a drop in Cr(VI) absorption after pH 4-5 because their pH only ranged from 1 up to 4.

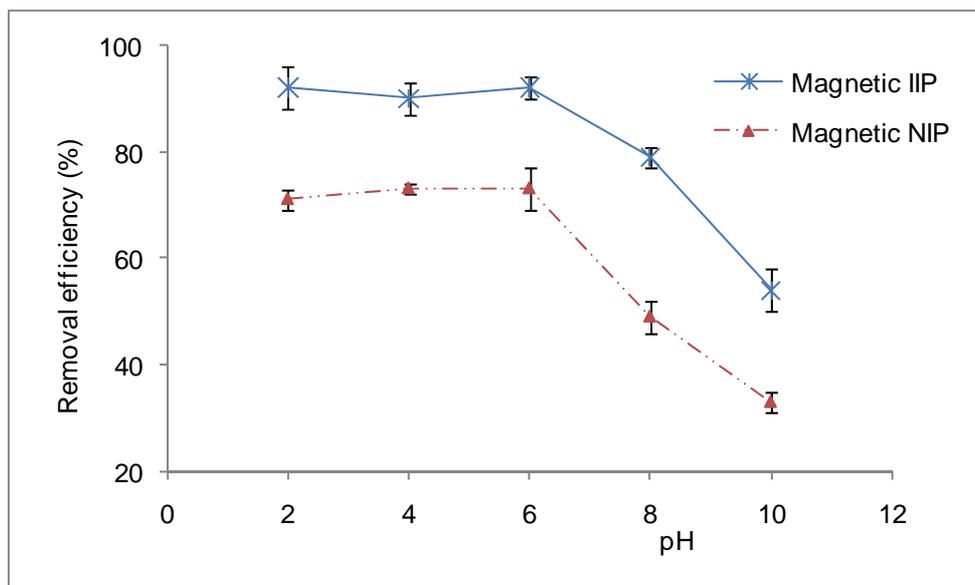


Figure 5.78: Effect of sample pH. Experimental conditions: Polymer amount, 20 mg; sample volume, 25 mL; chromium concentration, 5 mg L⁻¹; contact time, 45 minutes; stirring speed, 600 rpm; temperature, room temperature.

5.2.5.2 Effect of the amount of the adsorbent

The removal of chromium by magnetic polymers at different adsorbent doses (5-120 mg) from a Cr(VI) concentration of 5 mg L⁻¹ was investigated. The results (Figure 5.79) showed that, initially, the percent removal of Cr(VI) increased with the increase in the dose of magnetic polymers due to the greater availability of the adsorption sites within the adsorbent. For the magnetic IIP, the increase in adsorbent dosage from 5.0 to 20 mg resulted in an increase from 47 to 95% in adsorption efficiency of Cr(VI) ions whilst an increase from 83 to around 90% was observed for the dose from 5.0 to 65 mg for the magnetic NIP. The optimum amounts of magnetic polymer were then chosen to be 20 and 65 mg for the magnetic IIP and NIP respectively. Considering an initial volume of 25 mL for both the magnetic IIP and NIP, the normalized volume became 0.8 g L⁻¹ and 2.6 g L⁻¹ respectively.

Investigating the effect of polypyrrole/Fe₃O₄ nanocomposite dosage on adsorption of Cr(VI) from aqueous solution showed that Cr(VI) removal efficiency increased with an increase in polypyrrole/Fe₃O₄ dose (Bhaumik *et al.*, 2011). The extent of Cr(VI) removal from 50 mL of 200 mg L⁻¹ Cr(VI) solution changed from 16.3% at a dose of 25 mg to 100% at a dose of 100 mg which is equivalent to an optimum of 2 g L⁻¹ of polypyrrole/Fe₃O₄. In another study by Hadjmohammadi *et al.* (2011), who used pine needles powder as a biosorbent, the uptake of Cr(VI) from 50 mL of 50 mg L⁻¹ solutions, the adsorbent dose reached a plateau at 0.5 g of sorbent. This translated to 10 mg L⁻¹. Using tetraethylenepentamine on Fe₃O₄ magnetic polymer adsorbent, Yao *et al.* (2012) found a proportion of 20 mg per 250 mL (0.8 mg L⁻¹) water sample would ensure efficient preconcentration of Cr(VI).

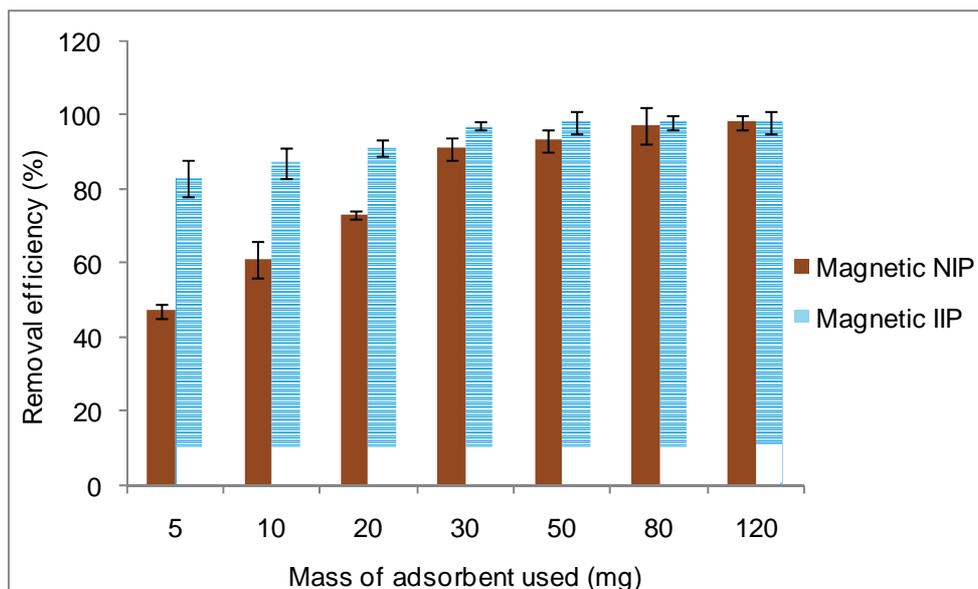


Figure 5.79: Adsorption percentages obtained by varying the mass of magnetic polymers for chromium adsorption. Experimental conditions: Sample pH, 4; sample volume, 25 mL; chromium concentration, 5 mg L⁻¹; contact time, 45 minutes; stirring speed, 600 rpm; temperature, room temperature.

5.2.5.3 Effect of contact time

Cr(VI) removal by magnetic polymers as a function of contact time is shown in Figure 5.80. Cr₂O₇²⁻ uptake was not fast and the maximum uptake was observed within 30-35 min for both the magnetic IIP and NIP. Before this time, there was a high rate of accumulation of the analyte in the adsorption sites within the magnetic polymer matrix. After reaching equilibrium, there was no further increase of adsorption of Cr(VI) as all the adsorption sites were saturated. A similar trend was observed by Yao *et al.* (2012) who used tetraethylenepentamine on Fe₃O₄ magnetic polymer as an adsorbent. Their results showed that the rate of Cr(VI) uptake was initially high, followed by a much slower subsequent adsorption quantity leading gradually to an equilibrium condition. A contact time of 60 min of stirring was considered enough to reach maximum values of separation and preconcentration of Cr(VI) ions (Yao *et al.*, 2012).

