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**AN ION IMPRINTED POLYMER FOR THE DETERMINATION OF Ni (II)
IONS FROM MINE TAILING SAMPLES**

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LIST OF ABBREVIATIONS

AAP - 2,2'-Azobis-(2-amidinopropane) dihydrochloride

ACHC - 1,1'-Azobis(cyclohexane carbonitrile)

ACPA - 4,4'-Azobis(4-cyanopentanoic acid)

AIBN – Azobisisobutyronitrile

ADP - Ammonium pyrrolidine dithiocarbamate

AQ - Amino quinoline

CRM - Certified reference material

DCQ – Dichloroquinoline

DMG – Dimethylglyoxime

DMG-NIP – Non imprinted polymer

DVB - Divinyl benzene

EDTA - Ethylenediaminetetraacetic acid

EE - Extraction efficiency

EF - Enrichment factor

EGDMA - Ethylene glycol dimethacrylate

ETAAS - Electrothermal atomic absorption spectrometry

FAAS - Flame atomic absorption spectrometry

HEMA - 2-Hydroxyethyl methacrylate

HCl - Hydrochloric acid

HPLC - High performance liquid chromatography

HQ - Hydroxy quinoline

8 HQ - Hydroxy quinoline
ICP-OES - Inductively coupled plasma-optical emission spectrometer
IIPs - Ion imprinted polymers
ISE - Ion-selective electrode
LLE - Liquid-liquid extraction
LOD - limit of detection
LOQ - Limit of quantification
MAA – Methacrylic acid
MAH – Methacryloylamidohistidine
MIBK - Methyl isobutyl ketone
MIPs - Molecular imprinted polymers
MQ - Mercapto quinoline
Ni(II) IIP – Nickel(II) ion imprinted polymer
NIP - Non imprinted polymer
NIPA - N-Isopropylacrylamide
Ni(II)-DMG IIP – Ni(II)-Dimethylglyoxime ion imprinted polymer
NiSO₄·6H₂O- Nickel(II) sulfate hexahydrate
PEG - Polyethylene glycol
RSD - Relative standard deviation
SAX - Strong anion-exchange
SCX - Strong cation-exchange
SEM - Scanning electron microscopy
SPE - Solid-phase extraction
THF – Tetrahydrofuran
VP - Vinylpyridine
4-VP – 4-Vinyl pyridine

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DEDICATION

I will like to dedicate this thesis to my late eldest brother, Seaego 'Shao' Rammika and my mum Steolo Pauline Madumetse whom recently left this world. May their souls rest in peace.

ABSTRACT

A Ni(II)-dimethylglyoxime ion imprinted polymer {Ni(II)-DMG IIP} was synthesized by the trapping method using the bulk polymerisation format. The structures of the imprinted and non-imprinted polymer were evaluated by infrared spectroscopy and the morphology was observed by scanning electron microscopy. The Ni(II)-DMG IIP was optimised for pH, mass, time and by the uniform design experimental method for the molar ratios of monomer to crosslinker to porogen and template to ligands as well as keeping these parameters constant and varying the quantities of initiator, 2,2'-azobisisobutyronitrile (AIBN). The optimum pH was 8.5, optimum mass was 50 mg, optimum time was 1 min and the optimum molar ratios of crosslinker to monomer, monomer to template and nickel(II) sulfate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) to 4-vinylpyridine to dimethylglyoxime were found to be 3.3:1.0, 0.6:1.0 and 1.0:0.6:3.6 respectively with 30 mg and 8 mL as the optimum amounts of initiator and porogen respectively. Through this optimisation, recovery of Ni(II) was increased from 98 to 100%. Selectivity of the ion imprinted polymer was evaluated by analysing, using an inductively coupled plasma-optical emission spectrometer, for Ni(II) ions that were spiked with varying concentrations of Co(II), Cu(II), Zn(II), Pd(II), Fe(II), Ca(II), Mg(II), Na(I) and K(I) in aqueous samples. Selectivity studies also confirmed that the ion imprinted polymer had very good selectivity characterised by % RSD of less than 5%. Co(II) was the only ion found to slightly interfere with the determination of Ni(II). The limits of detection and quantification were found to be 3×10^{-4} $\mu\text{g/mL}$ and 9×10^{-4} $\mu\text{g/mL}$ respectively. The method was evaluated by a custom solution of ground water certified reference material (SEP-3) and sandy soil reference material (BCR-142R) and the concentrations of Ni(II) obtained were not significantly different to the certified ones. The Ni(II)-DMG IIP was then evaluated in aqueous and soil samples where recoveries of 93 to 100% and 98 to 99% respectively were obtained with enrichment factors ranging from 2 to 18 in aqueous and 27 to 40 in soil samples. Finally, the Ni(II)-DMG IIP was used to analyse mine tailings samples and Ni(II) recovery of 99% was obtained with an enrichment factor of 2.

CHAPTER 1

1.0 INTRODUCTION

Heavy metals are stable and cannot be degraded nor destroyed. They therefore tend to accumulate in the environment from where they eventually get into the human food chain. The human body needs some of these metals at trace levels but further accumulation in the body results in various health effects. It is therefore important to determine their levels in the environment. Most of these heavy metals come from mine tailings [1-3].

Mine tailings are waste materials left after the process of separating the valuable mineral fraction from the mineral ore. As mining techniques and the price of minerals improve, mine tailings have to be reprocessed using new methods, or more thoroughly with old methods, to recover additional minerals. Mine tailings result in heavy metal pollution to the environment [4-5] and take land that could be put to better use. They have severe health implications on people and animals [6-7]. This is because depending on the composition of the ore and the process of mineral extraction method used on the ore, environment, weather and soil, there are some elements that are present in the tailings and some additives that are used during the extraction of mineral from tailings [8-9]. Several attempts including water constructed wetlands [10], planting metallophytes for biodiesel production or bioremediation [11-15], organic medium [16], electrokinetic and electro-dialytic remediation [17-18] have been used to rehabilitate mine tailings.

However, mine tailings can be used in agriculture as fertilizers for crops [19-20]. This is particularly important for elements such as nickel and iron which are below detectable levels in commonly used fertilizers such as urea and superphosphate [21] but contain elements such as copper and zinc as impurities in excessive levels for most crops [22]. Therefore to be used as fertilizers, mine tailings need to be characterized in terms of their elemental composition. This is because most mine

tailings are complex [23] to be introduced into the analytical instrument directly. Hence sampling, sample cleanup as well as preconcentration methods to enhance selectivity prior to their determination for elements such as nickel and iron are needed as they are found in mine tailings [24-25].

1.1 Extraction methods

There are various methods that are used to extract metal ions from solutions or matrices. These include normal digestion, microwave digestion, slurry techniques, electrodeposition, chemical precipitation, cementation, ultra filtration, ion exchange, activated carbon adsorption, liquid-liquid extraction and solid phase extraction.

1.11 Normal and microwave digestion

Normal digestion is usually carried out by putting the sample into a beaker, adding concentrated acids and sometimes oxidising materials such as hydrogen peroxide and heating the solution for a specified period of time on a hot plate or digestion block. This method is labour intensive, requires a little bit of skill and experience, time consuming and leads to samples loss [26]. Microwave digestion is similar to normal digestion except that a microwave is used instead of a hot plate or digestion block as in normal digestion [27]. When the three methods (microwave digestion, dry ash digestion and wet oxidation digestion) were compared, it was realised that all the three methods gave similar results; however, microwave is preferred in that it is fast, simple, safe, uses less reagent/sample and is relatively easy to use [28]. However, the microwave method requires the operator to have the skill to operate the microwave. The microwave digester is also expensive and can only load 12 samples hence time savings diminishes with the increasing number of samples.

1.12 Slurry techniques

Slurry technique is similar to direct solid sampling because of the small quantities of sample involved. However, it differs from the solid sampling in that pipettes can be used to quantify volumes hence it can be said to be between solid and liquid

sampling. It is relatively easier as compared to solid sampling. In a study where the slurry formation by sonication and atomic absorption determination was used to determine Cd in different solid samples, the method was good and showed to be comparable to conventional digestion methods and had advantages such as less time preparation, reduced sample contamination and loss, less reagents/analytes needed [29]. Good precision was obtained for all samples analysed [29]. Ultrasound-assisted extraction, slurry sampling and microwave-assisted digestion were once compared for cadmium, copper and lead determination in biological and sediment samples by electrothermal atomic absorption spectrometry (ETAAS) and the results showed that precision of ultrasound-assisted extraction and slurry analysis were not significantly different but were better than digestion results [30]. The ultrasound-assisted extraction procedure does not decompose the sample and contamination takes place during pre-treatment. Cd in brown bread, chlorella and tuna homogenate could only be detected with ultrasound-assisted extraction and slurry sampling due to high detection limits compared with decomposed samples [30]. However, this method is less homogenous as compared to liquid sampling and build-up of carbonaceous residues typically occurs in slurry sampling of biological materials [31].

1.13 Electrodeposition

Electrodeposition is the process of producing a coating on a surface by the action of electric current [32]. The deposition of a metallic coating onto an object is achieved by applying a negative charge on the object to be coated and immersing it into a solution which contains a salt of the metal to be deposited. The metallic ions of the salt carry a positive charge and are thus attracted to the object. When they reach the negatively charged object it provides electrons to reduce the positively charged ions to metallic form. An example is where copper and nickel were electrodeposited on InBi alloy electrodes using classical baths and good deposits were obtained provided that the current density did not exceed 1000 A/m^2 [33]. A low limit of detection (LOD) of $5.0 \times 10^{-10} \text{ M}$ was achieved for short gold deposition times (10 min for carbon paste electrode and 5 min for glassy carbon electrode) with this method [34]. However, it must be said that generally the method is not selective and therefore prone to interference and long time needed for preconcentration [35,36].

1.14 Cementation and chemical precipitation

Cementation reaction is a spontaneous electrochemical reaction that involves electrochemical precipitation of a noble metal from solutions of its salts on a more electronegative metal, which correspondingly dissolves [37]. Cementation is a feasible method when the concentration of the metal needed to be recovered is not very high. Chemical precipitation is the formation of a solid in a solution during a chemical reaction [38]. It involves the addition of a chemical agent to an aqueous solution and stirring for a certain period of time. The metals are converted into insoluble compounds by reactions between the chemical agent and the dissolved metal ion. The precipitates are then removed by settling and filtering. It is simple and low cost.

Marchioretto et al. successfully removed lead, chromium, copper and zinc from anaerobically digested sludge by sulfide and hydroxide precipitation (in single and combined ways) followed by filtration at bench scale [39]. The results showed that the combination of hydroxide and sulfide precipitation before physical separation was capable of promoting an efficient removal of heavy metals from anaerobically digested sludge. Recoveries of 100, 99.9, 99.7 and 99.9% for lead, chromium, copper and zinc respectively were achieved. In another study, cobalt, lead, copper, iron and zinc were co-precipitated with Ni(II)-2-Nitroso-1-naphthol-4-sulfonic acid prior to their determination by flame atomic absorption spectrometry (FAAS) [40]. Recoveries were more than 95% and the LODs were 1.05×10^{-3} , 2.67×10^{-3} , 1.30×10^{-3} , 1.38×10^{-3} and 0.50×10^{-3} $\mu\text{g/mL}$ for cobalt, lead, copper, iron and zinc respectively. The drawback of this method is that it only works well for precipitates that can be efficiently removed by filtering. It can also be applied efficiently to only a few metals (arsenic, barium, cadmium, chromium, lead, mercury, selenium, silver, nickel, copper, manganese, cobalt zinc, calcium, iron and strontium).

1.15 Ultrafiltration

Ultrafiltration is the passing of a solution through a network of semi-permeable membranes that permits soluble compounds of various molecular size ranges to

pass through their pores. An ultrafiltration filter has pore sizes of around 0.01 micron. Ultrafiltration is an expensive and equipment-intensive method. In most cases it is used to separate aquatic humic solutes from low molecular organic compounds and inorganic salts. In one study, a sodium salt of 2-(2-carboxyethyl)-3-decyl maleic anhydride was used to trap Cu(II), Zn(II), Cd(II), and Ni(II) ions from aqueous solution containing either a single metal species or mixtures of metal ions [41]. The 2-(2-carboxyethyl)-3-decyl maleic anhydride showed good binding capacities for copper with a rejection coefficient of 98%, zinc with 89.11 to 98.71%, cadmium with 95.58 to 99.53% and nickel was the lowest with 75.89 to 95.33%. In one application, it was reported that an ultrafiltration extraction method was used to determine zinc ions [42]. Ligands nitrilotriacetic acid, ethylenediamine tetraacetic acid (EDTA), humic acid, 8-hydroxyquinoline-5-sulphonic acid and 8-hydroxyquinoline (8-HQ) were packed in columns with cation-exchange resins chelex-100, anion-exchange resin dowex 1-X8 and C-18 reversed phase mode and % uptake of up to 100 was achieved. The disadvantage of the method is the selectivity. This is shown in the study where under competitive binding condition, polycarboxylic acid type bio-surfactant, 2-(2-carboxyethyl)-3-decyl maleic anhydride shows variations in rejection coefficients for metal binding affinity. Most of the ultrafiltration membranes are made of polysulfone or cellulose resins which have very low resistance to bacterial degradation. Other problems of using ultrafiltration are that a high concentration is a problem, shear damage can occur and quantitative recoveries are rare.

1.16 Ion exchange

Ion exchange is a process in which ions are exchanged between a solution and an insoluble solid. In ion exchange, the positively charged metal ions are exchanged with proton or sodium ions within anionic or chelating groups contained in resins. If the resin containing ion A and ion B is dissolved in the water passing through it, then the following exchange takes place, the reaction proceeding to the right (R represents the resin):



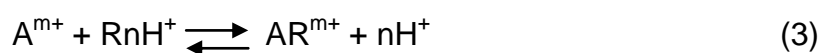
When the resin exchange capacity nears exhaustion, it will be mostly in the BR form. Therefore the reaction quotient for the equilibrium is

$$Q = \frac{[BR][A]^n}{[AR][B]^n} \quad (2)$$

Q is a constant specific for the pair of ions and the type of resin.

Ion-exchange processes are used to separate and purify metals. The advantage is that they are cheap, require little energy and if resin beds are maintained well, they can last for years.

In one study, Co(II) was fixed on amberlyst 15 ion exchange resin was extracted with 2-thenoyltrifluoroacetone in the presence of pyridine bases in various organic solvents [43]. It was found that 2-thenoyltrifluoroacetone or pyridine alone could not remove cobalt ion fixed on resin but having a mixture of the two was effective and percentage extraction was close to 100%. Shao et al. used a chelating ion-exchange resin in conjunction with a semi-permeable membrane for extracting metals from industrial waste streams and a continuous membrane dialysis process using ion-exchange resin was developed [44]. The membrane was able to retain the resin and its metal complex while allowing the free metal ion to permeate freely. The reaction mechanism of metal ion for this kind of chelating resin is expressed in eqn 3;



where R represents the resin structure radical, A^{m+} denotes the free metal ions, and AR^{m+} and RnH^+ are of the resin phase.

Increasing the concentration of H^+ in the solution reverses the reaction. The resin chelates metal ions from the solution or releases metal ions to the solution with changes in pH.

In one study, uranyl ion was selectively preconcentrated by silica gel phases modified with chelating compounds as inorganic polymeric ion exchangers from different aqueous solutions as well as ore samples [45]. The method was good especially the application of silica gel phase (IV) for direct and selective preconcentration of uranyl from uranium samples and was found to give excellent recovery values (91 to 93%) with less interference of the matrix. The main disadvantage of using ion exchange resins is with regard to impurities that can cause

problems; for example some ions in the sample can foul the resin and give erroneous results. Non-ionised organic contamination is also a major concern.

1.17 Activated carbon adsorption

This is a process of removing pollutants out of liquid by attaching on to activated carbon. This method has been used for the recovery of metal ions in aqueous industrial discharges. Adsorption of metal ions is characterized by breakthrough behaviour. A metal ion concentration wave moves through the carbon bed in the direction of flow. Eventually this wave reaches the exit. When the metal ion concentration at the exit reaches 5% of the inlet concentration, breakthrough is said to have occurred. On the other hand, when the concentration attains 95% of inlet, the adsorption capacity is lost and the carbon must be replaced or regenerated. The adsorption efficiency can be increased by addition of chelating agents like EDTA and nitrilotriacetate. The advantage of this method is the large specific surface area, simplicity, high adsorption capacity, universality and that it can be applied to all types of pollutants. Wilson et al. designed granular activated carbons with good metal ion adsorption characteristics from peanut shells using pyrolysis and steam activation, followed by air oxidation [46]. Carbon yield was calculated as;

$$\text{Carbon yield (\%)} = \left(\frac{W_{tc}}{W_{tps}} \right) \times 100 \quad (4)$$

Where W_{tc} is dry weight in gram of the carbon after acid and water washes, W_{tps} is the dry weight in gram of the peanut shells.

These steam-activated, air-oxidised peanut shells showed adsorption properties similar to the best commercial coal-based carbons and were simpler and cheaper in production.

Ghaedi et al. developed a sensitive and simple method for the simultaneous preconcentration of Cu(II), Ni(II), Pb(II) and Co(II) via the formation of metal complexes by 4,6-dihydroxy-2-mercaptopyrimidine loaded on activated carbon [47]. LODs of 3.5×10^{-3} , 3.4×10^{-3} , 2.9×10^{-3} and 8.4×10^{-3} for Ni(II), Co(II), Cu(II) and Pb(II) $\mu\text{g/mL}$ respectively were achieved. The method was simple, reliable, sensitive and did not need an elaborate cleanup procedure. The same group also separated and

preconcentrated Cr(III), Fe(III), Cu(II), Ni(II), Co(II) and Zn(II) on bis salicyl aldehyde, 1,3 propan diimine loaded on activated carbon [48]. The method was used to determine these metal ions in meat and cow liver samples and the recoveries ranged from 96 to 106% in meat and 98 to 105% in cow liver with minimal interference from varying amounts of a variety of diverse ions. The LODs were 0.28×10^{-3} , 0.27×10^{-3} , 0.29×10^{-3} , 0.30×10^{-3} , 0.28×10^{-3} and 0.33×10^{-3} $\mu\text{g/mL}$ in Fe(III), Cu(II), Ni(II), Co(II), Cr(III) and Zn(II) respectively. The modified activated carbon could be reused without any loss of its adsorption properties. Generally, the disadvantages of using activated carbon adsorption are that it needs to be regenerated, lack of selectivity and it requires a series of complexation steps.

1.18 Liquid-liquid extraction

Liquid-liquid extraction (LLE), also known as solvent extraction and partitioning, is a method used to separate compounds based on their relative solubilities in two different immiscible liquids. It separates components based upon chemical differences rather than differences in physical properties. The two immiscible liquids are usually water and an organic solvent. It is an extraction of a substance from one liquid phase into another liquid phase. It is good in that it is a basic technique just involving pouring the liquids into a separating funnel and shaking them for a certain period of time to make the analyte distribute between the two phases and preferentially into a liquid in which it is more soluble. In LLE, liquid-liquid equilibrium must be considered. This is best represented by equating the chemical potential of both liquid phases;

$$\mu_i^{\text{LI}} = \mu_i^{\text{LII}} \quad (5)$$

where μ is the chemical potential of the liquid phases, LI is the liquid phase 1 and LII is the liquid phase 2.

This relationship reduces to an expression, which is dependent only on the liquid mole fractions and activity coefficients;

$$\gamma_i^{\text{LI}} x_i^{\text{LI}} = \gamma_i^{\text{LII}} x_i^{\text{LII}} \quad (6)$$

Where γ represent activity coefficient and x are mole fractions. Variables that are responsible for the extraction process are operating temperature, operating

pressure, stirring/agitation, time of contact and composition of the phases. But as with other separation processes, the pressure and temperature conditions play a big role in the effectiveness of the separation. In order for a good split, the pressure and temperature must be such so as to ensure that all components remain in the liquid phase.

Separation costs may be desirable in contrast to distillation and other separation processes where LLE is applicable. Very large number/volumes of samples can be extracted with a minimum amount of energy used, it provides very clean sample extracts (which reduces burden on the mass spectrometer ion source), heat sensitive analytes are processed at ambient temperature and there is no need to withdraw water using energy intensive evaporation process. However, there are limitations of using LLE; the two liquids must be immiscible into each other, the organic solvent must be low cost, nontoxic, and nonflammable, the solute or analyte must be soluble in the water and at the same time completely or partially soluble in the solvent, temperature should be higher since solubility increases, but temperature not be higher than the critical solution temperature. The drawbacks of LLE are that it requires time for separation to occur, it uses large volumes of samples and toxic solvents, it requires ultra pure solvents as it forms emulsions. The separation of adjacent rare earth metals by LLE is difficult because such extractive separation processes are based on only the differences in the complex formation ability between the rare earth metals and their extractant.

Zinc and nickel ions were once separated using LLE in a strong acid [49]. Three kinds of organic solutions; tri-*n*-butyl phosphate, cyanex 272 and cyanex 301 were used as extractants. The extraction of zinc (constantly over 99%) was better than that of nickel (only up to 20%) throughout the experiments. This was good considering the fact there is not so much difference in the chemical and physical properties between zinc and nickel. Cyanex 301 showed the excellent characteristics of Zn/Ni separation. However, only extractants with higher concentrations showed better extraction characteristics. This is a drawback as these solvents are harmful to the environment. This system is not good for quantitative enrichment of nickel. LLE

was also used for the separation of copper (II), cadmium (II) and lead (II) using tripodal N-donor pyrazole ligands [50]. The ions were obtained from aqueous solutions using methylene chloride as a solvent. Copper(II) and lead(II) had better extraction percentages (62% and 64% respectively) while cadmium (II) was lower (below 10%). Therefore the method is not selective and had low recoveries.

In another application, perfluorocarbon-based LLE was used for the separation of Fe(III), Co(II), Ni(II) and Cu(II) ions from aqueous and organic phases to a perfluorocarbon phase (FC-72) with perfluorinated β -diketone (1,1,1,5,5,6,6,6-octafluoro-2,4-hexanedione) [51]. 100% extraction of iron was achieved in both aqueous and organic phases, followed by copper 70-100% in aqueous and nickel 30-40% also in aqueous phase. The nickel extraction values were low and necessitated work to improve these values if the system is to be employed for nickel extraction. LLE for the separation of nickel at macro-level concentration from sulphate/chloride solutions was done using phosphoric acid based extractants (Di-(2-ethylhexyl) phosphate, 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester and cyanex 272) [52]. Nickel extraction of 78.5% was achieved. However, the extraction efficiency decreased with increase in $\text{Na}_2\text{SO}_4/\text{NaCl}$ concentrations. This showed that the system cannot be used in salty seawater or industrial water which often contains higher concentrations of these elements as they will interference.

In an attempt to try and address the concern of high consumption of solvents in LLE, separation of metal ions Ni(II), Fe(III), Cd(II), Co(II), Zn(II) and Cu(II) was performed without the use of organic solvents [53]. This was an excellent attempt to avoid the use of too much solvents used LLE. However, there was a decrease in recoveries as only Zn(II), Co(II) and Cd(II) were quantitatively extracted and Cu(II) was enriched by almost 80%. Recoveries of iron and nickel were 60 and 30% respectively. Therefore this system is not applicable to nickel which is the main element of interest in this thesis. Another attempt was made to try and make LLE more selective by combining it with the conversion of metal species with a chemical reaction [54]. EDTA was used as a metal complexing system and separation of adjacent rare earth metals improved due to the difference of the complex formation ability between metals and EDTA. However, this approach still employed large volumes of organic solvents. The

use of a chelating agent made the system more expensive and complex as LLE is preferred for its simplicity and low cost.

1.19 Solid phase extraction

Solid-phase extraction (SPE), also known as solid-liquid extraction is a separation technique that is used to remove analyte from a mixture, using their physical and chemical properties. It can be described as the transfer of analytes from the active sites of liquid phase into the solid phase before elution of the analyte from the solid sites after interferences have been removed [55]. A typical SPE procedure involves four steps. First, the cartridge is equilibrated with a polar, moderately polar or non polar solvent, which wets the surface and penetrates the bonded phase. Then water, or a buffer of the same composition as the sample, is typically washed through the column to wet the sorbent surface. The sample is then added to the cartridge. As the sample passes through the stationary phase, the analytes in the sample will interact and retain on the sorbent while the solvent, salts, and other impurities pass through the cartridge. After the sample is loaded, the cartridge is washed with buffer or solvent to remove further impurities. The buffer or solvent disrupts the non specific interactions between the sorbent and other analytes but doesn't disrupt the specific interactions between the sorbent and the specific analyte. The analyte is eluted with a more, moderate or less polar solvent or a buffer of the appropriate pH. The elution step disrupt the specific interaction between the analyte and sorbent. This method is so far the most commonly used because it uses less solvent, it is simple, has higher and more reproducible recoveries, no emulsions formed, faster, more selective and flexible as compared to LLE which has been used previously [55]. There are four ways in which analyte are retained by the sorbent; normal phase, reverse phase, ion exchange and adsorption.

1.191 Normal phase

In this procedure, the liquid phase is nonpolar while the solid phase has been modified to become polar [55]. Therefore hydrophilic interactions are involved between the analyte and solid phase. The interactions involved are polar-polar,

hydrogen bonding, pi-pi interactions, dipole-dipole interactions, dipole-induced dipole interactions. A stationary phase of polar functionally bonded silicas with short carbon chains frequently makes up the solid phase. Examples are diol bonded silica (LC-Diol), aminopropyl bonded silica (LC-NH₂) and sometimes cyanopropyl bonded; endcapped silica (LC-CN) which can also be used in reverse phase described below. This stationary phase will adsorb polar analytes which can be collected with a more polar solvent.

In a rare case of application, Diol (2,3-dihydroxypropoxypropyl) was used to retain arsenic species and the % of retained species ranged from 6 to 41 [56]. However, it must be said that the interaction between the sorbent and analyte was mainly due to the organic moieties that were in the arsenic species. This is shown by increasing % of retainment in the species; arsenochline (12%), monomethylarsonic acid (18%), tetramethylarsonium ion (21%) and trimethylarsine oxide (41%) which have an increasing organic (CH₃) group (except in tetra and tri where the overall charge in the tetramethylarsonium ion change the dynamics of retainment of the analyte by the sorbent. Therefore though a Diol is mainly used in normal phase SPE, in this case it was mainly the hydrophobic interactions that were responsible for the retention of the analyte especially that Diol is a both non polar and polar sorbent. Hence the SPE phase used was reverse except in the case of retention of As(V) which hydrophilic interactions were mainly the ones responsible for the retainment of the analyte and %retainment was very low (6%). It must be said that in general, reverse phase SPE is the mostly used compared to normal phase SPE.

1.192 Reverse phase

In this procedure the liquid phase is polar while the solid phase has been modified to become nonpolar [55]. Therefore hydrophobic interactions are involved between the analyte and solid phase. The interactions involved are nonpolar-nonpolar and van der Waals or dispersion forces. A stationary phase of silicon with carbon chains is commonly used. Examples include octadecyl bonded; endcapped silica (LC-18), octadecyl bonded; endcapped silica (ENVITM-18), octyl bonded; endcapped silica (LC-8), octyl bonded; endcapped silica (ENVI-8), butyldimethyl bonded; end-capped silica (500Å pores) (LC-4), phenyl bonded silica (LC-Ph), hydrophobic surface

enclaved by a hydrophilic network (Hisep™) and sometimes cyanopropyl bonded; endcapped silica (LC-CN) which can also be used in normal phase described above. This stationary phase will adsorb non polar or relatively non polar molecules which can be collected with a non polar solvent which will disrupt the specific interactions between the analyte and the stationary phase.

Reverse phase SPE was used for separation of four mercury species in with zorbax eclipse XDB C18 column [57]. The method was used for determination of mercury species in river waters and the separation were performed in less than 5 min. Yu et al. also performed inductively coupled plasma mass spectrometry study of the retention behaviour of arsenic species on various solid phase extraction cartridges [56]. The sorbents included reverse phased C18 and C8 which had good retention % (56-80 for C18 and 73-77 for C8) [56].

1.193 Ion exchange

Ion exchange sorbents separate analytes based on electrostatic interactions between the analyte of interest and the positively charged groups on the stationary phase [55]. For ion exchange to occur, both the stationary phase and sample must be at a pH where both are charged. Ion exchange is used for compounds that are charged when in solution (both aqueous and organic). There are two types of ion exchange; anionic and cationic ion exchange.

In anionic ion exchange, sorbents are derivatized with positively charged functional groups that interact and retain negatively charged groups [55]. Strong anion-exchange (SAX) sorbents contain quaternary ammonium groups that have a permanent positive charge in aqueous solutions, and weak anion exchange sorbents use amine groups which are charged when the pH is below 9. An example of a strong anionic sorbent is quaternary amine bonded silica with Cl⁻ counterion (LC-SAX) while aminopropyl bonded silica (LC-NH₂) which is also used in normal phase is a weak anionic sorbent. A SAX, quaternary ammonium group with CH₃COO⁻ counter-ion was used to extract anionic NO₃⁻ which was interfering in the charge-based fractionation analysis of As, Cr, Mo, Sb, Se and V leached from cement-based materials [58]. More than 90% of the anionic species were extracted from a sample

containing up to 0.016 $\mu\text{g/mL}$ of NO_3^- by passing the aliquot through five identical SAX tubes. Shams and Goodarzi did a study where ambertjet 4200 Cl, an industrial strong base anion resin, was used for an improved and selective recovery of platinum from a spent dehydrogenation platinum α -alumina supported catalyst [59]. The purity of the platinum obtained was 83% and no other platinum group metals were found and the purity increased to 99.4% when using the hydroxylated resin.

In cationic ion exchange sorbents are derivatized with negatively charged functional groups that interact and retain positively charged groups [55]. Strong cation-exchange (SCX) sorbents contain aliphatic sulfonium acid groups that carry a negative charge in aqueous solutions, and weak cation exchange sorbents use aliphatic carboxylic acid groups which are charged when the pH is above 5. An example of a strong cationic sorbent is sulfonic acid bonded silica with Na^+ counterion (LC-SCX) while carboxylic acid bonded silica with Na^+ counterion is a weak cationic sorbent. Mulugeta et al. used a SCX, sulfonate group with H^+ counterion was used to extract anionic Cr(III) which was interfering in the charge-based fractionation analysis of As, Cr, Mo, Sb, Se and V leached from cement-based materials [58]. In the study, percolating the sample aliquot through three identical SCX cartridges gave more than 99% retention of Cr(III) from leachates containing a high concentration of interfering metal ions.

1.194 Adsorption

Adsorption is the interaction of analytes with unmodified materials. Hydrophobic and hydrophilic interactions may apply depending on which solid phase is used [55]. Selective SPE of palladium was reported by this mode of interaction with the sorbent 5(p-dimethylaminobenzylidene)rhodanine (which is specific for palladium) complex on silica gel-polyethylene glycol (PEG) [60]. The adsorbed complex was eluted using hydrochloric acid—acetone mixture and an LOD of 0.54×10^{-3} $\mu\text{g/mL}$ and the enrichment factor of 125 were achieved. The major limitation in this method was that PEG alone was not tested but it is known that it can adsorb metals [61]. This is shown by a study where extraction of metal ions such as copper, nickel and cobalt was performed by emulsion liquid membrane using PEG as a bi-functional surfactant

from aqueous solution. These metals are close to palladium in the periodic table therefore they are expected to have some similar chemical properties. Therefore PEG alone can also adsorb palladium. In another application, SPE for the separation of chromium(VI) from aqueous solutions was performed by adsorption of its diphenylcarbazide complex on an Amberlite XAD-4 resin column [62]. Diphenylcarbazide is a ligand that gives a very sensitive and selective color reaction with chromium(VI) and therefore the change in color intensity means that a cheap but less quantitative visible spectrophotometric instrument could be employed. The adsorbed complex could be eluted using an acetone–sulfuric acid mixture and a preconcentration factor of 27 with a LOD of $6 \times 10^{-3} \mu\text{g/mL}$ was achieved. Nevertheless, the method had a high LOD and less quantitative visible spectrophotometry was employed to determine the concentration of the metal.

All the three-mentioned modes of attraction between the analyte and sorbent employ silica-based packing while the last mode ie adsorption uses five packing which are;

- (1) Silica-based packing eg silica gel with no bonded phase; (LC-Si).
- (2) Alumina-based packing which include sorbents LC-Alumina-A (acidic), LC-Alumina-B (basic) and LC-Alumina-N (neutral pH).
- (3) Florisil-based packing which include sorbents LC-Florisil and ENVI-Florisil.
- (4) Graphitized carbon-based packing sorbents which include ENVI-Carb and ENVI-Carb C.
- (5) Resin-based packing for example ENVI-Chrom P.

An example is where SPE was used for the separation of Zn(II), Cu(II), Ni(II) and Pb(II) on poly(vinyl chloride) modified with 3-ferrocenyl-3-hydroxydithioacrylic acid, and their subsequent determination by ETAAS [63]. The method was able to remove interference from elements mostly found in water samples and LODs of 1.17×10^{-6} , 41.50×10^{-6} , 5.92×10^{-6} , and $51.04 \times 10^{-6} \mu\text{g/mL}$ respectively for Zn(II), Ni(II), Cu(II) and Pb(II) were achieved. Selectivity was a major limiting factor as the ligand was used for four metals with recoveries of more than 95%. An on-line SPE system using polytetrafluoroethylene packed column for the FAAS determination of copper was

performed in water samples [64]. The LOD of the method was $0.05 \times 10^{-3} \mu\text{g/mL}$ and recoveries of 94 to 102% were achieved. However, the method employed the use of many solvents including methyl isobutyl ketone (MIBK) which is most commonly used in LLE systems which employ a lot of solvents. Ammonium pyrrolidine dithiocarbamate (ADP) employed is also not selective to copper as shown by a study where solubility product constants of some divalent metal ions (Cu(II), Pb(II), Ni(II), Zn(II) and Cd(II)) were determined with ADP using MIBK as a solvent [65]. It was found that ADP forms very insoluble precipitates of the same degree of stability for all the divalent metal ions investigated [65]. The on-line SPE system using polytetrafluoroethylene packed column for the FAAS determination of copper also had slightly higher LOD.

In another application, SPE for the separation of nickel as methylthymol blue complex was performed on naphthalene adsorbent prior to FAAS determination [66]. The method was used for determination of nickel in ore and water samples and the recoveries ranged from 95 to 98% with a LOD of $3.6 \times 10^{-3} \mu\text{g/mL}$. However, methylthymol blue is not selective to nickel as shown in a study where it was to determine calcium in peanuts [67] and was also used for spectrophotometric determination of iron(III) [68]. The naphthalene adsorbent cannot be recycled as naphthalene is prone to microbial degradation [69]. The method did not show the performance of naphthalene alone (control). This is because a simple, sensitive, rapid and reliable preconcentration method for spectrophotometric determination of trace concentrations of arsenic using naphthalene-methyltrioctyl ammonium chloride adsorbent was developed [70]. Naphthalene-methyltrioctyl ammonium chloride was also successfully used for solid phase extraction of zinc and nickel [66,71].

SPE can be applied to a variety of matrices, uses less solvents, has high recoveries, good reproducibility and is amenable to automation. The main problem is that the analyte is co-extracted with interfering compounds as currently used sorbent like silica gel, glass beads, silica, cellulose etc are not selective. It is also difficult to master its usage. This is because there is wide range of chemistries with many choices for manipulating solvent and pH conditions. There are more steps and

method development time required than in other sample preparation techniques. It is also expensive.

However, SPE can be combined with ion imprinted polymers (IIPs) in order to improve selectivity [72-74]. An example is where an on-line IIP for selective SPE of nickel and lead from seawater prior to their determination by ICP-OES was synthesised [72]. Good extraction efficiencies (99%) were achieved for both metal ions and the LOD was 0.33×10^{-3} $\mu\text{g/mL}$ for nickel and 1.88×10^{-3} $\mu\text{g/mL}$ for lead. However, the synthesized IIP for lead exhibited undesirable imprinting characteristics compared to those offered by nickel IIP, and an enrichment factor of 5 is achieved for lead. The Ni(II) IIP had high extraction efficiencies for copper, chromium, iron, lead, vanadium and zinc. Interferences studies were not performed to get the influence of the closely related metal ions especially lead as the polymer was also for lead determination.

SPE-IIP method for the determination of Cu(II), Ni(II), Pb(II) and Zn(II) in seawater after an ionic imprinted polymer based SPE was performed [73]. A pre-concentration factor of 100 was achieved and the LODs of the method were 0.14×10^{-3} , 0.15×10^{-3} , 0.18×10^{-3} and 0.03×10^{-3} $\mu\text{g/mL}$, for Ni(II), Cu(II), Pb(II) and Zn(II) respectively. Recoveries ranging from 95-104% were achieved. However, there was an interference from closely related cations as the recoveries of Cu(II), Pb(II) and Zn(II) together with Ni(II) was 99%.