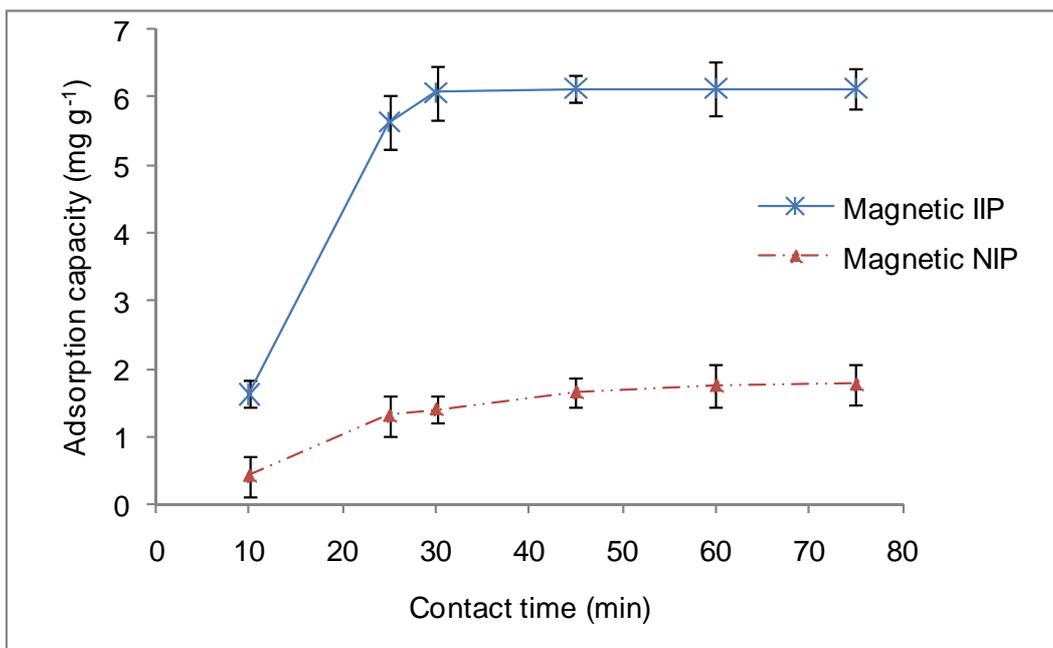


Figure 5.80: Effect of contact time on the uptake of chromium by magnetic polymers. Experimental conditions: Sample pH, 4; sample volume, 25 mL; chromium concentration, 5 mg L⁻¹; polymer weight (20 mg for magnetic IIP and 65 mg for magnetic NIP); stirring speed, 600 rpm; temperature, room temperature.

5.2.5.4 Effect of initial Cr(VI) concentration

The results obtained for the effect of initial concentration on the uptake of chromium by magnetic IIP and NIP are presented in Figure 5.81. An initial chromium concentration of 1-20 mg L⁻¹ was investigated. In this experiment, the magnetic polymer dose was fixed as well as the contact time and solution pH of which the values are indicated in the caption of Figure 5.80. It was observed that the magnetic polymers' Cr(VI) removal increased significantly from 1-2.5 mg L⁻¹ and 1-1.5 mg L⁻¹ for the magnetic IIP and NIP respectively. An initial Cr(VI) concentration of 5 mg L⁻¹ was taken to be the optimum. After this value, equilibrium was attained as there was no appreciable increase in the amount of the analytes adsorbed on the magnetic polymers. The maximum adsorption capacities for the magnetic polymers corresponding to the considered optimum Cr(VI) concentration of 5 mg L⁻¹ were 6.20 and 1.87 mg g⁻¹ for the magnetic IIP and NIP respectively.

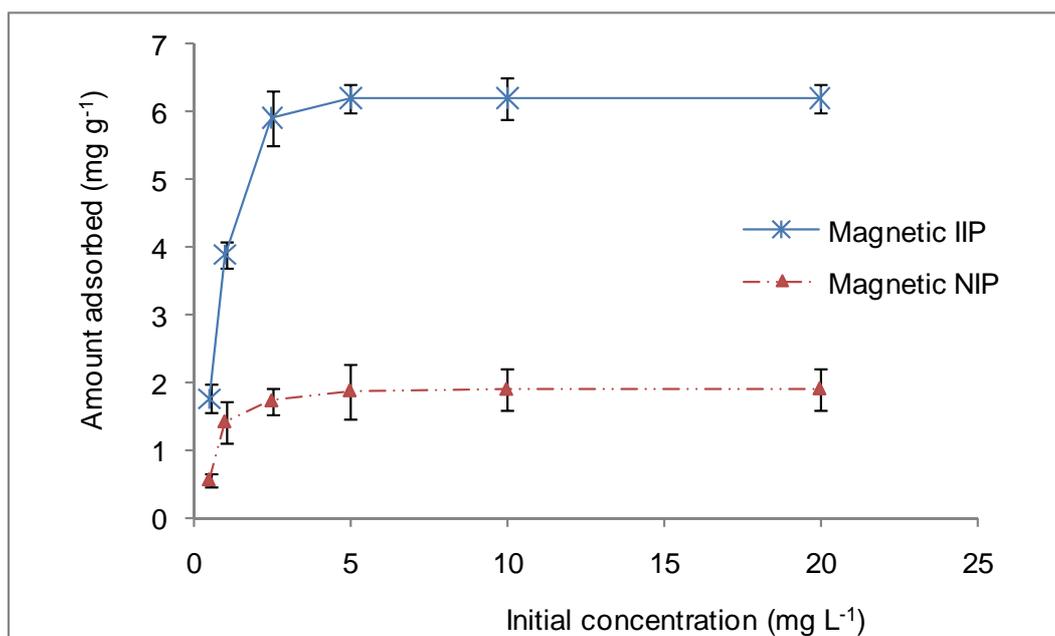


Figure 5.81: Effect of initial concentration on the uptake of chromium by magnetic IIP and NIP. Experimental conditions: Sample pH, 4; sample volume, 25 mL; polymer weight, (20 mg for magnetic IIP and 65 mg for magnetic NIP); contact time 35 min; stirring speed, 600 rpm; temperature, room temperature.

5.2.5.5 Selectivity of Cr(VI)

Competing anions are known to influence Cr(VI) uptake. However, because HCl was used as a leachant, it was likely that the chloride ion would have interfered with the selectivity studies, hence it was not used. The other ions selected, such as the sulphate and phosphate ions were selected as potential competitors because of their chemical similarities to the dichromate ion with respect to charge and oxy-ionic nature. Figure 5.82 is an example of the IC chromatogram of a 5 mg L⁻¹ anionic mixture standard. Similar chromatograms of 1, 10 and 20 were obtained and were used to construct calibration curves for the respective anions, Figure 5.83. For the binary mixture, Cr₂O₇²⁻/anionic competitor, the anion was also determined by IC and an example is illustrated for the fluoride ion in Figure 5.84. However, the equilibrium dichromate concentrations for all binary systems were determined by use of FAAS after the construction of a calibration curve, Figure 5.85. The selectivity performances of the magnetic polymers are summarized in Figure 5.86 and Table 5.23. The order of selectivity of the investigated anions followed the sequence: Cr₂O₇²⁻ > SO₄²⁻ > F⁻ > NO₃⁻.