In another study, a selective SPE of lead(II) from biological and natural water samples using surface-grafted lead(II)-imprinted polymers was also performed [74]. The LOD for the method was found to be 0.20×10^{-3} $\mu\text{g/mL}$ and recoveries of samples ranged from 97.8 to 101.1%. However, the preparation of this ion-functionalized silica gel sorbent was long (23 h) and relatively expensive considering the reagents used especially for industrial applications.

SPE-IIP is an attractive method for sample concentration and cleanup. Therefore IIPs can be synthesised and optimised to be used to trap metal ions from mine tailings.

OBJECTIVES

This thesis describes the design, synthesis, characterization and optimization of a Ni(II) IIP for mine tailing samples using bulk polymerisation. The specific objectives of the research were:

- (1) To determine the effectiveness of dimethylglyoxime as a trapped ligand for the preparation of an Ni(II) IIP using bulk polymerisation,
- (2) To optimise the Ni(II) IIP for pH, time, mass and ratio of monomers to template, crosslinker to monomer and amount of initiator,
- (3) To validate the Ni(II) IIP using certified reference materials
- (4) To test for interference of Co(II), Cu(II), Zn(II), Pd(II), Fe(II), Ca(II), Mg(II), Na(I) and K(I) in the determination of Ni(II) when using the Ni(II) IIP,
- (5) To use the Ni(II) IIP to trap Ni(II) ions from aqueous and soil samples and finally
- (6) To use the Ni(II) IIP to trap Ni(II) ions from mine tailing samples.

CHAPTER 2

2.0 IMPRINTED POLYMERS

2.01 Molecularly imprinted polymers

Molecularly imprinted polymers (MIPs) are highly selective cross linked polymeric materials synthesized by complexing a template and a functional monomer in the presence of a crosslinker. The reaction proceeds via a free radical initiator in an appropriate solvent normally referred to as a porogen. The imprinting effect is due to the 'memory' of the template (molecule) that has been previously used before its subsequent removal. The memory is a result of the effect of the shape, size and charge of the molecule that was present in the cavity during polymerisation. The functional mechanism is similar to that of antibodies or enzymes. However, MIPs have advantages over antibodies in that they are cheap and can be used in or with a variety of solvents at high temperature, pressure and pH where antibodies or enzymes would not tolerate. Since their inception in 1972 by Wulff and Sarchan [75], MIPs have been used in many areas to trap molecules from various media. These polymers show chemical affinity for the original molecule. The choice of a complexing ligand is of great importance, as it directly influences selectivity of the sorbent and porogen.

2.02 Composition of molecularly imprinted polymers

A polymerisation mixture of consist of a template which is the target analyte, functional monomer, which specifically interact with the template and the cross-linking monomer, which link the template-functional monomer together into a highly cross-linked network. There is also the porogen, which is the medium in which the polymerisation reaction takes place and the initiator, to start up the reaction photo chemically at room temperature or thermo chemically above 60 °C. Changing any of the above in relation to others affect the quality of an imprinted polymer.

2.03 Types of binding sites

There are three types of binding sites that can be established between the functional monomer and the template depending on the polymerisation method (as shown in Fig. 1). The first one is covalent imprinting method, which was developed by Wulff and Sarchan [75], the second method is a non-covalent method that was reported by Arshady and Mosbach [76] and the third one is sacrificial spacer approach, which was introduced by Whitcombe et al. [77]. Fig. 1 is a schematic diagram of a non covalent and covalent imprinting process.

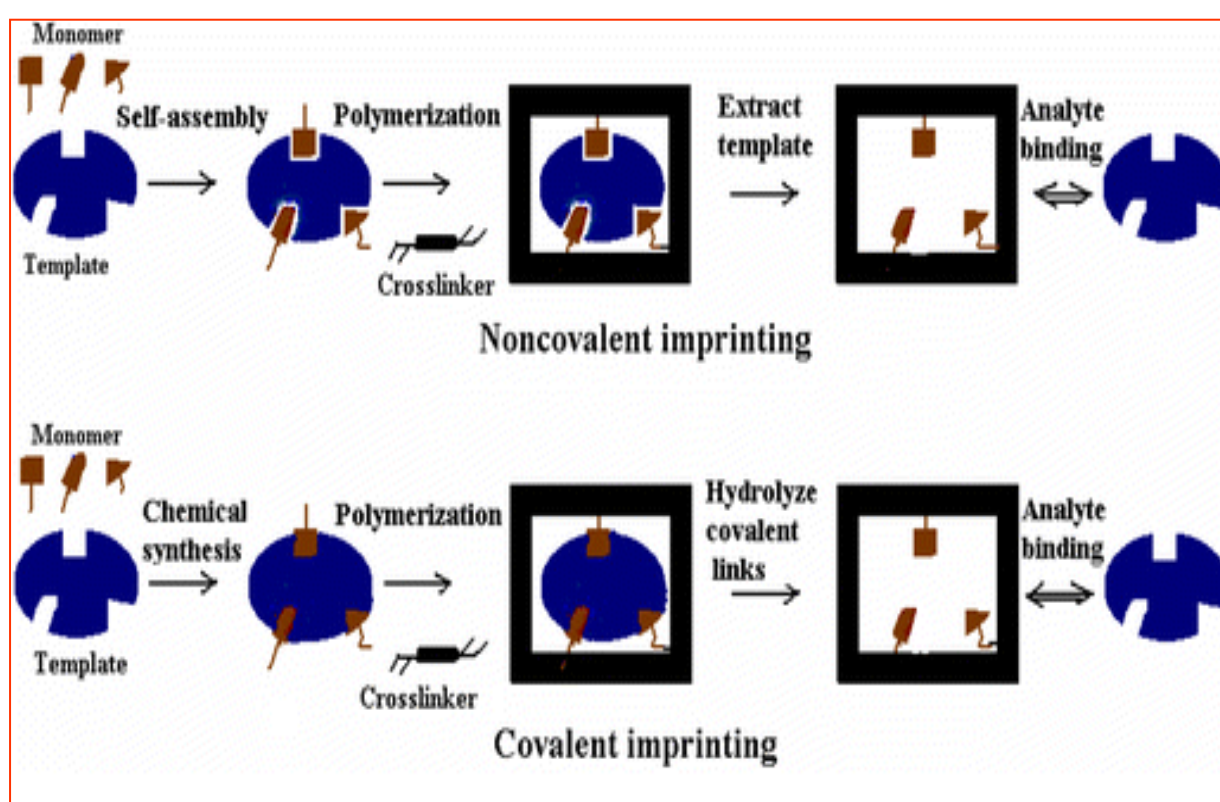


Fig. 1. Non covalent and covalent imprinting scheme (From Ref. [78])

Among the three methods, the non-covalent approach is found to be highly adoptable due to the simple methodology involved during the synthesis of the imprinted polymers. Covalent binding sites are formed through irreversible covalent bonds, noncovalent binding sites are formed by self-assembly noncovalent bonds (ionic, hydrophobic and hydrogen bonds are involved) [79]. Semi-covalent binding combines the advantages of covalent and noncovalent. Covalent bonds are used for binding whilst noncovalent bonds are used for rebinding. The noncovalent binding

method is the mostly used because it resembles antigens from which the idea of molecular imprinting was derived. Non-covalent protocol is also easily conducted, removal of the template is generally much easier and a greater variety of functionality can be introduced into the binding site using non-covalent methods. The requirements of covalent imprinting are different than those for non-covalent imprinting, particularly with respect to ratios of functional monomer, crosslinker, and template.

2.1 Imprinting formats

Imprinted polymers can be prepared by seven main formats. These are bulk, precipitation, suspension, two-step swelling, emulsion, core-shell and dispersion polymerisation formats.

2.11 Bulk polymerisation format

In bulk polymerisation format, the polymerisation mixture (template, monomer, cross-linker and initiator) are mixed in a porogen then polymerised before the obtained block polymer is ground in a pestle and mortar to obtain irregular particles of sizes between 20 and 100 μm . Particles are then sieved. The polymerisation process usually takes two to six hours. The main drawback of the bulk polymerisation format is that some binding sites are destroyed due to grinding and it is inefficient as about 70% of the polymer is lost during the process and it is also labour intensive. Therefore this polymerisation format is not good for industrial processes where a large quantity of polymer will be produced. This is owing to its high heat produced during the process. An example showing the application of bulk polymerisation format is a IIP that was synthesised and characterised for the separation and preconcentration of uranyl (UO_2^{2+}) ions from aqueous systems using a bulk polymerisation format [80]. Though the synthesis procedure was long with not so impressive extraction efficiencies, the polymer was very good with acceptable selectivity factors. The trapped ligand used N,N'-Ethylenebis(pyridoxylideneiminato) was good considering the number of nitrogen and oxygen donors. However, it is too

bulky and long which may affect its stability as long, bulky molecules are not stable especially considering the crushing and grinding that is involved in the bulk polymerisation format. This might be shown by low recoveries obtained at temperatures of 65 and 70 °C. Therefore the method can be improved by changing the ligand. Metilda et al. reported a bulk polymerisation format to prepare an IIP based sensor for monitoring toxic uranium in environmental samples [81]. The sensor showed good selectivity for uranyl ion over alkali, alkaline earth, transition and heavy metal cations. This shows that bulk polymerisation format is simple and good for preparing polymers.

2.12 Precipitation polymerisation format

Precipitation polymerisation format is the same as bulk polymerisation except that it is performed in a larger volume of porogen, about two to ten times the volume used in bulk polymerisation. This reduces the chance of contact between the template and the functional monomer hence is it performed for longer periods of time than bulk polymerisation. It is done in about twelve hours and above. The polymerisation process is well suited to industrial processes as it produces less heat due to the distance between the functional monomer and template. Smaller polymer particles of sizes 0.3 to 10 µm can be obtained from this polymerisation format. It is also more efficient than bulk. The main drawback is that it takes place over a long period of time and require specialised conditions. Precipitation polymerisation format was employed to prepare an IIP based SPE for the determination of Cu, Ni, Pb and Zn in seawater [73]. The polymer was good and recoveries were 99% for all the metals. However, as earlier pointed out selectivity was a problem. MIP microspheres for the selective extraction of carbamazepine and oxcarbazepine from human urine were synthesised by precipitation polymerisation format in [82]. Carbamazepine was used as a template molecule, methacrylic acid (MAA) as functional monomer and either DVB-80 or a mixture of DVB-80 and ethylene glycol dimethacrylate (EGDMA) as crosslinking agents. Good recoveries of 90% and 83% for carbamazepine and oxcarbazepine respectively were obtained with an LOD of 7×10^{-3} µg/mL for carbamazepine and 20×10^{-3} µg/mL for oxcarbazepine. This shows that precipitation polymerisation format is another good method especially for smaller particles than bulk polymerisation format.

2.13 Suspension polymerisation format

In suspension polymerisation format, a mixture of monomers, template and porogen is added to a dispersion solvent to form an emulsion. The dispersion solvent may be aqueous or organic fluorocarbon solvent. It is more reliable and can be done in less than two hours. However, some reactions take up to six hours. The amounts of template and monomers (functional and cross-linking) are higher in order to compensate for the loss in the dispersion phase which is not involved in the polymerisation process and this means that the initiator must be soluble in the monomer-containing phase but not in the dispersion phase. Regular polymer beads of sizes between 5 and 50 μm have been obtained depending on the stirring speed and the mass/volume of surfactant. The main drawback of suspension polymerisation format is the use of specialised fluorinated surfactant which are very expensive though they can be recycled. Mayes et al. used suspension polymerization format employing a liquid perfluorocarbon as the dispersing phase to make simple and reproducible MIP beads [83]. However, the perfluorocarbon liquid was found to be expensive. Another suspension polymerization format was reported in [84] where 2,4-dichlorophenoxyacetic acid MIP particles were synthesised in silicon oil. The advantages of silicon oil as a dispersion phase are high viscosity; suitable density; nonpolarity, insolubility with pre-polymerization mixture and low cost. The synthesised polymer particles exhibited regular shape in the micro-scale range polymer but it must be said that this synthesis procedure was long. Therefore suspension polymerisation format can be used depending on the intentions of synthesis.

2.14 Two-step swelling polymerisation format

In two-step swelling polymerisation format, seed polymer beads are first synthesised using emulsion polymerisation, then the seed particles are equilibrated with a solution containing the monomers that have been chosen to form a polymer shell around the core. Then the second emulsion polymerisation step is initiated. The polymer particles obtained by this format are usually monodisperse in size and shape. It is also easy to control the final size and the number of particles. Polymer

particles of size range 2-50 μm have been produced using this format. The drawback of this method is the increased surface area for non-specific binding because of aqueous suspensions used. The reaction conditions required are also complicated. Masci et al. prepared uniform-sized clenbuterol MIPs with two-step swelling and thermal polymerization technique with either MAA or acrylamide as the monomer and EDGMA as the crosslinker at different monomer/crosslinker ratios [85]. The quality of the microbeads, in terms of shape, size distribution, rigidity, and monomer incorporation was good proving that although the synthesis procedure for this type of polymers is long, it is sometimes worth the benefits obtained.

2.15 Emulsion polymerisation format

In emulsion polymerisation format, water is used as a continuous phase and particles obtained are monodisperse with sizes ranging from 0.05 to 2 μm . It is mostly done using oil-in-water interface and therefore it can be used in surface imprinting. Kanazawa et al. performed a synthesis of a thermosensitive microgel adsorbent, which adsorbs and desorbs Cu(II) ions by changes in temperature by the emulsion polymerization format using anionic polymerizable surfactant [86]. N-Isopropylacrylamide (NIPA) and N-(4-vinyl)benzyl ethylenediamine were used as the primary monomer and the chelating monomer, respectively. The synthesis went well as Cu(II) ions were adsorbed quickly in response to the temperature change. Other imprinted polymers were prepared using different formats (bulk, precipitation, and emulsion) for the determining of organotin compounds in environmental samples [87]. Results showed that although MIPs prepared by bulk polymerisation had excellent pre-concentration and were good at matrix elimination, those prepared by emulsion polymerisation have shown very good morphological characteristics (high pore volume, homogeneous and regular particle size) for their potential applicability as chromatographic stationary phase.

2.16 Core-shell polymerisation format

Core-shell particles are normally obtained by emulsion polymerisation format. They have a structured morphology that allows the incorporation of any added property into the core of the particle without interfering with the imprinted shell. The continuous medium during polymerisation is water. Particles obtained by this format are monodisperse and can be produced in a colloidal size range of 0.05–2 μm . In one application of this format of polymerisation, a study where core-shell polymer particles with protonizable shells were prepared and characterised by oxyanionic polymerization was reported [88]. The synthesis was successful as poly[2-(dimethylamino) ethyl methacrylate] shells could be protonated at a low pH and the core-shell particles could adsorb negatively charged modified magnetite articles. At higher pHs, the magnetite particles could be released again and this process was reversible. It must be said that the method was long and a little bit complex for industrial applications. The core-shell polymerisation format was also used to form imprinted spherical particles which were prepared by using a conventional polymer solution coating method [89]. The imprinted silica particles were used as a stationary phase in high performance liquid chromatography (HPLC) mode. The imprinted polyimide-coated silica particles showed higher retention and imprinting factors for estrone than for any other structural analogues. Compared to the grafting method, this approach was good in that various spherical inorganic particles can be used as core materials and the thickness of the shell can be controlled easily.

2.17 Dispersion polymerisation format

Dispersion polymerisation format is a format in which a dilute homogenous mixture of the template, monomer and initiator are dispersed in a porogen. The point at which a growing polymer network precipitates out of solution is determined by a solubility of the polymer within the polymerization solvent. Say et al. prepared Cu(II)-imprinted poly(ethylene glycol dimethacrylate-methacryloylamidohistidine/Cu(II)) (poly(EGDMA-MAH/Cu(II))) microbeads for dermination of Cu(II) in aqueous samples by dispersion polymerisation format [90]. The microbeads were good as the selectivity of Cu(II) was high even in the presence of Zn(II), Ni(II) and Co(II) ions

which have the same ionic radii as Cu(II). However, the synthesis procedure was long with many reagents used which render the method less suitable for industrial applications.

Most polymers are prepared by bulk polymerisation format as it is simple, universal, cheap and takes less time when compared to others which require expensive apparatus, complicated processes and takes long times.

2.2 Factors affecting the performance of an imprinted polymer

There are several factors that influence the polymerisation, and hence the subsequent performance of the imprinted polymers such as; the nature and masses of monomers [91-106], crosslinkers [91-92,95-96,99-103], porogen [91-93,98-100,102-104], template [95,97,99-102], initiator used [103-105], as well as the temperature [94,103], pressure [94], method of initiation [99] polymerization time [94,103], magnetic field [97], and the dielectric constant [94,106] of the components of monomer mixture employed.

2.21 Nature and amount of monomer

The monomer is chosen so as to provide complementary interactions with the template. A better fit between the site and the template will increase the affinity and selectivity in the recognition. A higher number of interactions with the template will be more advantageous. One study reported an investigation where the influence of monomer–template ratio and sample load on retention and selectivity was done [101]. The investigation showed that working with higher molecular to template ratios should lead to more homogeneous receptor populations.

2.22 Nature and amount of cross-linker

The performance of imprinted polymers is not only dictated by the interaction of template with the functional monomer pre- and post-polymerisation at a molecular

level, but also by the physical make up of the polymer at a macro level. The cross-linker is important in controlling the morphology of the polymer matrix, stabilizes the imprinted binding site and imparts mechanical stability to the polymer matrix. An investigation of the influence of cross-linkers' concentration on the performance of the piezoelectric sensor modified with molecularly imprinted polymers was done in [96]. Scatchard analysis was employed to estimate the binding parameters of the niacinamide polymers. The estimated parameters binding were given by eqn 7;

$$\frac{Q}{[NA]} = \frac{Q_{\max} - Q}{K_D} \quad (7)$$

Where Q is the amount of niacinamide bound to the polymer at equilibrium; Q_{\max} is the apparent maximum number of affinity-binding sites; [NA] is the niacinamide concentration at equilibrium and K_D is the equilibrium dissociation constant. Results showed that the dissociation constant and the apparent maximum number of affinity-binding sites increased with the increment of the ratio of EDGMA to MAA until the ratio reaches 20.