Pakade *et al.* (2011) investigated the influence of coexisting ions on the uptake of Cr(VI) onto 1, 4 dichlorobutane quaternized linear copolymer. Their findings were that the selectivity order was Cr₂O₇²⁻ > SO₄²⁻ > F⁻ > PO₄³⁻ > NO₃⁻ > Cl⁻. After considering two Cr(VI) competitors, Neagu and Mikhalovsky (2010) found that there was also a rather remarkable selectivity towards hexavalent chromium over the sulfate anion. The full order of selectivity was Cr₂O₇²⁻ > SO₄²⁻ > Cl⁻ which was almost what was obtained in our studies. However, the same authors reported that the adsorption selectivity for the common anions

onto commercial styrene anion exchangers and it followed the order: $\text{SO}_4^{2-} > \text{I}^- > \text{CrO}_4^{2-} > \text{Br}^- > \text{Cl}^-$. Fang *et al.* (2007) also performed some selectivity studies on three competitor ions for Cr(VI) and found the selectivity order of $\text{PO}_4^{2-} > \text{SO}_4^{2-} > \text{NO}_3^-$. For the two Cr(VI) competitors investigated by Bayramoglu and Arica (2011), it was demonstrated that (4-vinyl pyridine-co-hydroxyethyl methacrylate) particles showed excellent selectivity for Cr(VI) and the adsorption capacity of IIP particles for Cr(VI) anions was 13.8 and 11.7 fold greater than those of the Cr(III) and Ni(II) ions respectively.

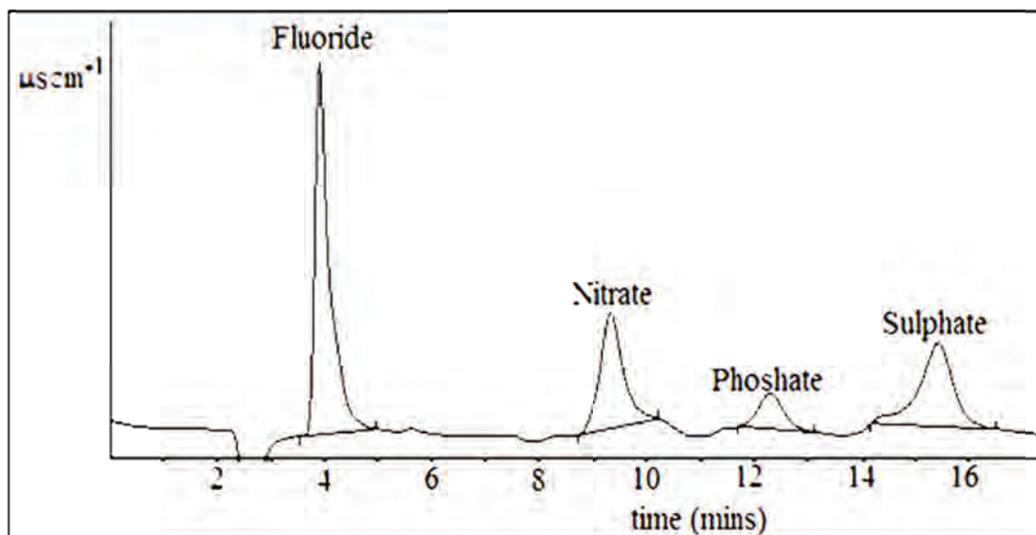


Figure 5.82: A 5 mg L^{-1} anionic mixture standard.

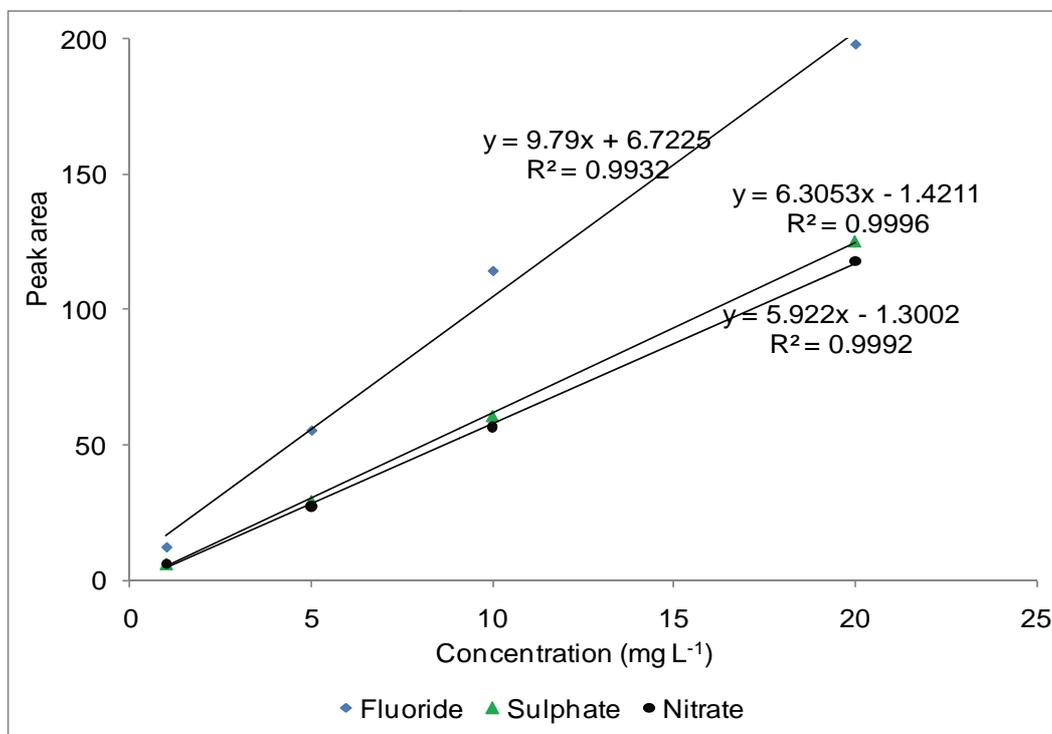


Figure 5.83: Calibration curve for four dichromate anionic competitors.

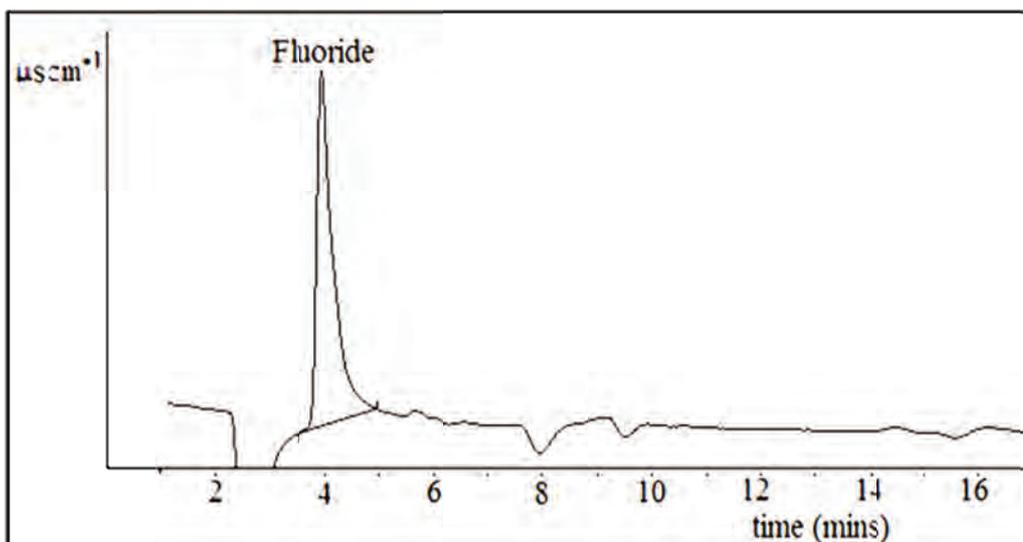


Figure 5.84: An example of a fluoride ion dichromate competitor.

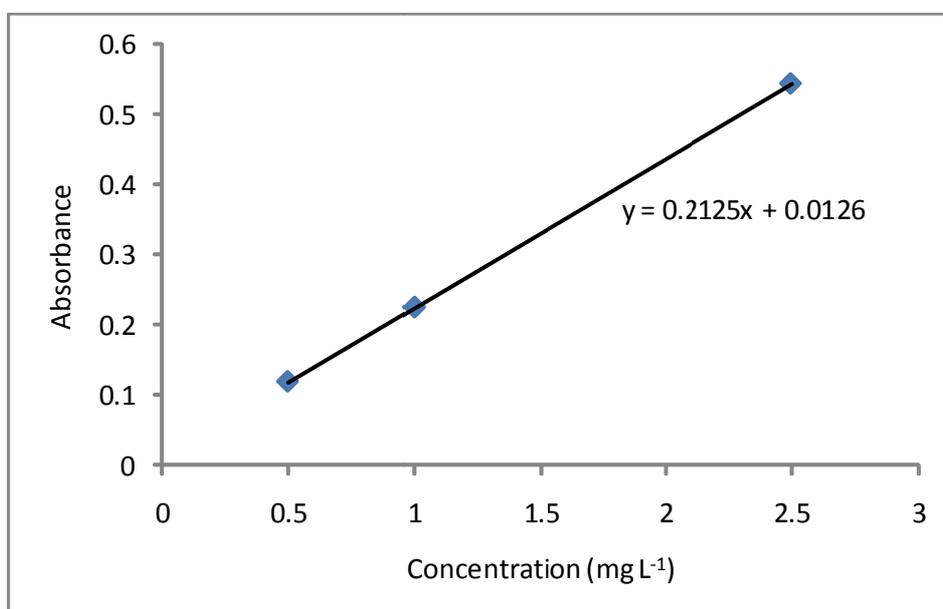


Figure 5.85: Calibration curve for the dichromate anionic standards.

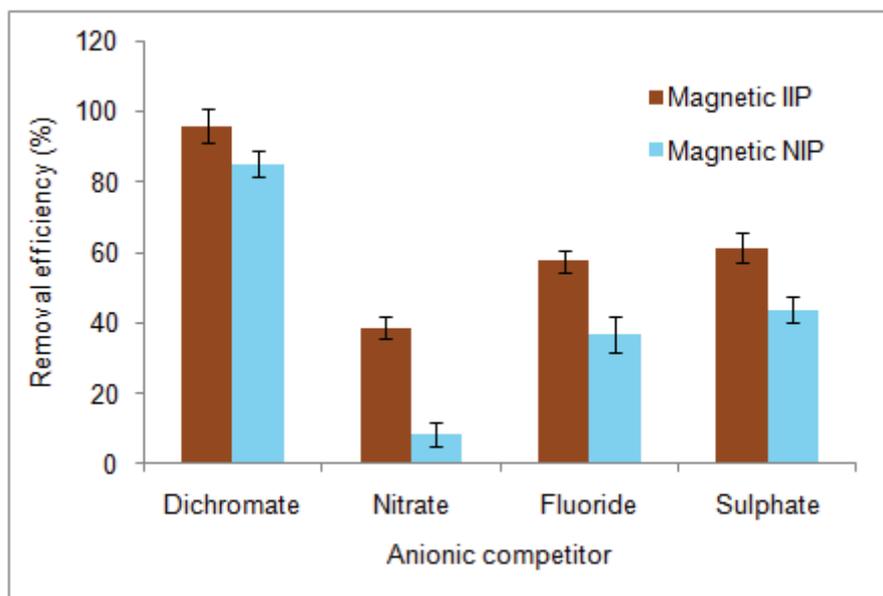


Figure 5.86: Extraction efficiencies of anions extracted by the magnetic Cr(VI) IIP and NIP from 2 mg L⁻¹ spiked binary mixtures of solutions.

Table 5.23: K_d, K and K['] values for the magnetic Cr(VI) IIP and NIP in binary mixtures.

Cr ₂ O ₇ ²⁻ ion Competitor	K _d (L g ⁻¹)				K		K [']
	Cr ₂ O ₇ ²⁻ IIP	Cr ₂ O ₇ ²⁻ NIP	Magnetic IIP	Magnetic NIP	Magnetic IIP	Magnetic NIP	Magnetic NIP
SO ₄ ²⁻	11.70	3.06	1.98	0.30	5.91	10.20	0.58
F ⁻	23.50	1.90	1.69	0.22	13.91	8.64	1.61
NO ₃ ³⁻	33.00	5.53	0.79	0.035	41.77	158	0.26

5.2.5.6 Reusability of Cr-magnetic polymers

Since the reusability of the magnetic polymers is an important factor, six adsorption-desorption cycles were performed, Figure 5.87. What was observed was that the magnetic polymers maintained their stability as well as their chromium abstraction capacity of 98.5% and 89% for the magnetic IIP and NIP respectively. This high robustness of the imprinted polymers has the significance that they can be cleaned, thereby regenerating their adsorption capabilities. For up to 5 cycles, the IIP synthesized by Pakade *et al.* (2011) was still stable as it showed 96% extraction efficiency.