2.23 Porogen

The nature and level of porogenic solvents determines the strength of non-covalent interactions and influences polymer morphology which directly affects the performance of an imprinted polymer. The template molecule, initiator, monomer and cross-linker must be soluble in the porogen. Increasing the volume of porogenic solvents increases the pore volume. The porogen should also be less interactive with the template and monomer so as not to interfere with the binding interactions between the template and monomer. The polarity of the porogen determines the level of interaction between template and the functional monomer. A highly polar porogen will interact with the template or functional monomer or both and give a less chance for the template and functional monomer to interact. This leads to fewer imprinting sites and reduces the absorption effectiveness of the imprinted polymer. A less polar porogen will have a less interaction with either the template or the functional monomer. The interaction of the template and the functional monomer will be strong and the formed imprinted polymer will precipitate quickly due to less

polarity of the porogen so a medium polar porogen is needed. This helps uniform imprinting sites in the imprinted polymer. The volume of a porogen affects the concentrations and the gel point of the polymer and this will change the morphology and hence the adsorption performance of the imprinted polymer. One study investigated the effect of porogenic solvent on selective performance of molecularly imprinted polymer for quercetin [98]. Quercetin was used as a template molecule, acrylamide as a functional monomer and EDGMA as a cross-linker in the presence of four different porogenic solvents: 1,4-dioxane, tetrahydrofuran (THF), acetone, and acetonitrile. The results showed that the MIP prepared in THF gave the highest capacity and selectivity.

2.24 Nature and amount of template

The template should have the highest number of polymerizable sites that will interact well with the monomer as much as possible but should be chemically inert during the polymerization reaction. Template with a high number of binding sites yields binding sites of higher specificity and affinity for the template. Zhang and Li reported a study on molecular self-assembly and its effect on selectivity [97]. It was found that an increase in the monomer–template ratio will result in a higher level of adsorption until a saturation point is reached after which a further increase in monomer–template ratio will lead to a dramatic decrease in this selectivity. Adsorption process was modelled the using Langmuir, Freundlich and Temkin models.

Langmuir model;
$$\frac{C}{Q} = \frac{1}{K_A Q_m} + \frac{1}{Q_m} C \quad (8)$$

Freundlich model;
$$\ln Q = \left(\frac{1}{n}\right) \ln C + \ln K_F Q_m \quad (9)$$

Temkin model;
$$Q = K_T \ln C + K_T \ln f \quad (10)$$

Where Q and Q_m are the actual and the maximal adsorption amounts, C is the equilibrium concentration of substrate, K_A , n , K_F , f and K_T are constants.

The linear correlation fitted well for the Freundlich and Temkin models but not for the Langmuir model. This results indicated that interactions among adsorbed substrates themselves and that between MIP and substrate were largely involved in the process. This experiment confirmed a known fact that the Temkin model is generally accepted as the most suitable model for chemical adsorption.

2.25 Initiator

The initiator starts the polymerisation by providing a source of free radicals. This is generated by thermal or photolytic cleavage of azobis(nitriles) or peroxides. It is important that the temperature of initiation is lower than the boiling point of the porogen. An example is a study on the effect of initiators {(AIBN, 2,2'-azobis-(2-amidinopropane) dihydrochloride (AAP), 4,4'-azobis(4-cyanopentanoic acid) (ACPA) and 1,1'-azobis(cyclohexane carbonitrile) (ACHC))} on the emulsion polymerization of 2-hydroxyethyl methacrylate (HEMA) [101]. It was found that the polymerization rate increased with the initiator mass, but the polymerization rate showed little dependence on the particle number. A study on the influence of initiator and different polymerisation conditions on performance of molecularly imprinted polymers was done where it was concluded that lower quantities of initiator lowered the temperature generated during polymerisation and formed MIPs with better recognition properties [103].

2.26 Temperature

Lowering the polymerization temperature always favours complexation due to a reduction in the influence of residual vibrational modes and increase in the strength of polar interactions. However, lower temperatures also increase the adverse contributions of conformational and van der Waals forces. Piletska et al. investigated the influence of the polymerization conditions on the performance of molecularly

imprinted polymers [94]. They explained the formation of complexes to be under thermodynamic control, and its energies were described by eqn 11;

$$\Delta G_{\text{bind}} = \Delta G_{\text{t+r}} + \Delta G_{\text{r}} + \Delta G_{\text{h}} + \Delta G_{\text{vib}} + \sum \Delta G_{\text{p}} + \Delta G_{\text{conf}} + \Delta G_{\text{vdW}} \quad (11)$$

where the Gibbs free energy changes are: ΔG_{bind} , complex formation; $\Delta G_{\text{t+r}}$, translational and rotational; ΔG_{r} , restriction of rotor upon complexation; ΔG_{h} , hydrophobic interactions; ΔG_{vib} , residual soft vibrational modes; $\sum \Delta G_{\text{p}}$, sum of interacting polar group contributions; ΔG_{conf} , adverse conformational changes; and ΔG_{vdW} , unfavorable van der Waals interactions. It was concluded that polymerization temperature affects the affinity and specificity of MIPs, both of which could be significantly improved by selecting a lower polymerization temperature.

2.27 Pressure

Pressure affects the intramolecular associations and kinetics of a polymerization reaction. Imprinted polymers made at high pressure had higher affinities compared with the corresponding polymers prepared at ambient pressure. This is because polymers prepared at higher pressures result in enhanced retentions of the template. An example is where an investigation was done on the influence of pressure on polymerisation and the influence of temperature and pressure on the rate coefficients of free-radical polymerization [94]. These influences can be described by eqn 12;

$$\frac{d(\ln k_p)}{dP} = \frac{\Delta V^\ddagger}{RT} \quad (12)$$

Where R is the gas constant, T the absolute temperature, P the pressure, k_p is the propagation rate coefficient and ΔV^\ddagger is the change in activation volume. It was concluded that polymerization at higher pressure generates more rigid polymers with better defined shapes of imprinting cavities and therefore higher specificity.

2.28 Polymerization time

Increasing polymerization time lead to a greater degree of conversion in the polymerization reaction with fewer unpolymerized double bonds remaining in the

polymer. An analysis on the effect of polymerization time on the affinity and specificity of MIPs was done and it was concluded that increasing the polymerization time leads to more rigid polymers and improves the specificity of MIPs [94].

2.29 Dielectric constant

The dielectric constant is the ratio of the permittivity of a substance to the permittivity of free space. It is an expression of the extent to which a material concentrates electric flux, and is the electrical equivalent of relative magnetic permeability. Dielectric constant, $\varepsilon(\omega)$ is given by eqn 13;

$$\varepsilon_r(\omega) = \frac{\varepsilon(\omega)}{\varepsilon_0} \quad (13)$$

Where $\varepsilon(\omega)$ is the complex frequency-dependent absolute permittivity of the material and ε_0 is the electric constant.

Generally, substances with high dielectric constants break down more easily when subjected to intense electric fields, than do materials with low dielectric constants. An investigation into the principal component analysis of the influence of solvent properties on molecularly imprinted polymer-ligand rebinding was done where it was observed that dielectric constant made a significant contribution to describing the observed binding [106]. It was also discovered that the dielectric constant of the solvent used for polymer preparation should be lower than the dielectric constant of the cross-linker [94].

2.3 Ion imprinted polymers

The idea of MIPs have led to the inception of metal ions being used as templates. IIPs are similar to MIPs, except that they recognize metal ions after imprinting, while retaining all the virtues of MIPs, [107]. The coordination geometry and number of a metal ion together with the charge and the size of the ion play important roles in obtaining selective IIPs. Since their inception in 1976 by Nishide and Deguchi [108],

IIPs seem to have found applications in the field of separation science just like their predecessor, MIPs.

The concentration of a metal ion bound to the ion imprinted polymer known as binding capacity, Q is calculated as shown in eqn 14;

$$Q (\mu\text{mol}) = \frac{V(C_i - C_s)}{W} \quad (14)$$

Where V represents the volume of the solution (mL), C_i initial solution concentration ($\mu\text{mol/mL}$), C_s the solution concentration after adsorption and W is the mass of the polymer used for extraction.

The %extraction efficiency (%EE) is calculated by eqn 15;

$$\%EE = \left(\frac{C_i - C_s}{C_i} \right) \times 100 \quad (15)$$

C_i and C_s are the same as defined in eqn 14.

The selectivity coefficient for the binding of a specific metal ion (M) in the presence of competitor species is given by eqn 16;

$$k = \frac{K_d(M)}{K_d(X)} \quad (16)$$

where k is the selectivity coefficient and X represent competitor metal ions.

Relative selectivity coefficient k' is given by eqn 17;

$$k' = \frac{k_{\text{imprinted}}}{k_{\text{nonimprinted}}} \quad (17)$$

where $k_{\text{imprinted}}$ is a selectivity coefficient of the imprinted polymer and $k_{\text{non imprinted}}$ is a selectivity coefficient of the non imprinted polymer.

2.31 Types of polymerization methods

There are four methods of preparing IIPs;

- (i) Linear chain polymers carrying metal-binding groups being cross-linked with a bifunctional reagent, [109]. This type of polymerization method was introduced by Nishide et al. who crosslinked poly(4-vinylpyridine) with 1,4-dibromobutane in the presence of metal ions Cu(II), Zn(II), Co(II), Ni(II), Hg(II) and Cd(II) as templates [108]. The polymer preferentially adsorb metal ion which had been used as template.
- (ii) Chemical immobilization by preparation of binary complexes of metal ions with ligands having vinyl groups, isolation and then polymerization with matrix-forming monomers, [110]. This type of polymerization method was utilized for the first time by Kato et al. who polymerised a metal complex of 1-vinyl-imidazole with 1-vinyl-2-pyrrolidone and divinyl benzene (DVB) [111]. The metal-vinyl imidazole complex was copolymerized and crosslinked with 1-vinyl-2-pyrrolidone by γ -irradiation and the template metal ion was removed by treating the polymer complex with an acid.
- (iii) Surface imprinting conducted on aqueous–organic interface [112]. Yu et al proposed the method by preparing ion imprinted microspheres of Cu(II), Ni(II) and Co(II) by the use of seed emulsion polymerisation [113]. Seed emulsion was obtained by the polymerisation of styrene, butylacrylate and methacrylic acid in water. DVB, butylacrylate and water were added to the polymerisation mixture. The emulsion was then combined with a metal ion solution to complex metal ion and carboxyl group on the surface and then polymerised by γ -rays at room temperature.
- (iv) Trapping of non-vinylated chelating ligand via imprinting of binary/ternary mixed ligand complexes of metal ions with non-vinylated chelating agent and vinyl ligand [81]. This method was employed by Biju et al. who prepared dysprosium particles via thermal polymerisation by copolymerisation ternary mixed ligand complex [Dy-5,7-dichloroquinoline-8-ol (DCQ)₃-4-vinylpyridine (VP)₂] with styrene monomer, DVB crosslinker in the presence of 2,2'-azobisisobutyronitrile initiator, (AIBN) [114]. The

metal ion was removed by leaching with 6.0 M HCl. The imprinting scheme showing the synthesis of a Dy IIP via the trapping method is shown in Fig. 2;

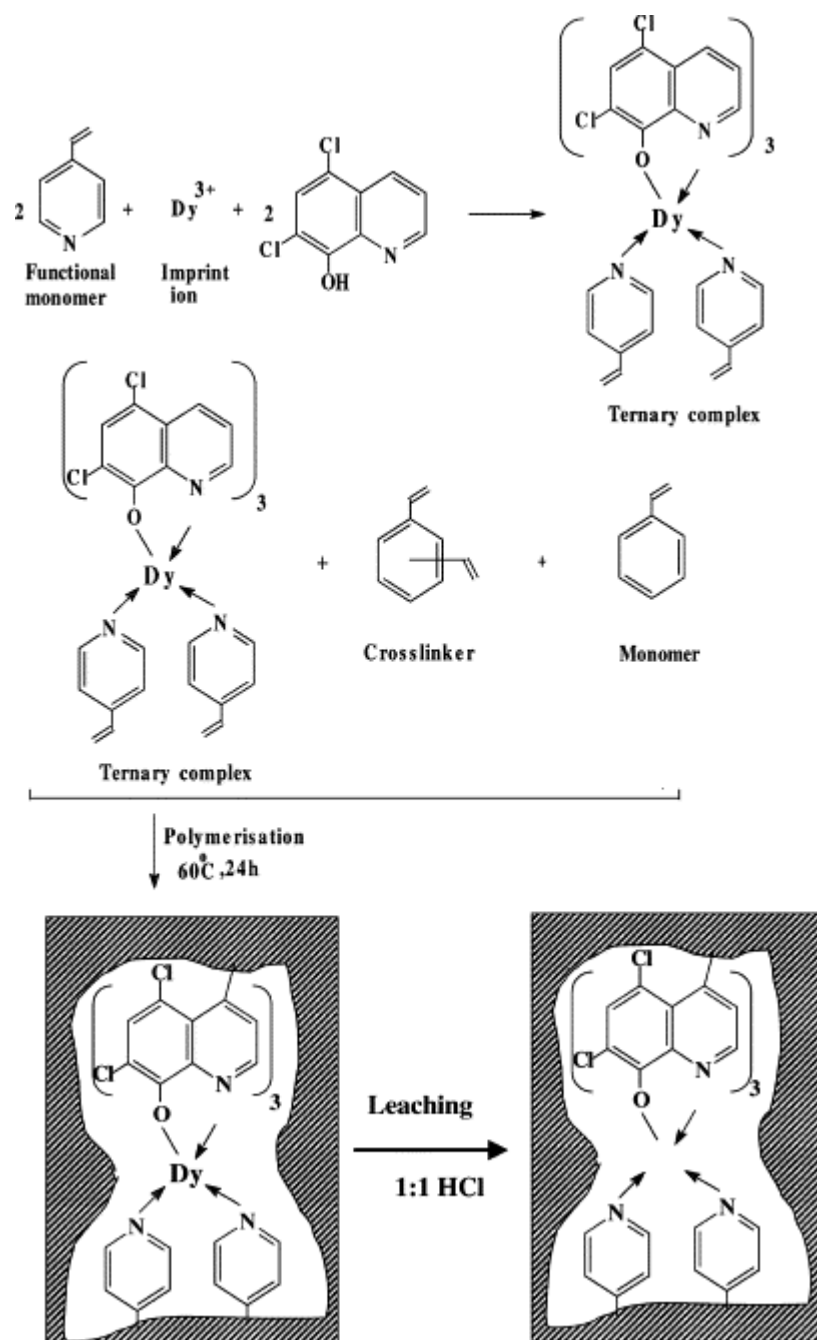


Fig. 2. Schematic representation of Dy IIP synthesis via trapping.

(From Ref. [114])

The most commonly used method is trapping. This is because all other methods require complexing ligand showing vinylated groups which are scarce.

CHAPTER 3

3.0 APPLICATIONS OF ION IMPRINTED POLYMERS

IIPs have been used in a variety of analytical applications such as preconcentration/separation or purification processes and sensors. These applications have taken advantage of the good characteristics already discussed in the preceding sections.

3.1 Preconcentration

Numerous studies on IIPs and their applications for selective preconcentration and separation of metal ions have been reported. One such successful preconcentration was done for the separation of palladium(II) using palladium(II) IIP particles formed with different quinoline derivatives [115]. The polymer was formed by polymerising ternary complexes of palladium(II) with amino (AQ) or hydroxy (HQ) or mercapto (MQ) derivatives of quinoline and 4-vinylpyridine (4-VP), 2-Hydroxyethyl methacrylate (HEMA) was used as a functional monomer, EDGMA as a crosslinker, 2-methoxy ethanol as a porogen and AIBN as initiator. The method was successful with an LOD of 5.0×10^{-3} $\mu\text{g/mL}$. This is not surprising considering the number of donor ligands that were bonded to the imprinted palladium metal ion. However, this high number of donor ligands had a disadvantage in that template bleeding is likely to occur. This was evident in leaching of the imprinted polymer which was performed by stirring with 100 ml of 50% (v/v) HCl for 18 h.

Another application was reported where silver was successfully enriched and separated from waste by a metal ion imprinted membrane [116]. The results on the experiment of competitive adsorption indicated that Ag(I) IIP had specific recognition of Ag(I). The polymer had large adsorption capacity for Ag(I) (in comparison to Cu(II), Pb(II) and K(I)) which indicates that Ag(I)-ion imprinted polymer can be used in silver enrichment and separation from waste solutions. Özkütük et al. selectively separated and preconcentrated phosphate ions on the phosphate-imprinted

chitosan-succinate beads [117]. Chitosan-succinate was used as a complexing monomer, phosphate as a template and epichlorohydrin as a crosslinking agent. The phosphate-imprinted polymer showed higher selectivity towards phosphate over thiocyanate and fluoride in a couple of mixtures of these ions. It can also be used many times without decreasing adsorption capacity significantly. The polymer was used for specific removal of phosphate ions from aqueous solution. Another phosphate selective method was reported where *N*-allyl-*N*-methyl-thiourea or 1-allyl-2-thiourea were used as functional monomers for the synthesis of a selective polymer for phosphorus from water used in agriculture [118]. The imprinted polymer showed high binding ability to and selectivity for phosphate and 70% of highly concentrated phosphate could be recovered. This is considering the fact that only hydrogen bonding was involved for binding and rebinding (recognition). This is contrary to ionic bonds that are mostly formed in IIPs that involve a metal ion.

The bulk polymerisation format was used to prepare IIP particles for the preconcentration of copper from water and biological samples [119]. Morin was used as a copper complexing reagent, 4-VP as a monomer, EDGMA as a crosslinker and AIBN as an initiator. Good recoveries ranging from 97.3 to 99.6% were obtained with an LOD of 0.12 µg/mL. The use of oxygen donors which are good for copper helped increase the selectivity for over Cd(II), Zn(II), Ni(II), Pb(II) and Co(II). However, the morin ligand is slightly bulky and has several oxygen atoms which may create non specific binding for copper. Another case study was reported where the synthesis of Cu(II)-ion IIP that was used for preconcentration of Cu(II) from aqueous solutions was done [120]. The polymer had a good selectivity for Cu(II) ions even in the presence of complex matrices, such as sea water (with recoveries ranging from 98.4 to 99.9%). The IIP was repeatedly used in adsorption–desorption experiments for seven times with recoveries around 95%. However, the synthesis was long with use of many reagents making the synthesis expensive for industrial applications. The stability and rigidity of imprinted site in polymer is questionable since polymerisation only occurs from one side. Double-imprinted particles were synthesized by the ionic imprinted technique for selective SPE of trace Cd(II) from aqueous solution [121]. It was found that the ion imprinted material had increased affinity toward Cd(II) ion

over other competitor metal ions with the same charge. The method had an LOD of 0.23×10^{-3} $\mu\text{g/mL}$ with a maximum adsorption capacity for Cd(II) ions of 548 mg/g. Though most of these applications are for positively charged metal ions, the work by Özkütük et al. [117] and A. Kugimiya et al [118] have proved that IIPs can also be used for negatively charged molecules/non metals.

3.2 Sensors

IIPs have been used as selective sequestering agents and as components of electrochemical and optical sensors. The advantage of using IIPs is that they are simple and inexpensive. Metilda et al. synthesized IIP (biomimetic) based potentiometric sensor by dispersing the uranyl IIP particles in 2-nitrophenyloctyl ether (plasticizer), which is embedded in polyvinyl chloride matrix for monitoring toxic uranium in environmental samples [81]. The sensor could detect uranium ion in a wide concentration range from 2.0×10^{-8} to 1.0×10^{-2} M with LOD of 2.0×10^{-8} M. The selectivity of the proposed uranyl ion sensor was far superior to several other ionophore based sensors, which can be attributed to size and shape specific binding sites in uranyl ion imprinted polymer particles. The sensor was successfully tested for the monitoring of toxic uranium in tap and sea water samples and recoveries ranging from 100 to 101.25% were obtained.

Another example is where a carbon paste electrode modified with IIPs was used for qualitative evaluation of rare earth ionic recognition of the imprinted polymers using cyclic voltammetry [122]. The recognition ability of the IIP to uptake rare earth ions was demonstrated. Ion imprinting processes showed excellent control on the orientation and spatial uniformity of ionic recognition sites that enhanced the absorption ability and recognition of the template ion. Prasad et al. designed an IIP based ion-selective electrode (ISE) by dispersing the dysprosium(III) IIP particles in 2-nitrophenyloctyl ether plasticizer and then embedded in a polyvinyl chloride matrix [123]. The electrode was used for the trace determination of dysprosium(III) ions by potentiometric (EDTA) titration. It was then successfully used to determine fluoride in mouth wash solution with a LOD of 2×10^{-6} M and was able to work in a wide concentration range of 8.0×10^{-6} to 1.0×10^{-1} M. The recoveries ranged from 100 to 105%. The sensor had a very fast response time (~ 10 s) and offered high selectivity

compared to conventional chemical sensors towards dysprosium(III) with respect to several alkali, alkaline earth and transition metal ions as the selectivity was 10–100-fold better. The dysprosium(III) IIP ISE was found to be stable (deviation was less than 1 mV for 5×10^{-5} M of dysprosium) for 3 months and could be reused for more than 20 times without any loss in sensing ability.

An ion imprinted mesoporous silica based fluorescence turn-on sensor array for the discrimination of Zn(II) and Cd(II) metal ions was designed in [124]. The sensor was able to discriminate two template metal ions (Zn(II) and Cd(II)) plus three non-template metal ions; Mg(II), Ca(II) and Al(II) at two different concentrations. For Zn IIP, the fluorescence intensity reached 85% of the equilibrium value within 0.5 min after the addition of Zn^{2+} while for Cd IIP, the fluorescence intensity reached 95% of the equilibrium value within 0.5 min after the addition of Cd^{2+} .

These applications show that there are still a lot of avenues, improvements and new opportunities that can be explored with IIPs. For IIPs to be explored extensively, the inherent weak characteristics of IIPs, need to be improved. These include template bleeding, slow rebinding kinetics, multi-step procedure and high cost of functionalised monomer and copolymer.

CHAPTER 4

4.0 NI(II) BASED ION IMPRINTED POLYMERS

4.1 Previous studies on Ni(II) ion imprinting

Nickel is one of the most widely imprinted ions by different methods of polymerization. Most nickel ion imprinting studies have been carried out using the trapping method [72-73,125-129] with different chelating agents such as HQ [72-73,125] or modified HQ [128] and its derivatives (mainly 5,7-DCQ) [126], dithizone [130] and vinylimidazole [131]. Other methods like surface imprinting and chemical immobilization have also been employed [129,132-134].

Ersoz et al. synthesised Ni(II) IIP using Ni(II)-methacryolhistidinedihydrate complex monomer with EDGMA crosslinker for selective separation and preconcentration of Ni(II) from aqueous solutions [135]. Recoveries of samples ranged from 98.2 to 100.1% with minimal interference from closely related ions and an LOD of 3.0×10^{-4} µg/mL was achieved. Nevertheless, methacryloylhistidinedihydrate is a large molecule (which may affect the stability of the polymer) but binds to the metal through two nitrogen atoms. The polymer also involved binding of nickel to oxygen while it is known that nickel doesn't bind to oxygen better than other metals like copper. Therefore, an improvement can be made by employing a smaller but effective ligand that can maximally bind to nickel. The synthesis procedure was also very long (132 h) and polymerisation time alone was 9 h. Though it was found that increased polymerisation time increased the rigidity of the polymer structure and facilitated the formation of imprinted cavities with better defined shapes, too much time means a lost opportunity in an industrial situation. Many steps and reagents were involved which will in the long run make it uneconomical for industrial applications. Dispersion polymerisation is a little complex as compared to bulk.

5,7-DCQ-8-ol embedded styrene–EDGMA polymer particles for SPE preconcentration of cobalt and nickel in aqueous, soil and sediment samples were designed by the bulk polymerisation format [126]. 5,7- DCQ-8-ol was a trapped

ligand, styrene as a monomer, DVB as a crosslinker and 2-methoxy ethanol as a porogen. The synthesis of the polymer was good with few steps and polymerisation time and the results were good. The recoveries of aqueous samples ranged from 98 to 100% and the LOD was 2.0×10^{-4} $\mu\text{g/mL}$. However, the synthesis involving the use of crosslinker EDGMA was chosen for detailed characterization and analytical applications studies but DVB has been shown to have an increased specific adsorption capacity than crosslinker EGDMA, trimethylolpropane triacrylate, 1,6-Hexanediol diacrylate and tripropylene glycol diacrylate [99]. Polymers prepared using DVB as a crosslinker were shown to have a better binding of the analyte and lower non specific binding than EDGMA [95]. This was attributed to the less polar nature of DVB as compared to EDGMA, which avoids the interaction of the crosslinker and template and promotes the complexation between the template and the monomer. The method did not show how the two metal ions ie Co(II) and Ni(II), interfere in the determination of each especially that the method was used for enrichment of the two metal ions. This is because the two metals have similar chemical properties.

Another IIP synthesis was reported where an Ni(II)-imprinted amino-functionalised silica gel sorbent was designed for SPE of trace Ni(II) in water samples [129]. The polymer was good as it involved surface imprinting and involved nitrogen donors which are good for nickel. The recoveries of water samples ranged from 98 to 103% with an LOD of 1.60×10^{-4} $\mu\text{g/mL}$. However, the synthesis procedure was long (124 h, with polymerisation time of 20 h) and involved the use many steps and reagents which make it not favourable for industrial application. This is shown by the use of an expensive and time consuming (time lost during its preparation and extraction of nickel ion) reagent, EDTA to remove the template instead of the cheap acid commonly used in leaching IIPs.

Precipitation polymerisation format used for the synthesis of a Ni(II) IIP for SPE of Ni(II) from seawater was also reported [125]. 8-HQ was used as a trapped ligand, 2-(diethylamino) ethyl methacrylate as a monomer, DVB as a crosslinker and 3:1 acetonitrile;toulene as a porogen. The method was good with LOD of 5.0×10^{-5} $\mu\text{g/mL}$. 2-(diethylamino) ethyl methacrylate monomer used its nitrogen donor atom

which is a little bit sterically hindered as it is surrounded by three single bonds unlike if it had a double bond and single bond in which it will have more space to interact with the nickel. This makes binding with nickel a little bit 'stressed'. And interference studies of closely related metal ions were not performed to evaluate selectivity of this polymer for nickel. Precipitation polymerisation is also a little bit complex (with longer polymerisation times, 26 h in this case) as compared to bulk polymerisation.

Nickel and lead IIPs were synthesised using 8-HQ as a trapped ligand for selective SPE of nickel and lead from seawater. The precipitation polymerisation format was used with 2-(diethylamino) ethyl methacrylate as a monomer, DVB as a crosslinker and 3:1 acetonitrile/toluene as a porogen [72]. The method was good with a LOD of 3.30×10^{-4} $\mu\text{g/mL}$. However, it would have been interesting to see the influence of Pb(II) on the determination of Ni(II) since the method was used for the two metal ions. It must also be said that recoveries of other metals like copper, chromium, lead, vanadium and zinc were high and it would have been interesting to evaluate their interference. Precipitation polymerisation also takes a lot of time (polymerisation time alone was 26 h), is not simple and needs sophisticated apparatus/conditions.

The trapping method with bulk polymerisation format was employed by Saraji et al. who synthesised a Ni(II) IIP for water samples using dithizone as a trapped ligand, 4-VP as a monomer, EGDMA as a crosslinker and chloroform as a porogen [130]. The method was good with recoveries of aqueous samples ranging from 87.3 to 100.6% and a LOD of 1.60×10^{-4} $\mu\text{g/mL}$. However, it involved the use of the cross linker, EGDMA which has a lower binding of the analyte and lower non specific binding [95]. Dithizone ligand is also bulky (with two benzene rings) and therefore binding sites are likely to be affected by grinding that is involved in bulk polymerisation. The synthesis involved the use of chloroform which is less polar (with polar index of 4.1) but medium polar solvents are desirable because they result in the formation of uniform imprinting sites and better molecular recognition ability in the IIP [98]. Low polarity solvent was found to decrease the stabilisation energy of the template and the functional monomer [98]. Though bulk polymerisation was used, the polymerisation time was very long (48 h). The polymerisation time was even longer

than precipitation time. This long period of time defeats one of the advantages of bulk polymerisation which is less time of preparation of IIPs.

Romani et al. synthesised a Ni(II) IIP for SPE of Cu(II), Ni(II), Pb(II) and Zn(II) from sea water by the precipitation polymerisation format [73]. The trapped ligand was 8-HQ as a ligand, 2-(diethylamino) ethyl methacrylate as a monomer, DVB as a crosslinker and 3:1 acetonitrile;toulene porogen. The method was good as shown by recoveries of samples and the LOD was 1.40×10^{-4} $\mu\text{g/mL}$ for Ni(II). However, there was interference from closely related cations as their recoveries of Cu(II), Pb(II) and Zn(II) together with Ni(II) were 99%. But there was an increase in selectivity when the same method was used but with 5-vinyl-8-hydroxyquinoline bi-functionalised ligand and the recoveries of Cu(II), Pb(II) and Zn(II) dropped to 74.9, 76.2 and 70.8% respectively and LOD was found to have increased to 2.60×10^{-4} $\mu\text{g/mL}$ [128]. It must be said that the recoveries of these closely related cations are still too high. The synthesis involved the use of 2-(diethylamino) ethyl methacrylate monomer whose disadvantage has already been discussed. The synthesis involved precipitation format which takes a long time with polymerisation time of 26 h in this case.

Recently, an IIP was synthesised by the bulk polymerisation format using 4-vinyl benzoic acid as a monomer, EDGMA as a crosslinker and 2-methoxy ethanol as a porogen [136]. The polymer was synthesised in a short period of time and did well in the presence of closely related metal ions with LOD of 6.0×10^{-3} $\mu\text{g/mL}$. Nevertheless, the method involved the use of crosslinker, EDGMA that has less binding of the analyte and higher non specific binding compared to DVB and 4-vinyl benzoic acid monomer which has oxygen donors that are not effective for nickel. The LOD was also a little bit high when compared to what has been obtained in other studies [72-73,125,128-129,130,135].

A slightly different approach of synthesis was reported in [110] where a selective sorbent for the enrichment of nickel ions from aqueous solutions was synthesised using a hierarchically hybrid organic-inorganic polymer based on the double imprinting concept. The use of a surfactant leads to the formation of polymers with

more porous surface only in the presence of template Ni^{2+} . This is because the orientation of specific binding sites containing functional groups is predetermined which makes cavities more selective. The method had an LOD of $1.6 \times 10^{-4} \mu\text{g/mL}$ and was used for Ni(II) determination in water samples and *Gingko Biloba* with satisfactory recovery values. The synthesis of the polymer was longer (87 h), complex and expensive considering reagents used when compared to what can be achieved using the bulk polymerisation method.

The disadvantages of these methods include the use of scarce vinylated groups, use of wrong cross linkers, monomers, porogens, low selectivity, high LODs, long synthesis procedures and time for rebinding. A majority of the studies did not perform Co(II) (or closely related cations) interference studies whose chemistry is similar to that of Ni(II). Therefore an improvement in these characteristics were needed hence the synthesis of Ni(II)-DMG IIP.

4.2 Ni(II)-Dimethylglyoxime IIP

4.21 Background of dimethylglyoxime and its reaction with Nickel(II)

Dimethylglyoxime ($\text{CH}_3\text{C}(\text{NOH})\text{C}(\text{NOH})\text{CH}_3$), DMG, sometimes known as 2,3-Butanedionedioxime, Diacetyldioxime, Chugaev's Reagent or 2,3-diisonitrosobutane is a colourless solid used as a chelating agent in the gravimetric analysis of nickel, [137-139]. It is also used in the analysis of palladium, [140]. Nickel complexes of DMG are very stable and sensitive [141] and are red in colour.

4.22 Use of DMG in ion imprinting

DMG has rarely been used as a ligand in ion imprinting polymerisation methods. This is despite the stable complexes it forms with Ni(II). However, DMG has been used for the determination of nickel using colorimetric and gravimetric techniques [137-139,133-144]. Daniel et al. [127] designed a Pd(II)-DMG IIP for the selective uptake of palladium ions from dilute aqueous solutions (Fig 2). The total time needed

to prepare the polymer was more than two days. Therefore new methods are needed to reduce this long time if DMG based IIPs are to be successfully used as SPE sorbents in the industry.

4.23 Ni(II)-DMG ion imprinting

DMG reacts with nickel and changes its white colour to red due to the d-d transitions. The formation of Ni(II)-DMG IIP is similar to the formation of Pd(II)-DMG IIP as shown in Fig. 3:

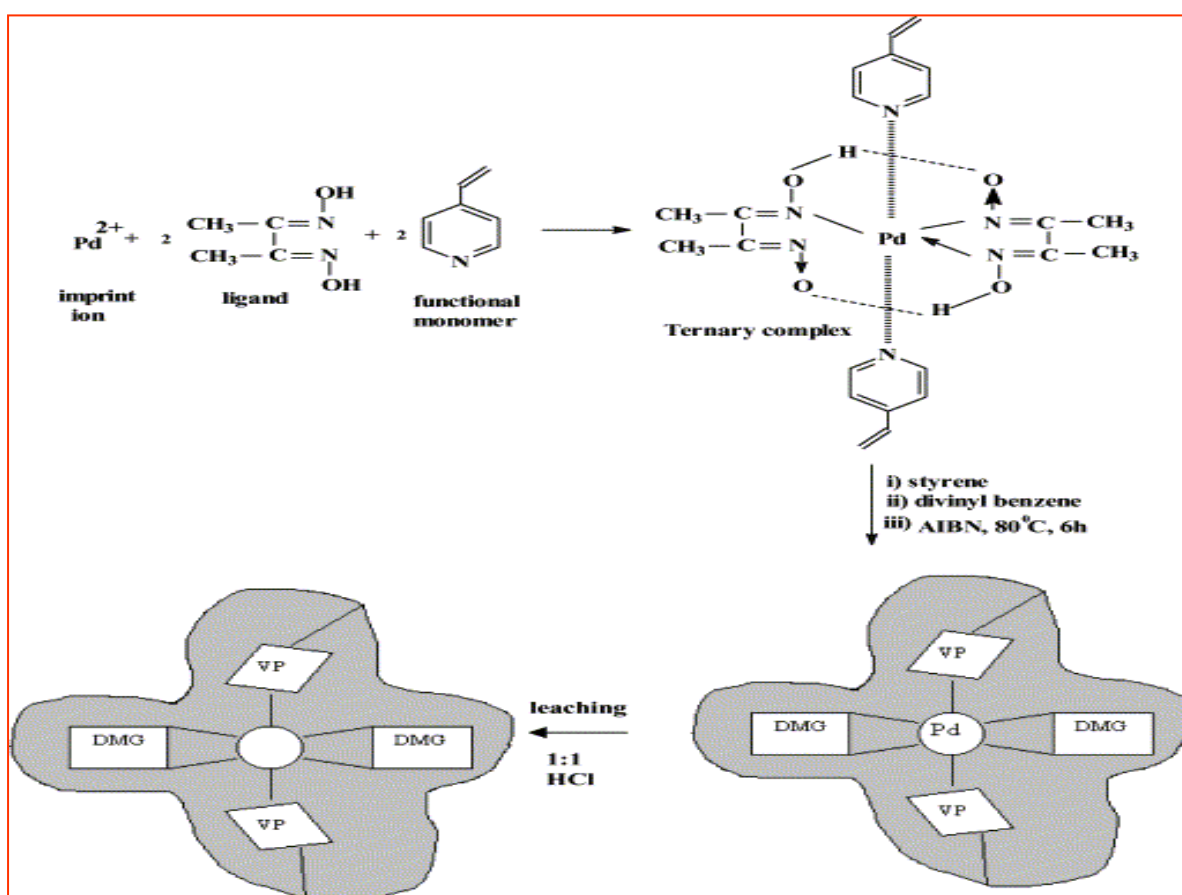


Fig. 3. Pd-DMG ion imprinting scheme (From Ref. 122)

1 mole of Ni(II) reacts with 2 moles of 4-VP and 2 moles of DMG to form a square planar Ni(II)-DMG IIP complex. Actually, DMG, through the nitrogen of its imine groups donates a lone pair to the Ni(II) metal and this cause d-d electron transitions

which is responsible for change in colour of DMG from white to red. 4-VP is used as second ligand to help keep the metal ion in place and create a cavity that is specific in size and charge to Ni(II). The donation of electrons by DMG to Ni(II) change the bond length of imide group and this change is expected to be seen in the Ni(II)-DMG IIP spectra but not in the DMG alone or DMG-NIP. There is also hydrogen bonding between the two DMG molecules and therefore OH vibrations will also be expected to be seen in Ni(II)-DMG IIP spectra but not in the DMG alone or DMG-NIP.

CHAPTER 5

5.0 ENHANCING THE PERFORMANCE OF AN IMPRINTED POLYMER

5.1 Optimization of pH

pH is the concentration of hydrogen ions or $-\log[H^+]$.

$$\text{pH} = -\log[H^+] \quad (18)$$

This concentration of hydrogen ions is very important in IIPs because as mentioned earlier the selectivity of IIPs is based on size and charge. Therefore high concentration of the hydrogen ions interfere with the rebinding of the metal ion [145] to the cavity as the hydrogen ions also bind with the cavity and a low concentration of hydrogen ions means there are a lot of OH^- which usually form precipitates with ligands [146]. Hence it is very important to optimise pH in order to have maximum rebinding of metal ions on the cavity.

5.2 Optimization of mass

Sorbents or imprinted polymers have loading capacities [147]. This is the concentration of metal ion per mass of sorbent. Therefore it is important to know the mass of a sorbent needed per volume of sample. This is to avoid too much of sorbent or wasting when a low mass can be used. Obviously adding a low mass of sorbent will compromise the results obtained.