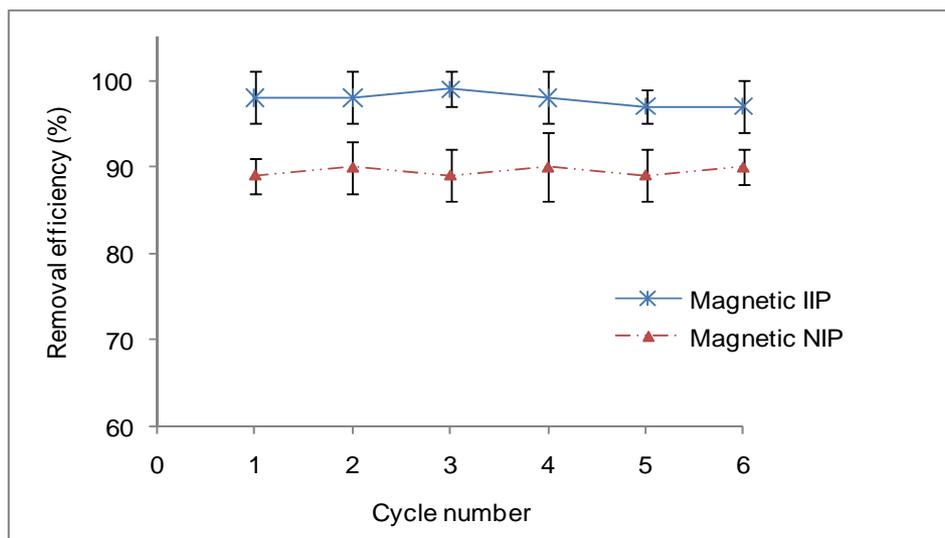


Figure 5.87: Reusability and stability magnetic IIP and NIP selective to chromium. Adsorption conditions: Sample pH, 4; sample volume, 25 mL; polymer weight, (20 mg for magnetic IIP and 65 mg for magnetic NIP); contact time 35 min; initial dichromate concentration, 5 mg L⁻¹; stirring speed, 600 rpm; temperature, room temperature, Desorption conditions: Solution volume, 20 mL; contact time, 20 min, [NaOH] leachant, 1 M.

5.2.6 Kinetic modelling

5.2.6.1 Pseudo-first order kinetics

The correlation coefficients values for the pseudo-first and second order kinetics were calculated from the plots of Figures 5.88 and 5.89 respectively.

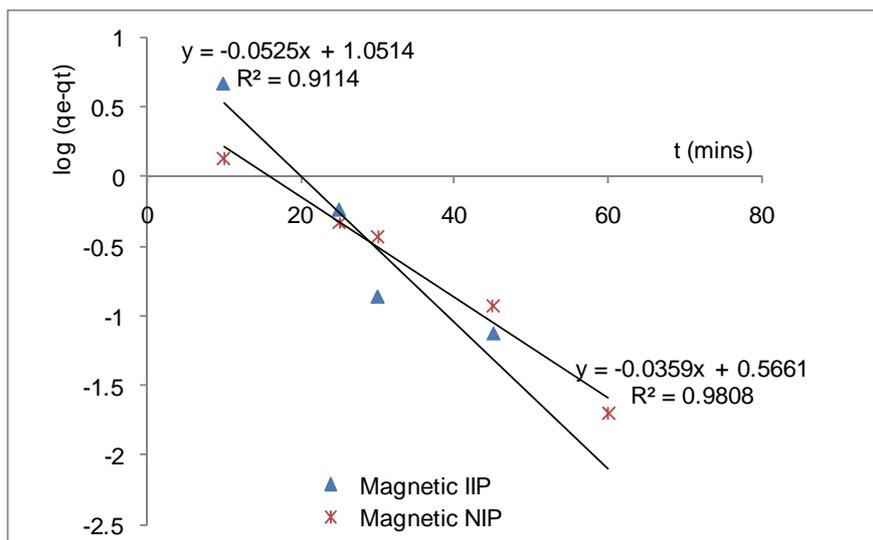


Figure 5.88: Pseudo first-order plots for the adsorption of chromium onto magnetic polymers.

5.2.6.2 Pseudo-second order kinetics

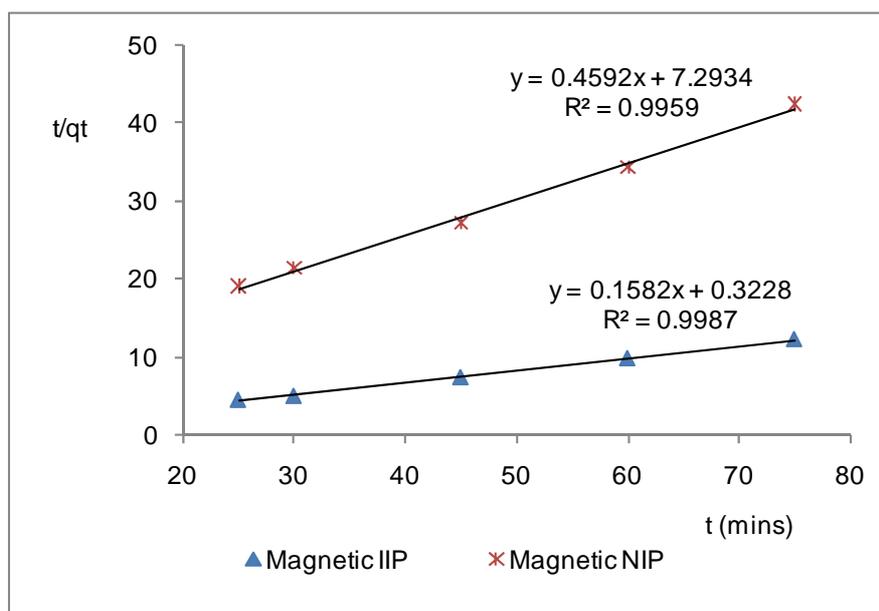


Figure 5.89: Pseudo second-order plots for the adsorption of chromium onto magnetic polymers.

Table 5.24: Calculated kinetic parameters of pseudo-first and second orders for initial Cr(VI) concentration of 5 mg L⁻¹.

Polymer	Pseudo first-order			Pseudo second-order		
	R ²	k ₁ (L min ⁻¹)	q _e (mg g ⁻¹)	R ²	k ₂ (g mg ⁻¹ min ⁻¹)	q _e (mg g ⁻¹)
IIP	0.9114	0.121	11.256	0.9987	0.078	3.098
NIP	0.9808	0.083	3.682	0.9959	0.029	2.178

It was observed that correlation coefficients values of the pseudo-second order kinetics produced better quality of linearization compared to the pseudo-first order kinetics. Moreover, the adsorption capacity values obtained by this method were much closer to those reported before in this work (6.20 and 1.87 mg g⁻¹ for the magnetic IIP and NIP respectively). A pseudo-second order further suggests that the type of interaction between the target template and the adsorbent surface was chemisorptions as a rate controlling step (Wang *et al.* 2011). This interaction was probably due to the exchange of electrons on the dichromate and the quaternized nitrogens.

5.2.7 Freundlich and Langmuir isotherm modelling

Figure 5.90 and 5.91 present the Freundlich and the Langmuir isotherm model for magnetic IIP and NIP respectively.

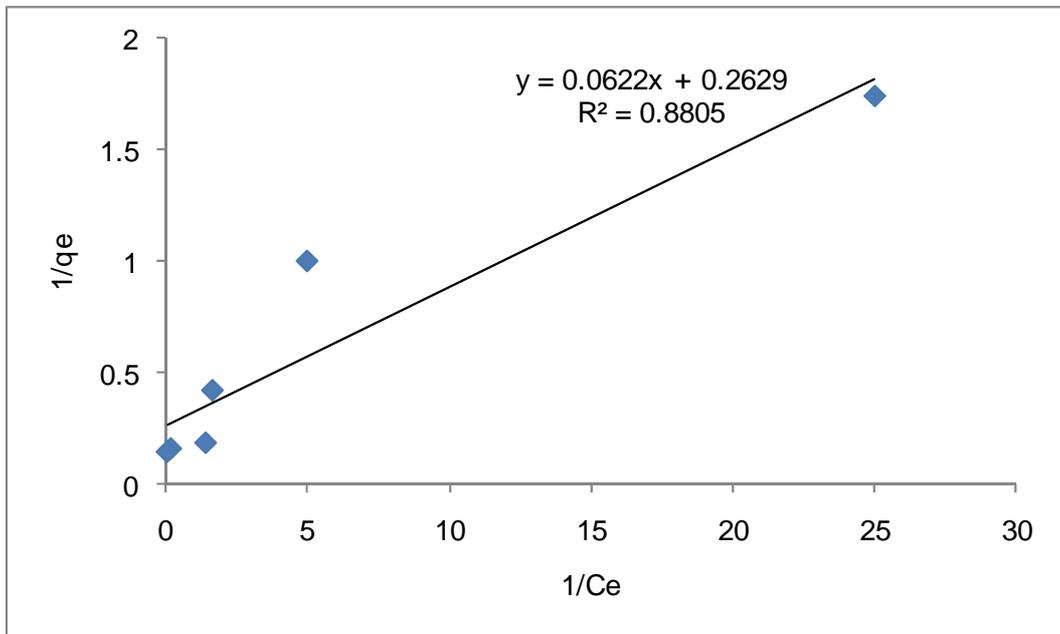
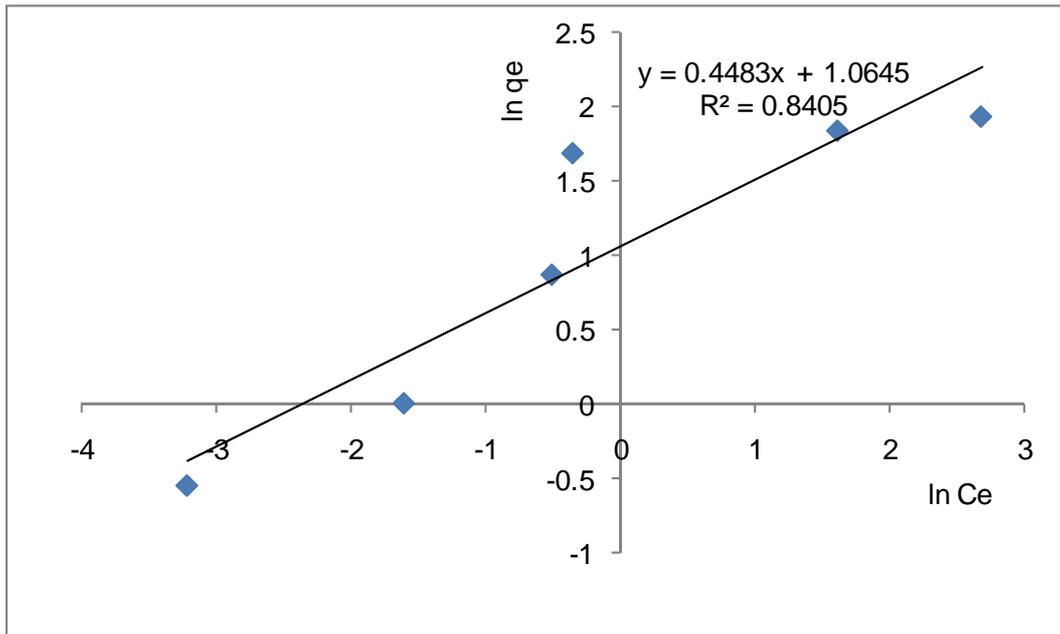


Figure 5.90: (a) Freundlich and (b) Langmuir isotherm model for magnetic IIP.

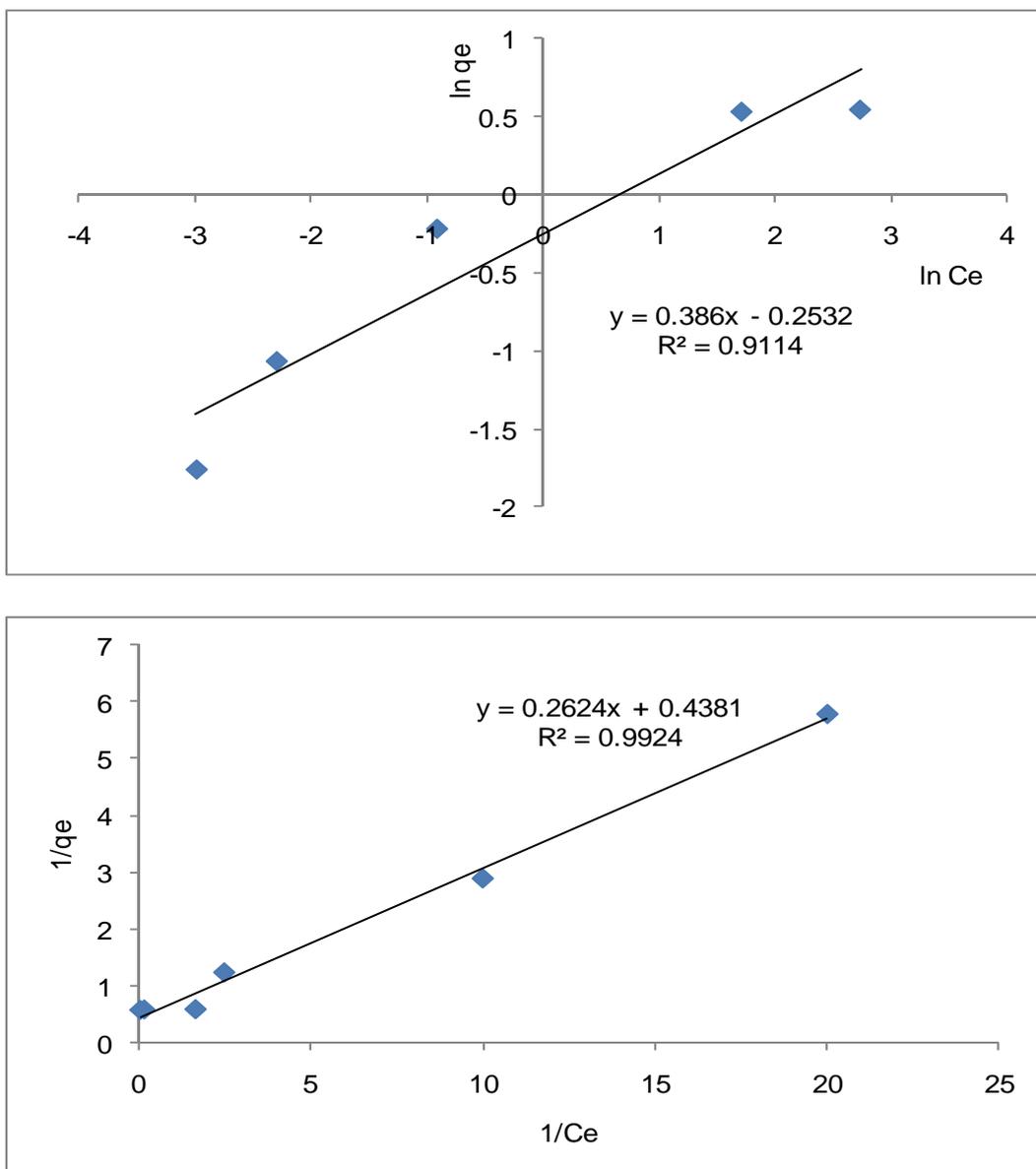


Figure 5.91: (a) Freundlich and (b) Langmuir isotherm model for magnetic NIP.