5.3 Optimization of time

Time is important in rebinding studies as sufficient time should be allowed for the metal ion to rebind to the sites. This is mainly because the binding sites are always not on the surface hence time is required for metal ions to move towards binding sites, [148].

5.4 Optimization of the ratio of monomer to crosslinker, crosslinker to template and initiator

The bonds formed between the template and the functional monomers in these polymerisation reactions are weaker non-covalent [76] as compared to stronger covalent [75] bonds. There are several factors discussed in Chapter 4 that influence the polymerisation, and hence the subsequent performance of the imprinted polymers. It is therefore important to optimise the parameters in order to drive the equilibrium of the polymerisation reaction towards complex formation so as to improve the formation and performance of the imprinted polymers. There are several approaches that can be used to optimise these parameters [91-106]. Most have reported an approach where a single parameter was varied with others kept constant [92,96-100,102-105]. However, other groups varied more than one parameter at a time [91,93-95,101]. The uniform design of experiments employed in this thesis [91] is a statistical approach that uses a combination of experimental parameters.

The most important parameters that determine the performance of imprinted polymers are the molar ratios of crosslinkers to monomers [79,91-92,96,99,149], monomers to template [79,92,95,97,99-101,149], the volume and type of porogen [79,92,98-99,104,149] and the initiator used [92,101]. The volume/mass of template used ought to be optimised because increasing the concentration of the components in the polymerization mixture will favour an increase in the pre-polymer complex, according to Le Chatelier's principle. This drives the equilibrium of the reaction towards complex formation and thus improves the performance of the polymer formed. The monomer complexes with the template and the process is dependent on the concentration of the monomer. Non-specific adsorption, however, occurs when the volume of the monomer is in excess and a very low concentration of the monomer results in a polymer with less functional groups and therefore insufficient binding sites. A better fit between the binding sites and the template leads to increase in the affinity and selectivity of the imprinted polymer in the analyte recognition. However, increasing the concentration of the monomer reduces the crosslinker to monomer ratio which affects the morphology and stability of the

polymer matrix and consequently, the imprinted binding sites. In this regard, the concentration of the crosslinker has to match that of the monomer.

The template, initiator, monomer and the crosslinker must be soluble in the porogen [92]. The nature and volume of the porogenic solvent determines the strength of non-covalent interactions and influences polymer morphology which directly affects the performance of an imprinted polymer [98]. Therefore the quantity of the porogen used is very important. The polymerisation reaction is started by an initiator which provides the free radicals. The free radicals are generated by thermal or photolytic cleavage of azobis(nitriles) or peroxides [150]. Lowering the mass of the initiator leads to reduction in temperature during polymerisation to form polymers with good imprinting cavities [94,103] and at the same time the polymerisation rate also increases with initiator amount [105]. Therefore a balance has to be struck to ensure that all the double bonds are broken with a minimum amount of initiator.

The choice of 4-VP as a monomer was based on the strong binding that occurs between nickel and nitrogen atoms on the ligand [151]. 4-VP is also known to be a good functional monomer for metals [108,125,127,130]. The crosslinker, DVB, was used as it is less polar hence interacts less with the template and the monomer. DVB has also shown to have an increased loading capacity than EDGMA, trimethylolpropane triacrylate, 1,6-Hexanediol diacrylate and tripropylene glycol diacrylate [99].

2-methoxy ethanol was used because it is moderately polar (with polarity index of 5.5) and found to have a much better selectivity coefficient (99%) than methanol (90.33%), tetrahydrofuran (37.66%), acetic acid (33.83%), dichloroethane (10.57%), N,N-dimethyl formamide (4.59%) and toluene (1.50%) [152]. Chapter 4 explains how the polarity of the porogen determines the level of interaction between the template and the functional monomer.

Ligands help keep the template in place. DMG was chosen as it binds with metal ions by donating electrons just like 4-VP and has been used for the determination of nickel in urea [153], sea water [154] and lately, in the determination of nickel in cell phones [155]. AIBN was used as it is soluble in 2-methoxy ethanol, the porogen used in this experiment, and has a temperature of initiation (65 °C) which is lower than the boiling point of the porogen (124-125 °C).

CHAPTER 6

6.0 EXPERIMENTAL

6.1 Chemicals and Reagents

Analytical grade ammonium acetate, 4-VP, AIBN, 2-methoxy ethanol, styrene, nickel(II) sulfate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$), DVB, DMG, trace metal grade nitric acid, hydrochloric acid (HCl), hydrogen peroxide and stock solutions of Ni(II), Cu(II), and Co(II) were obtained from Sigma Aldrich (Steinheim, Germany). Pd(II) was obtained from BDH laboratories Chemical Division (London, UK). Standard solutions of Ca(II), Fe(II), Mg(II), Zn(II), Na(I), and K(I) were freshly prepared from their nitrate salts also obtained from Sigma Aldrich. Filter paper was acquired from Whatman (Maidstone, UK). An A10 milli-Q system from Millipore RiOs (Bedford, USA) was used to generate ultrapure water. A custom solution of certified reference material (CRM) (SEP-3) was obtained from Inorganic Ventures (Christiansburg, USA) and Light sandy soil CRM, (BCR-142R) was obtained from the European Commission Joint Research Centre (Brussels, Belgium).

6.2 Instrumentation

Scanning Electron Microscopy (SEM) images were acquired by a TS5136ML Digital Vega Microscope from Tescan (Brno, Czech Republic). FTIR ($400\text{--}4000\text{ cm}^{-1}$) spectra were recorded on a PerkinElmer Spectrum 100 spectrometer (Massachusetts, USA) equipped with a universal ATR sampling accessory. Concentrations of metals were determined using an iCAP 6000 series ICP-OES from Thermo Electron Corporation (Cheshire, United Kingdom). The solution pH was measured using the Jenway 3510 pH meter (Essex, UK).

6.3 Preparation of the Ni(II)-DMG IIP

Ni(II)-DMG IIP was prepared by mixing NiSO₄·6H₂O (0.263 g), 4-VP (0.23 mL) and DMG (0.465 g) in 2-methoxy ethanol (10.0 mL) with stirring for 10 min to form a ternary complex. Subsequently, DVB (1.78 mL), styrene (1.15 mL) and AIBN (50.0 mg) were added. The mixture was cooled to 0 °C and purged with nitrogen gas for 10 min. Polymerisation was carried out by heating in an oil bath at 70 °C for 3 h. The red-coloured Ni(II)-DMG IIP was then homogenised using a pestle and mortar to obtain a fine powder. The powder was sieved through a 45 µm mesh before it was subsequently washed three times with 50% HCl and then three times with ultrapure water. The leached Ni(II)-DMG IIP was then dried at 55 °C for 12 h. The non ion imprinted polymer (NIP) was prepared by the same procedure except that NiSO₄·6H₂O was omitted.

6.4 Optimization of pH, mass and time

A set of three replicates 30.0 mL portions of 10 µg/mL Ni(II) solutions were prepared and their pH adjusted from 1.0 to 12.0. Then 40.0 mg of Ni(II)-DMG IIP was added into each solution and stirred for 5 min. To optimise for time needed for Ni(II) rebinding, equal volumes of Ni solutions (30.0 mL) were taken and adjusted to pH 8.0. Times for rebinding of Ni(II) ranging from 15 s to 1800 s were evaluated. For mass optimization, 10.0 to 100.0 mg of leached Ni(II)-DMG IIP were weighed into each solution and shaken for 30 min. The recoveries of Ni(II) in all the optimization steps were calculated after quantification with ICP-OES. To test for reusability of the IIP, three replicates of 30.0 mL portions containing 10 µg/mL Ni(II) were taken, buffered with ammonium acetate and their pH adjusted to 8.0. Then 50.0 mg of a leached Ni(II)-DMG IIP were weighed into each solution and shaken for 5 min. The Ni(II)-DMG IIP was recovered and washed with 50 %HCl and deionised water. The Ni(II)-DMG IIP was evaluated for reuse six times. In all the experiments, the amount of Ni(II) absorbed by Ni(II)-DMG IIP was desorbed with 50% HCl and the concentration of Ni(II) quantified by ICP-OES. This value was always not significantly different from the one obtained by taking the reduction in concentration of the Ni(II) solution as the amount trapped by the Ni(II)-DMG IIP.

6.5 Preparation of the different compositions of Ni(II)-DMG IIPs

For the uniform design experiments, a series of Ni(II)-DMG IIPs were prepared through the process described but with varying quantities of the reactants. The amounts of template, monomer, crosslinker, crosslinking monomer, ligand and porogen were varied from 0.105 to 0.526 g, 0.05 to 0.41 mL, 0.36 to 3.21 mL, 0.23 to 2.07 mL, 0.093 to 0.836 g and 2.0 to 18.0 mL respectively. The 'array' in the uniform design experimental method is as shown in Tables 1 and 2.

6.6 Sample collection and preparation

Sea, river, untreated sewage and treated sewage water samples were collected in polyethylene containers by grab sampling method. 100.0 mL portions of water samples doused with 2.0 mL conc. HNO₃ and 5.0 mL conc. HCl were digested by heating on a hot plate at 90 °C until the volume was reduced to 20.0 mL. The solution was then filtered through whatman No. 1 filter paper after allowing it to cool and diluted to 100.0 mL with ultrapure water prior to ICP-OES analysis [156]. Soil and mine tailing samples were collected in polyethylene bags from buildings around the Chemistry and Pharmaceutical Sciences (Rhodes University, Grahamstown) and Selibe Phikwe copper-nickel mine (Selibe Phikwe, Botswana) respectively. Soil samples were collected at any exposed surface ground without following any scheme as the environment is paved. For mine tailings, 1.0 kg of samples were taken at a depth of 15 cm using soil auger. One composite sample represented 1 ha and each composite sample consisted of 15 subsamples. Three composite samples were taken to the laboratory where they were air-dried, passed through a 2.0 mm sieve and homogenised in a mortar. Each sample was divided into three subsamples and 0.5 g was acid digested using a standard protocol [157] prior to ICP-OES analysis. CRMs were treated by the same procedure as the samples.

6.7 Analytical quality control

A custom-made CRM for groundwater (SEP-3) and light sandy soil (BCR-142R) were obtained from the European Commission Joint Research Centre (Brussels, Belgium) and Inorganic Ventures (Christiansburg, USA) respectively were used to validate the analytical procedure. Analytical calibrations, based on the recommended

concentration points and emission lines of each element, were carried out in aqueous standard solutions. Adsorption and desorption experiments were carried out using 50.0 mg of the Ni(II)-DMG IIP in 10.0 mL portions of the certified reference groundwater. Repeatability of the method was evaluated by comparing the signals obtained from 5 determinations of the reference material. The LOD and LOQ were evaluated as 3 and 10 times the estimated regression standard deviation respectively based on 5 replicate determinations.

6.8 Selectivity and interference studies

For selectivity, 50.0 mg of leached Ni(II)-DMG IIP or non imprinted polymers were placed into 30.0 mL portions of 10 µg/mL solutions of Ni(II), Mg(II), Ca(II), Na(I), K(I), Co(II), Cu(II), Zn(II), Fe(II) and Pd(II) were shaken for 5 min. The Ni(II)-DMG IIP was filtered off and the change in metal concentration was taken as the amount trapped by the Ni(II)-DMG IIP. The recoveries of each metal were calculated after quantification with ICP-OES. For interference, 50.0 mg Ni(II)-DMG IIP was placed into 30.0 mL aliquots of each of 10 µg/mL Ni(II), Mg(II), Ca(II), Na(I), K(I), Co(II), Pd(II), Cu(II), Zn(II) and Fe(II) were shaken for 5 min. The concentration of Ni(II) was kept at 10 µg/mL while each of Mg(II), Ca(II), Na(I), K(I), Co(II), Pd(II), Cu(II), Zn(II) and Fe(II) were varied from 10 to 20 µg/mL in successive experiments. A mixture containing 10 µg/mL of Mg(II), Ca(II), Na(I) and K(I) was also prepared and the interference on nickel recovery at 10 µg/mL and 20 µg/mL of these metal ions was evaluated. Lastly a solution containing all of the above elements were prepared at 10 µg/mL and at 20 µg/mL and the interference of this solution on recovery of Ni(II) was tested at these levels. The effect of Co(II) and Cu(II) on the recovery of Ni(II) and interaction between the two were evaluated using the scheme outlined by Montgomery [158].

CHAPTER 7

7.0 RESULTS AND DISCUSSION

7.1 Characterisation of the morphology of the imprinted polymers.

Fig. 4 shows the SEM images of the Ni(II)-DMG complex, Fig. 5 is Ni(II)-DMG IIP, Fig. 6 is NIP and Fig. 7 is leached DMG-IIP. The morphology of Ni(II)-DMG complex was fibrous while that of Ni(II)-DMG IIP had more agglomerates, the NIP was spongier and the leached Ni(II)-DMG IIP had a more porous morphology. Generally, literature has shown that IIPs prepared by bulk polymerisation are large sized swollen irregular agglomerates whereas the NIP consists of agglomerates and also spherical monodisperse particles whilst the leached IIP is expected to have some cracks and pores on the surface [125,128,131,134,159-162]. In this case, the spongier morphology of the DMG-NIP shows that it is 'relaxed' and has the ability to absorb Ni(II) ions and become 'stiff' like Ni(II)-DMG IIP. The morphology of the Ni(II)-DMG complex is expected to show needle like structures with a diameter of about 200 nm and length up to several micrometers [163-164] which is what was observed.

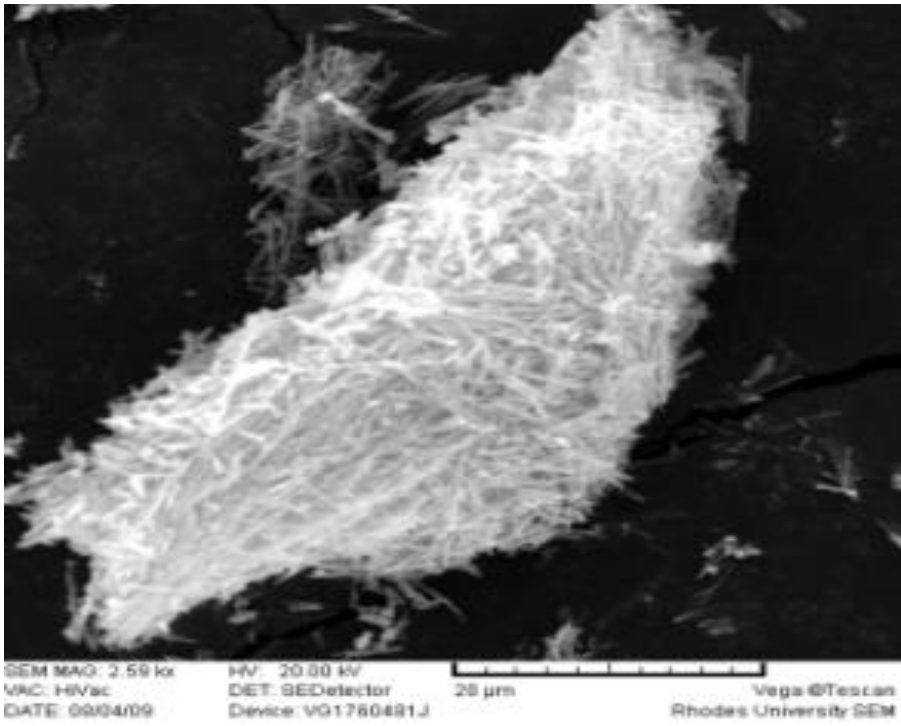


Fig. 4. SEM image of a Ni(II)-DMG complex.

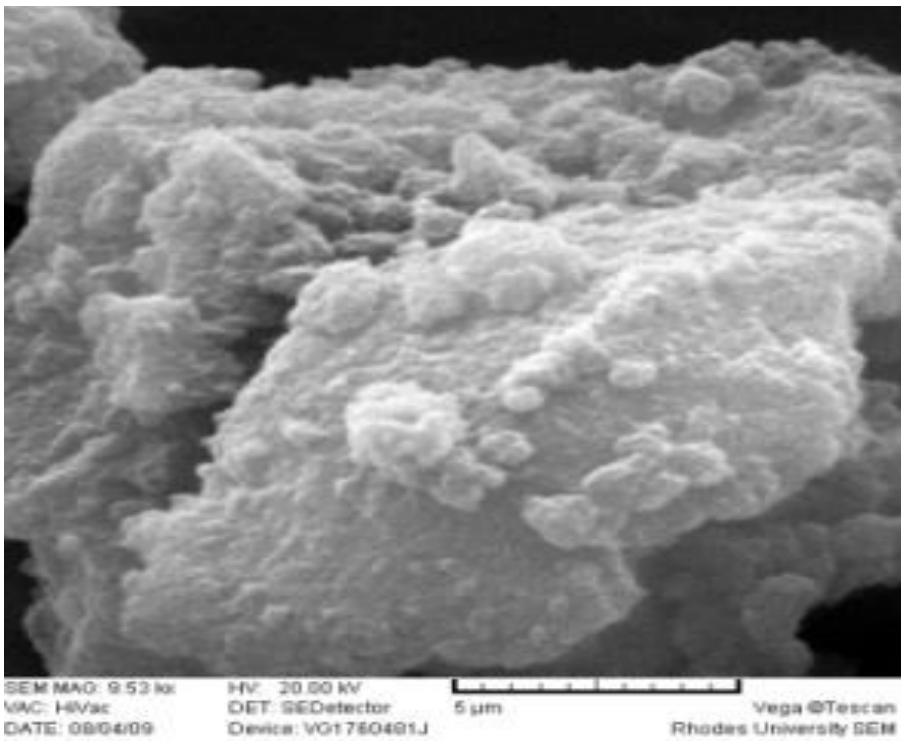


Fig. 5. SEM image of a Ni(II)-DMG IIP.