Table 5.25: The Langmuir and Freundlich constants for adsorption of Cr(VI) on magnetic polymers.

Magnetic polymer	Langmuir isotherm				Freundlich isotherm		
	b ($L g^{-1}$)	q_m ($mg g^{-1}$)	R_L	R^2	n	K_f ($L g^{-1}$)	R^2
Cr- IIP	4.23	3.8	0.05	0.881	2.23	2.90	0.841
Cr -NIP	1.67	2.3	0.11	0.992	2.59	0.78	0.911

Since the separation factors for both the magnetic IIP and NIP are within the range of zero and unity, Cr(VI) adsorption onto magnetic polymers was deemed favourable. This indicates the suitability of the adsorbent to extract the target from aqueous solution (Zhou *et al.*, 2012).

Chapter Six: Conclusions and Recommendations for future work

6.1 Conclusions

The imprinting technique proved that a memory of the targets U(VI) and Cr(VI) can be induced in the magnetic polymer such that in subsequent use, even in the presence of other competing ions in aqueous media, selectivity was enhanced. After adsorption the adsorbents were traditionally removed from the solutions *via* centrifugation and filtration. This approach is however not economically viable on a large industrial scale. The technique of endowing magnetic particles into the polymer matrix, as demonstrated in this research, makes the whole polymer particles magnetic and this necessitated their easy removal from solutions. The successful incorporation of the magnetite into the polymer was evident from the FTIR where a band at was observe implying that the general objective of this to synthesize magnetic polymers selective to U(VI) and Cr(VI) was realized.

Both magnetic IIPs and NIPs showed potential in the uptake of uranium and chromium from contaminated solutions as these imprinted magnetic polymers were successfully applied for the selective extraction of the respective analytes from various complex samples which were AMD and treated wastewater effluent. Adsorption capacities for the Cr(VI) magnetic IIP were 6.20 and 1.87 mg g⁻¹ for the magnetic IIP and NIP respectively and the order of selectivity for the U(VI) magnetic IIP was $\text{UO}_2^{2+} > \text{Fe}^{3+} > \text{Pb}^{2+} > \text{Ni}^{2+} > \text{Mg}^{2+}$ and that for the Cr(VI) magnetic IIP was: $\text{Cr}_2\text{O}_7^{2-} > \text{SO}_4^{2-} > \text{F}^- > \text{NO}_3^-$. Magnetic IIPs always expectedly showed a higher uranyl and dichromate uptake as compared to their corresponding magnetic NIPs.

The uptake of the uranyl was made possible by the presence organic ligands (functional groups) with oxygen and nitrogen atoms that provided lone pairs of electrons to the cationic uranyl ion through coordinate bonding. For the adsorption of the Cr(VI), quaternization enabled the extraction of anionic dichromate target.

6.2 Recommendations for future work

- There is need to carry out the polymerization reaction in aqueous media rather than the organic solvents in order to avoid the swelling and shrinkage of magnetic polymers. This however means changing of the initiator to those compatible with water.
- The application of the synthesized magnetic polymers can be applied to a pilot plant scale and ultimately to real environmental systems. It is therefore important to carry out the same adsorption studies in a continuous flow system that mimic a river system. In this approach, the magnetic polymers need to be contained in cartridges such as those used in SPE.
- To use natural adsorbents like chitosan, cellulose that can be compatible with magnetic materials. This is because synthetic polymeric reagents becomes expensive

especially when large quantities are required to decontaminate large volumes of wastewaters in real environmental situations. Most natural adsorbents are cheap and readily available.

- To try other methods for coating the magnetite wholly as this is important so that no part of the exposed magnetic core takes part in the adsorption of the uranyl and dichromate ions from solution. Adsorption studies of the uranyl and dichromate ion by a bare magnetite should also be carried out to show its contribution in the case of partial coating.
- In this study, only oxygen and nitrogen bearing functional monomers were used (for uranium magnetic IIP). It is however important that monomers with electron lone pair donating atoms like sulphur be investigated in order to see if there can be an improvement in the adsorption capacity.

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Appendix

A.1 Calculation of the amount of γ -MPS on the surface of the magnetite using CHNS Analysis

$$\text{Mass of the sample} = 2 \text{ mg}$$

$$\text{C in the sample} = 20.16\%$$

$$\text{Mass of carbon in the sample} = 20.16\% \times 2$$

$$= 0.4032 \text{ mg}$$

$$\text{Ligand concentration} = \frac{(0.4032 \times 10^{-3})}{12}$$

$$= 3.36 \times 10^{-5} \text{ moles (in 2 mg-sample)}$$

$$\text{Ligand concentration per g} = \frac{(3.36 \times 10^{-5})}{(2 \times 10^{-3})}$$

$$= 16.8 \text{ mmol C g}^{-1}$$

The three other values for the ligand concentration per gram were similarly calculated and the values were both $15.8 \text{ mmol C g}^{-1}$.

$$\text{Ligand concentration} = (11) \times (16.1)$$

$$= 177.1 \text{ mmol H g}^{-1}$$

$$\text{Mass of H per g} = (177.1) \times (1)$$

$$= 177.1 \text{ mg H g}^{-1}$$

$$= 17.71\%$$

A.2 Calculation of the amount of OA on the surface of the magnetite using CHNS Analysis

$$\text{Mass of the sample} = 2.05 \text{ mg}$$

$$\% \text{ C in the sample} = 4.627\%$$

$$\text{Mass of carbon in the sample} = 4.627\% \times 2.05$$

$$= 0.9485 \text{ mg}$$

$$\text{Ligand concentration} = \frac{(0.9485 \times 10^{-3})}{12}$$

$$= 7.9 \times 10^{-5} \text{ moles (in 2 mg-sample)}$$

$$\begin{aligned}\text{Ligand concentration per g} &= \frac{(7.9 \times 10^{-5})}{(2.05 \times 10^{-3})} \\ &= 38.1 \text{ mmol C g}^{-1}\end{aligned}$$

$$\begin{aligned}\text{Ligand concentration} &= (33) \times (3.85) \\ &= 42.35 \text{ mmol H g}^{-1}\end{aligned}$$

$$\begin{aligned}\text{Mass of H per g} &= (42.35) \times (1) \\ &= 42.35 \text{ mg H g}^{-1} \\ &= 4.24\%\end{aligned}$$

A.3 PXRD analysis: Particle size analysis

$$\begin{aligned}\bar{D} &= \frac{57.3 \cdot k \cdot \lambda}{\beta \cos \theta} \\ &= \frac{57.3 \cdot k \cdot \lambda}{\beta \cos \theta} \\ &= \frac{(57.3)(0.9)(1.5418)}{(0.7)(\cos 17.5)} \\ &= 119.1 \text{ \AA} \\ &= 11.9 \text{ nm}\end{aligned}$$

A.4 TEM micrograms of the uncoated and coated γ -MPS-magnetite.

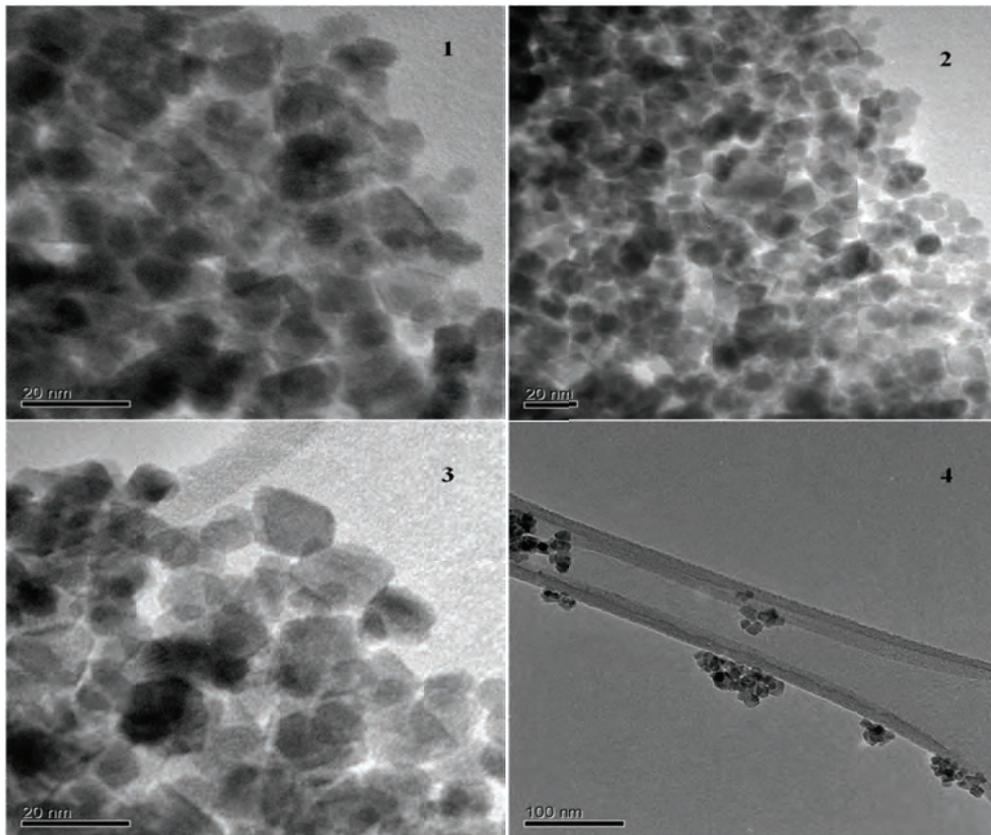


Figure A1: TEM micrograms of the uncoated magnetite.

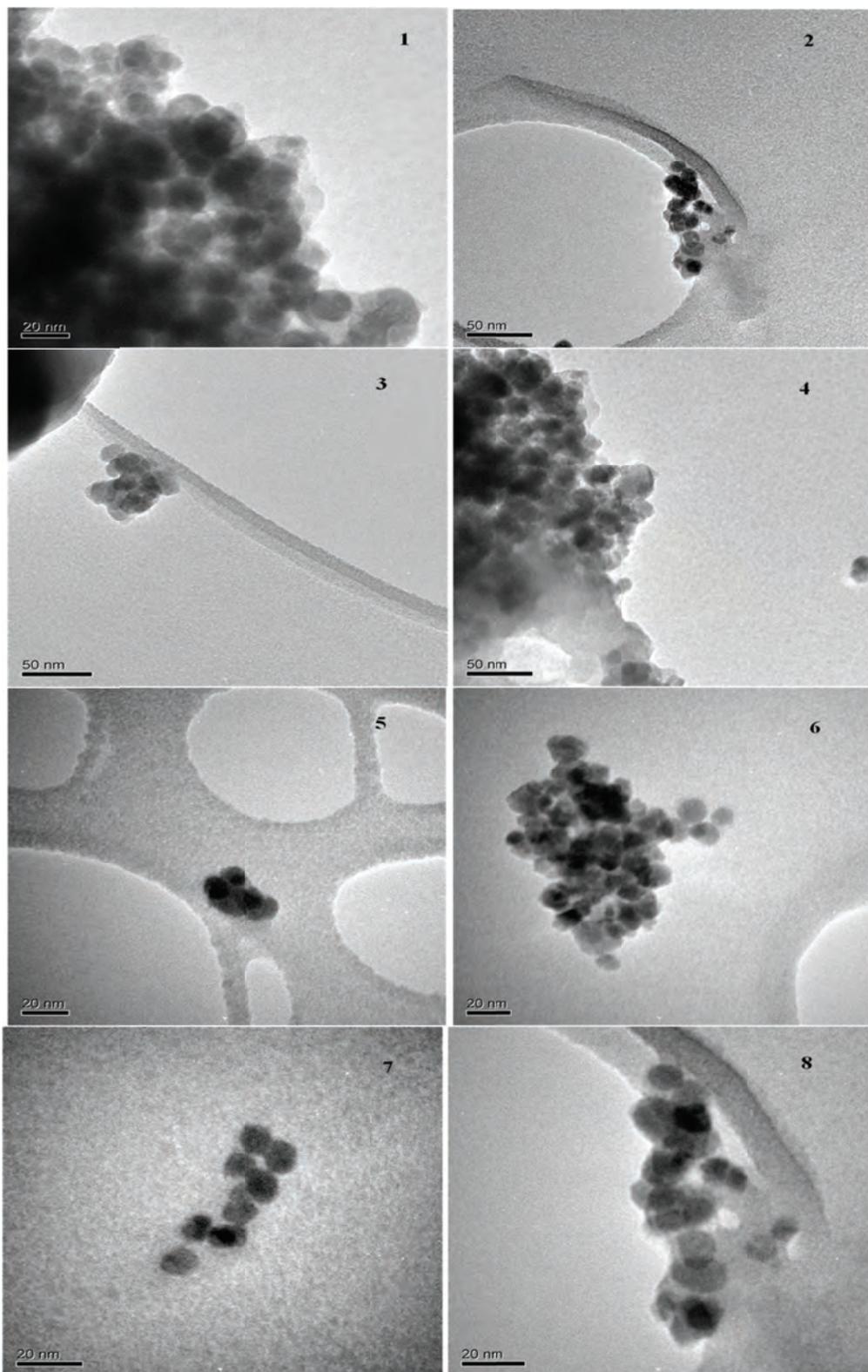


Figure A2: TEM micrograms of the coated γ -MPS-magnetite.