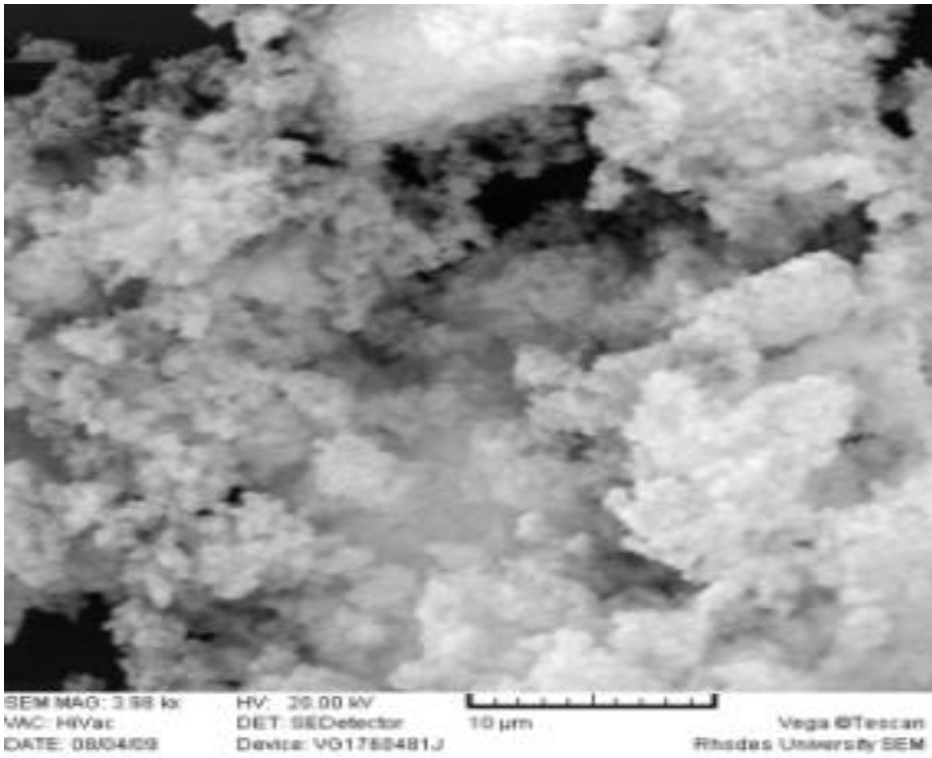


Fig. 6. SEM image of a non-imprinted polymer.

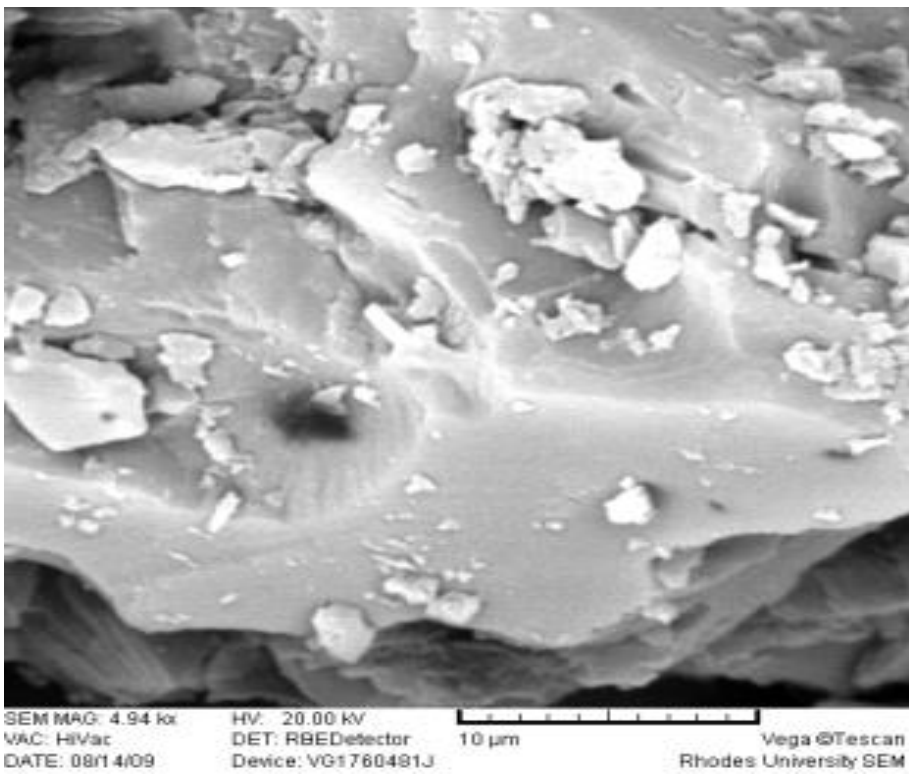


Fig. 7. SEM image of a leached imprinted polymer.

7.2 IR Studies

The IR spectrum of Ni(II)-DMG IIP (Fig 8C) indicates that Ni(II) is bound through the nitrogen atoms due to the change in (C=N) from around 1636 cm^{-1} and 1638 cm^{-1} respectively in the free DMG (as shown in Fig. 8A) and NIP (as shown in Fig. 8B) to 1628 cm^{-1} in the Ni(II)-DMG IIP (as shown in Fig. 8C). The IR spectrum of the Ni(II)-DMG IIP (as shown in Fig. 8C) also shows the presence of OH deformation band at 1737 cm^{-1} indicating the formation of a hydrogen bridge [165-167]. This hydrogen bridge confirms the formation of the red square planar Ni(II)-DMG IIP and is absent in the DMG and in the NIP (as shown in Figs. 8A and 8B).

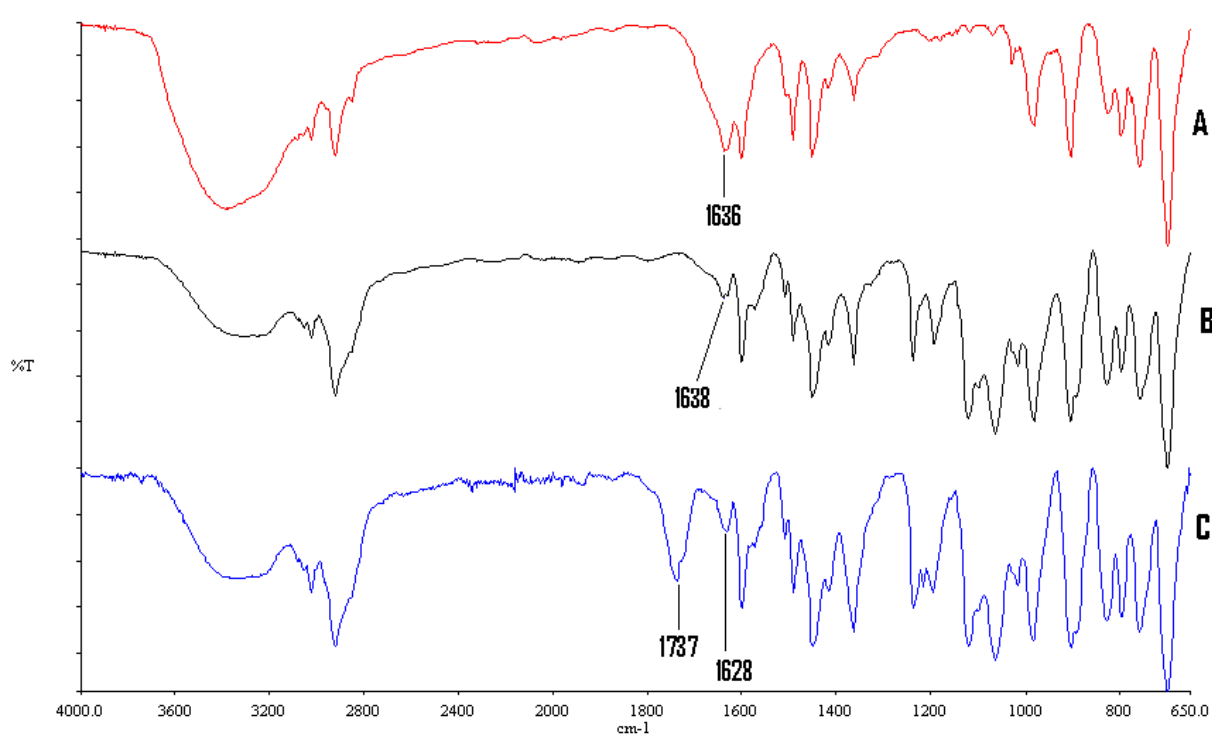


Fig. 8. IR spectra of DMG (A), NIP (B) and Ni(II)-DMG IIP (C).

7.3 Optimization of pH

At pH 0 to 4.0 the recoveries ranged from 13 to 24% and good recoveries (72-89%) were recorded in the pH range of 6.0 to 10.0 and beyond pH 10.0, the recoveries dropped (Fig. 9). This pH range obtained for optimal rebinding of Ni(II) is in agreement with that reported in literature [72-73,125-126,130-131,133,135,136,171]. Ni(II) is better adsorbed by DMG at mid to high pH values. This is because it is the conjugate base of DMG, that complexes the metal ions. At lower pH values, DMG is

protonated and cannot bind effectively with metals. Its binding capacity is rather enhanced when it is deprotonated at higher pH values. At pH higher than 10, there is too much hydroxide ions which usually form precipitates with ligands [146].

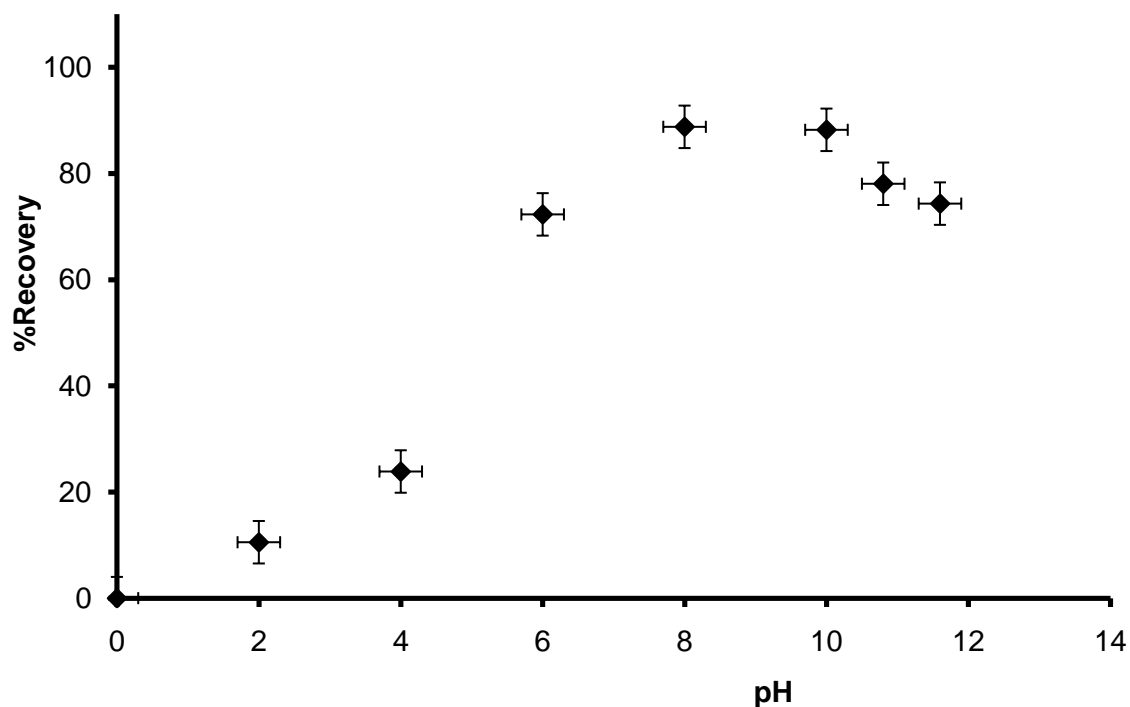


Fig. 9. Effect of pH on recovery of Ni(II).

7.4 Optimization of mass

50.0 mg of leached IIP was found to be the optimal mass of the Ni(II)-DMG IIP to achieve the maximum recovery of 98% (as shown in Fig. 10) and therefore 50.0 mg was used in this study, making up polymer-to-solution ratio of 5:3. The Ni(II)-DMG IIP performed exceptionally well, compared to some other IIPs as it used less quantities of polymer per volume of samples [125,128,135-136]. This is considering the higher concentrations of samples that were used in this study.

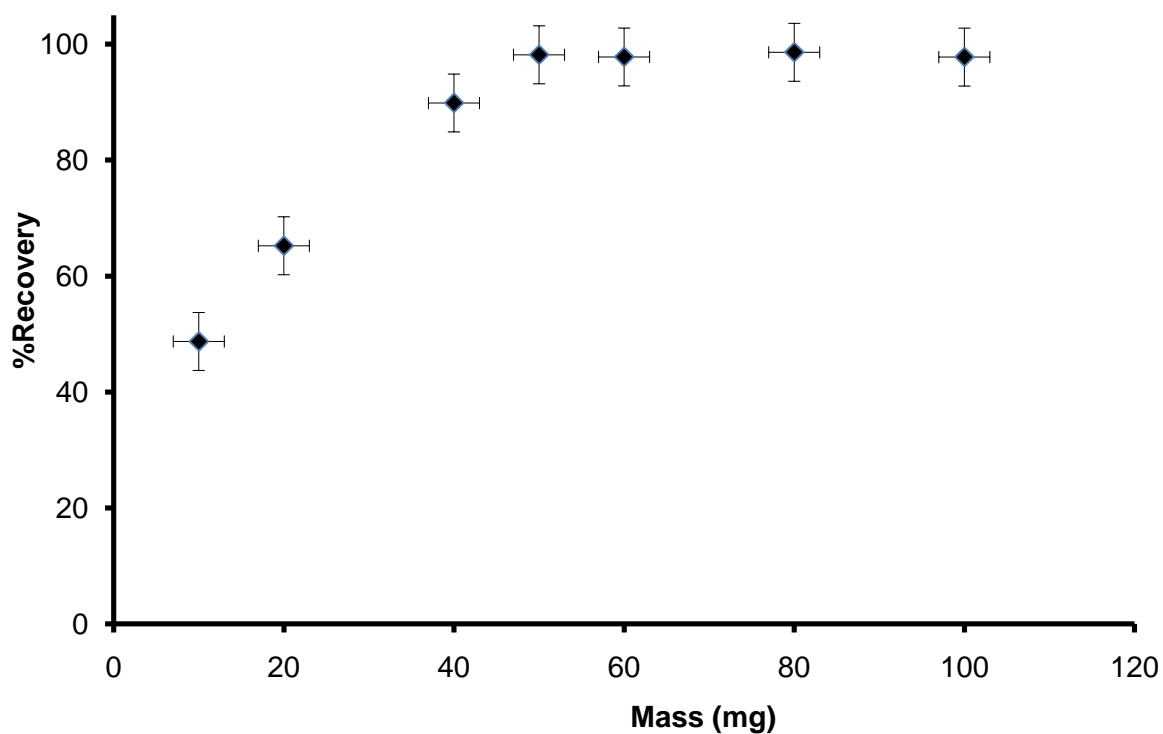


Fig. 10. Effect of mass on recovery of Ni(II) for Ni(II)-DMG IIP.

7.5 Kinetics of the Ni(II)-DMG IIP

As can be seen from Fig. 11 maximum of 1 min was the time needed to rebind all the nickel ions onto imprinted sites on the Ni(II)-DMG IIP. Considering the time taken by other polymers; 2 min [72], 5 min [126,129] and 20 min [131], this Ni(II)-DMG IIP showed good kinetics of rebinding.

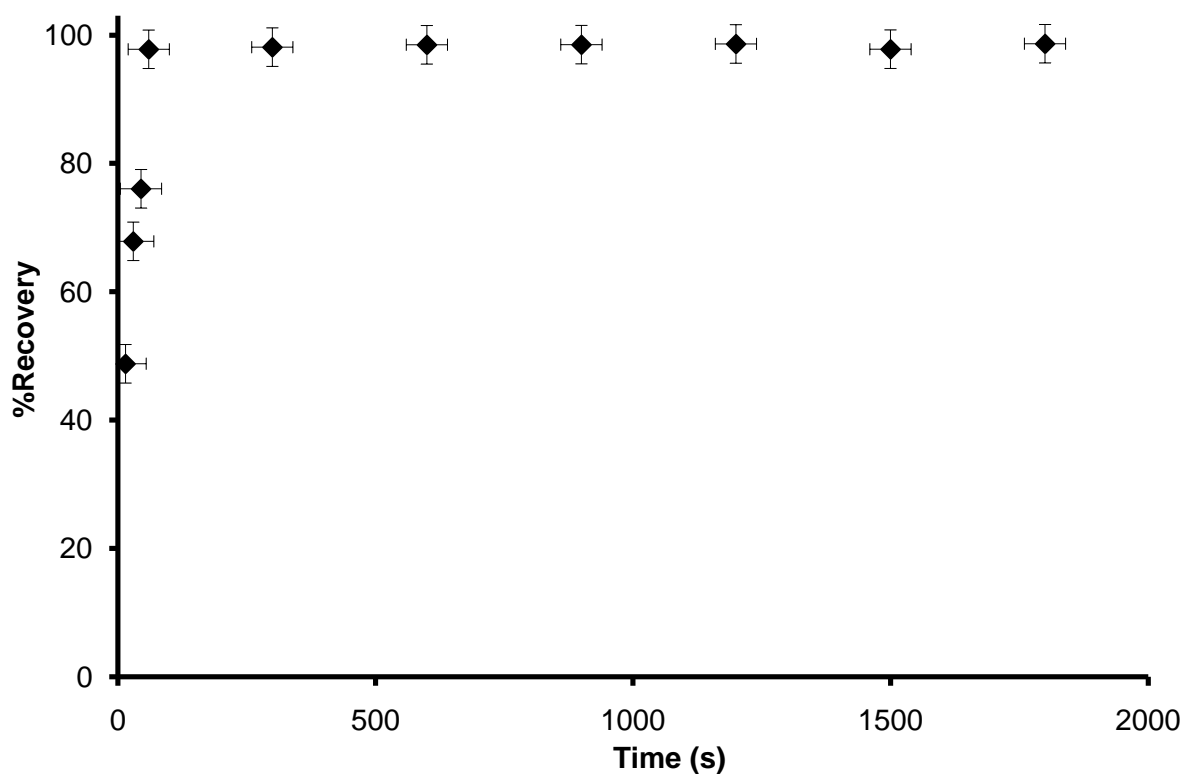


Fig.11. Effect of preconcentration time on recovery of Ni(II)-DMG IIP

7.6 Reusability kinetics of the Ni(II)-DMG IIP

Although some IIPs have been reported to be reusable [72-73,127-128], the percentage recovery of Ni(II)-DMG IIP dropped from 98% to 44% upon the sixth usage (as shown in Fig. 12). This is, however, not a major limitation as the solid SPE sorbents, which is the ultimate goal of synthesising this IIP, are used only once.

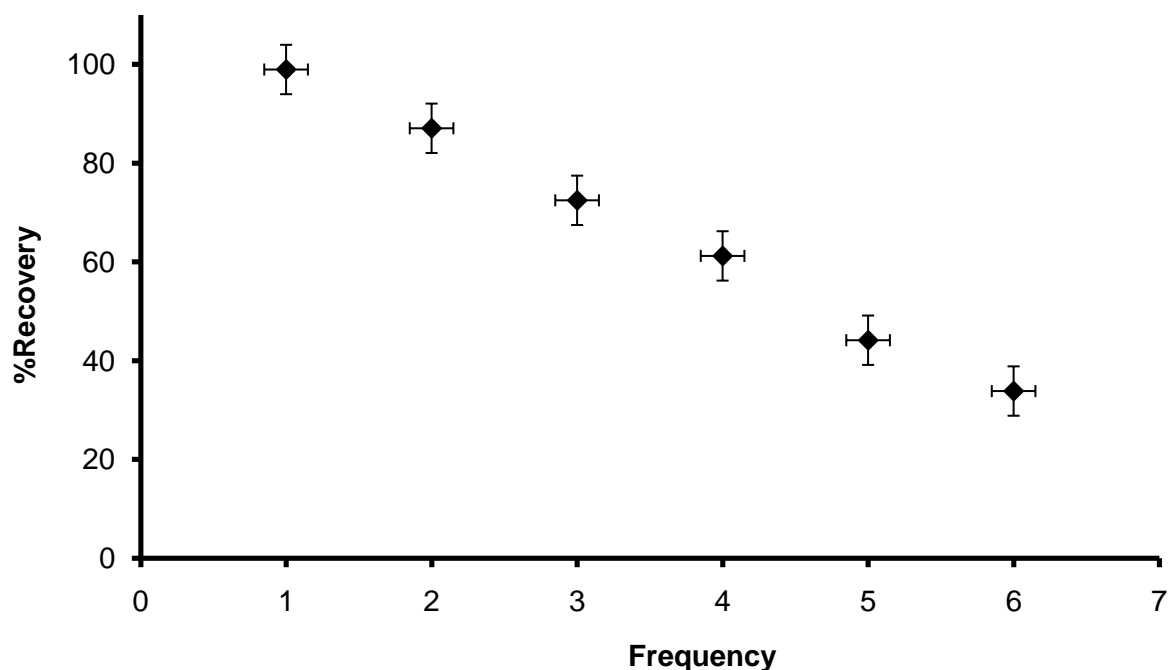


Fig. 12: Effect of repeated use of Ni-DMG IIP on recovery of Ni(II).

7.7 Optimisation of template, monomer, porogen, crosslinker, crosslinking monomer, ligand and initiator.

The uniform design experimental approach reduced the number of experiments that were initially proposed from 162 (or 189 if the initiator is included) to 54 by varying the concentrations of template, monomer, porogen, crosslinker, crosslinking monomer and ligand at 9 levels with three replicates. Initially the concentrations of the parameters including the initiator were to be varied one at a time while keeping others constant. By varying the quantities of crosslinking monomer, crosslinker and porogen, a recovery range of 98.26 to 99.35% was achieved (Table 1).

Table 1

The uniform design experiment showing the variations of styrene, DVB and 2-methoxy ethanol after recovery (n=3).

Run	^a Volume of Styrene (mL)	^b Volume of DVB (mL)	Volume of 2-methoxy ethanol (mL)	Molar ratio (b:a)	%Recovery
1	0.688	2.493	18	2.3:1.0	95.96
2	1.376	1.424	16	0.7:1.0	98.89
3	2.065	0.356	14	0.1:1.0	-
4	0.459	2.849	12	4.0:1.0	94.63
5	1.147*	1.781*	10*	1.0:1.0	98.26
6	1.835	0.712	8	0.2:1.0	99.35
7	0.229	3.205	6	9.0:1.0	94.87
8	0.918	2.131	4	1.5:1.0	92.81
9	1.606	1.068	2	0.4:1.0	96.45

*Amounts that were previously used.

These recoveries were achieved with a lesser total volume of the mixture (from 12.93 to 10.55 mL) though the volume of monomer was more than used before optimisation.

From Table 2, the recovery of Ni(II) increased from 99.35 to 99.91% after varying the amounts of template, monomer and ligand. Table 3 shows that the optimum crosslinker to monomer molar ratio was 3.3:1.0 which is in the range of 3.0:1.0 to 20.0:1.0 reported by others [79,89,91-92,96,149]. The lower ratio of crosslinker to monomer can be attributed to the fact that the styrene monomer was added as a crosslinking monomer. The effect of the styrene was evident in run 3 in Table 1 where the polymer did not form. This was mainly because the molar ratio of styrene to DVB which was used in run 3 was too high (1.0:0.1). However, the polymer formed, though with less recovery when the ratio was reversed, as can be seen in

run 7 in Table 1 where the molar ratio was changed to 9.0:1.0. The optimum volume of porogen was 8.0 mL compared to 10.0 mL that was used without optimisation.

Table 2

The uniform design experiment showing how the variations of NiSO₄·6H₂O, DMG and 4-VP after recovery (n=3).

Run	^a Mass of NiSO ₄ ·6H ₂ O (g)	^b Mass of DMG (g)	^c Volume of 4-VP (mL)	Molar ratio (a:c:b)	%Recovery
1	0.158	0.650	0.409	1.0:6.0:9.3	97.28
2	0.316	0.372	0.363	1.0:2.7:2.7	85.49
3	0.473	0.093	0.318	1.0:1.6:0.4	86.3
4	0.105	0.743	0.272	1.0:6.0:16	97.61
5	0.263*	0.465*	0.227*	1.0:2.0:4.0	99.35
6	0.421	0.186	0.182	1.0:1.0:1.0	88.63
7	0.526	0.836	0.136	1.0:0.6:3.6	99.91
8	0.210	0.557	0.091	1.0:1.0:6.0	99.13
9	0.368	0.279	0.045	1.0:0.3:1.7	94.37

*Amounts that were previously used.

The optimal monomer to template molar ratio that was obtained from this run was 0.6:1.0 which was different from 2.83:1.0 to 5.0:1.0 reported in other studies [79,92,95,97,99-101,149] or 2.0:1.0 that was used without optimisation. The optimal molar ratio of NiSO₄·6H₂O to 4-VP to DMG was 1:0.6:3.6 which was comparable to the predicted one of 1:2:2 (similar to the one in run 2) or 1:2:4 that was used in [73] employed with nickel chloride hexahydrate to 2-(diethylamino) ethyl methacrylate to 8-HQ. According to the scheme proposed by Daniel et al. [127] two molecules of 4-VP react with one metal atom and two molecules of DMG are used to hold the metal atom in place via donation of electrons by nitrogen atoms. The total masses of NiSO₄·6H₂O and DMG were higher than the ones previously used but the volume of 4-VP was very much less. Comparing the benefits of increasing the quantities of reactants to the increase in % recovery, it can be concluded that the quantities in run 8 can still be used with less quantities of reactants but achieving good recoveries.

Table 3Molar ratios of DVB to 4-VP and 4-VP to NiSO₄·6H₂O (n=3).

^a Moles of DVB	^b Moles of 4-VP	^c Moles of NiSO ₄ ·6H ₂ O (g)	Crosslinker:monomer molar ratio (a:b)	Monomer:template molar ratio (b:c)
0.0039989	0.003603	0.000600	1.1:1.0	6.0:1.0
0.0039989	0.003198	0.001200	1.3:1.0	2.7:1.0
0.0039989	0.002802	0.001800	1.4:1.0	1.6:1.0
0.0039989	0.002396	0.000400	1.7:1.0	6.0:1.0
0.0039989	0.002000	0.001000	2.0:1.0	2.0:1.0
0.0039989	0.001603	0.001600	2.5:1.0	1.0:1.0
0.0039989	0.001198	0.002000	3.3:1.0	0.6:1.0
0.0039989	0.000802	0.000800	5.0:1.0	1.0:1.0
0.0039989	0.000396	0.001400	10.1:1.0	0.3:1.0

7.8 Optimisation of initiator

From Fig. 13, the optimum mass of initiator was 40.0 mg. This mass is similar to what other authors reported, [72-73,125-126,135] but less than 150 mg and 120 mg used by others [128,130]. There was no polymer formed when 10.0 mg of initiator were used.

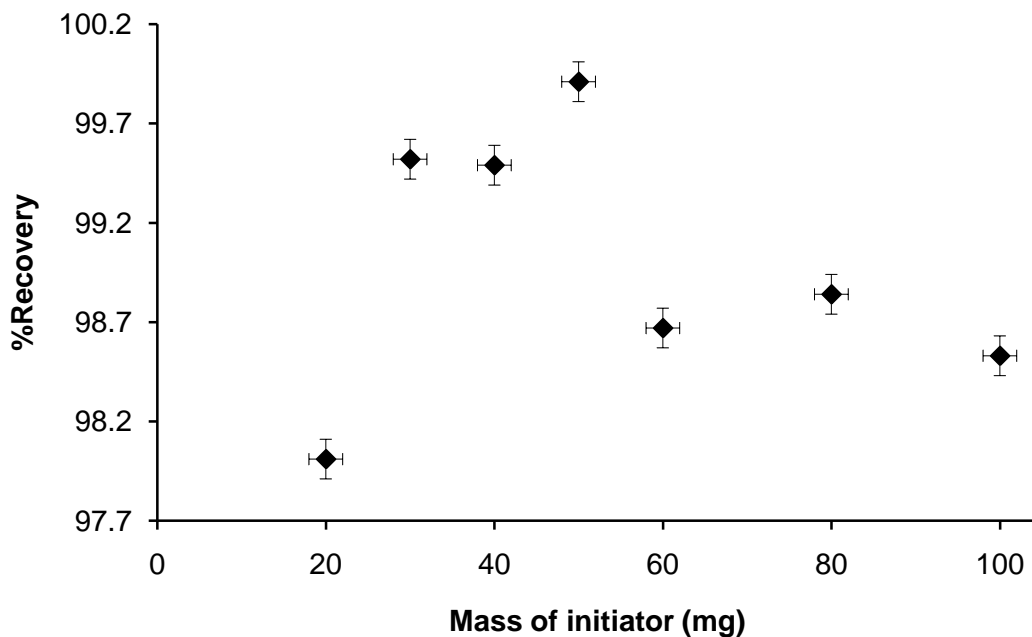


Fig. 13: Effect of the mass of initiator on recovery of Ni(II)-DMG IIP

The optimisation of initiator was conducted in 24 experiments with 8 levels and 3 replicates. This could have been less if the uniform design experimental method was used as this number of experiments is almost the same as that of the uniform design experimental method when it was performed (with 9 levels instead of 8 as is the case with the initiator) with 3 parameters as shown in Tables 1 and 3. Some of the deviations of these results from those obtained in the literature are mainly due to the fact that most of them did not perform optimization studies.

7.8 Selectivity and interference studies

The recovery of Ni(II) was much higher as compared to those of Co(II), Cu(II), Zn(II), Pd(II), Ca(II), Mg(II), Na(I) and K(I), demonstrating that the cavities in the Ni(II)-DMG-IIP had higher affinity for Ni(II) as shown in Table 4.

Table 4

%EEs of Ni(II) IIPs obtained from other sources compared to Ni(II)-DMG-IIP.

IIP	% EEs ^a									
	Ni(II)	Fe(II)	Co(II)	Pd(II)	Cu(II)	Zn(II)	Ca(II)	Mg(II)	Na(I)	K(I)
This work (n=3)	98 (66)	100 (100)	62 (37)	26 (22)	37 (42)	37 (37)	38 (59)	47 (62)	64 (62)	37 (52)
Ni(II)-HQ, [72]	99 (1)	82 (84)	-	-	93 (39)	90 (37)	-	-	-	-
Ni(II)-HQ, [73]	99 (10)	-	-	-	99 (23)	99 (19)	-	-	-	-
Pd(II)- DMG, [127]*	2 (2)			99 (48)	2 (2)	1 (1)	-	-	-	-
Ni(II)- Bifunctional ised 5- vinyl-HQ, [128]	99 (73)	84.8 (85)	63 (60)	-	75 (76)	71 (74)	-	-	-	-
Ni(II)- Dithizone, [130]	93 (37)	-	14 (8)	-	62 (68)	-	-	-	-	-

$${}^a\%EE = \left(\frac{C_i - C_s}{C_i} \right) \times 100$$

Where C_i is the initial solution concentration ($\mu\text{mol/mL}$) and C_s is the solution concentration after adsorption.

*This IIP was for palladium and is only shown here because DMG was used as a trapped ligand.

The values in brackets are for non imprinted polymers.

Despite the fact that Fe(II), Co(II) and Cu(II) [164,171-172] are known to interfere with the complexation of nickel with DMG, these metals did not show any interference with the extraction efficiency of Ni(II) when the Ni(II)-DMG-IIP was used. Although DMG is selective to both Pd(II) and Ni(II), it seems that in this case, Ni(II) specific cavities were created. This was evidenced by the lower %EEs recorded for Co(II), Cu(II), Zn(II) and Pd(II) which have about the same size and charge as Ni(II).

Fe(II) had a reasonably high recovery but it did not interfere with the determination of Ni(II). The selectivity of the Ni(II)-DMG IIP for Ni(II) in this study was much better compared to what was previously reported for some polymers [73,126,128]. Zn(II), Pd(II), Fe(II), Ca(II), Mg(II), Na(I) and K(I) in the water samples did not interfere with the binding of Ni(II) on the IIP as shown in Table 5.

Table 5

Ni(II) recoveries of Ni(II)-DMG-IIP after addition of different levels of different cations (n=3).

Element(s) added	Concentrations of elements added (µg/mL)	Concentration of Ni(II) (µg/mL)	% Recovery
Na(I)	10, 20	10	96, 98
K(I)	10, 20	10	98, 99
Ca(II)	10, 20	10	91, 93
Mg(II)	10, 20	10	91, 93
Ca(II), Mg(II), Na(I) and K(I)	10, 20	10	98, 94
Co(II)	10, 20	10	93, 81
Pd(II)	10, 20	10	90, 89
Cu(II)	10, 20	10	92, 87
Zn(II)	10, 20	10	93, 89
Fe(II)	10, 20	10	94, 91
All above	10,20	10	83, 74
Co(II); Cu(II)	10, 10	10	91
Co(II); Cu(II)	10, 20	10	92
Co(II); Cu(II)	20, 10	10	89
Co(II); Cu(II)	20, 20	10	87

To compute the main effect of Cu(II) on Ni(II) for the two factorial design experiments, the average response at all runs with Cu(II) at the high setting were computed and the average response of all runs with Cu(II) set at low were subtracted [158]. The same procedure was followed to evaluate for the main effect of Co(II).

Cu(II) and Co(II) interfered with the rebinding of Ni(II) and interference studies were performed on them and the results are shown in Table 5. Co(II) slightly interfered with the determination of Ni(II) and the interaction between the Cu(II) was too low.

According to Montgomery, for effect to be taken as significant, it has to be more than 5 [158]. Most Ni(II) ion imprinting work does not have these data which can help evaluate the effect of Co(II) on rebinding of Ni(II) as the two ions compete severely [169,173-174].

7.9 LOD and LOQ.

The evaluated LOD and LOQ were rather low, 3×10^{-4} and 9×10^{-4} $\mu\text{g/mL}$ respectively and much lower compared to some previously reported values as shown in Table 6. Those with both lower LOD and LOQ than the Ni(II)-DMG IIP had lower selectivity for Ni(II) or higher interference from closely related cations [73,126,128].

Table 6

LOD and LOQ obtained from other sources compared to the Ni(II)-DMG-IIP.

IIP	LOD ($\mu\text{g/mL}$)	LOQ ($\mu\text{g/mL}$)
This work (n=3)	3.00×10^{-4}	9.00×10^{-4}
Ni(II)-HQ, [72]	3.30×10^{-4}	1.10×10^{-3}
Ni(II)- HQ, [73]	1.40×10^{-4}	4.70×10^{-4}
Ni(II)- HQ, [125]	5.00×10^{-5}	
Ni(II)-Bifunctionalised 5-vinyl- HQ, [128]	2.60×10^{-4}	8.70×10^{-4}
Ni(II)-Dithizone, [130]	1.60×10^{-3}	-
Ni(II)-amino-functionalised silica gel, [129]	1.60×10^{-4}	-
Ni(II)-methacrylol histidinedihydrate, [135]	3.00×10^{-4}	-

7.10 Analysis of CRMs

The developed method was validated by analyzing a CRM of water (SEP-3) and light sandy soil (BCR-142R) as shown in Tables 7 and 8.

Table 7

Analytical quality control parameters determined using the SEP-3 certified referenced groundwater.

Wavelength (nm)	Calibration Linearity R ²	Certified concentration (mg/L)	Concentration found (n=3) (mg/L)	Relative error (%)	%RSD (n=6)	LOD (mg/L) (n=5)	LOQ (mg/L) (n=3)
231.60	0.9954	0.8980 (0.007)	0.8991 (0.0013)	+0.1225	4.29	0.0003 (0.0018)	0.0009 (0.002)

*Standard deviations in brackets.

The results showed that the values obtained from the method are within the error of the CRMs. The %RSD was found to be 4.29. The recoveries of the spiked samples were very good (99-100% and 99% for water and soils respectively) as shown in Tables 9 and 10).

Table 8

Analytical quality control parameters determined using the BCR-142R certified referenced sandy soil.

Wavelength (nm)	Calibration Linearity R ²	Certified concentration (mg/L)	Concentration found (n=3) (mg/L)	Relative error (%)	%RSD	LOD (mg/L)	LOQ (mg/L)
231.60	0.9994	64.5 (0.007)	62.6314 (0.0013)	-2.8971	2.2919	0.0003 (0.002)	0.0009 (0.002)

*Standard deviations in brackets.

Tables 7 and 8 give the quality control parameters regarding the determination of nickel concentrations in water and sandy soil CRM. Accuracy of the determinations, expressed as relative error between the certified and the observed values of the reference material were $\leq 0.2\%$. The precision of these measurements expressed as RSD on five independent determinations, was also satisfactory, being lower than 3% in all cases. The LOD of the Ni(II)-DMG IIP was found to be 0.0003 ± 0.0001 mg/L while the LOQ is 0.0009 mg/L.

Table 9

Analysis of SEP-3 CRM.

CRM	Certified Ni(II) conc. value (µg/mL)	Ni(II) conc. in sample (µg/mL) (n=3)	Amount of Ni(II) added (µg/mL) (n=3)	% Recovery
SEP-3	0.900	0.8991	0, 5, 10	-,99, 100

Table 10

Analysis of BCR-142R CRM.

CRM	Certified Ni(II) conc. value (µg/mL)	Ni(II) conc. in sample (µg/mL) (n=3)	Amount of Ni(II) added (µg/mL) (n=3)	% Recovery
BCR-142R	64.5	62.6314	0, 5, 10	-,99, 99

7.11 Analysis of water samples

The Ni(II)-DMG IIP was then used to determine the concentration of Ni(II) in water samples. The results are shown in Tables 11. Enrichment factor (EF) was found to range from 2 to 18.

Table 11

EFs of Ni(II)-DMG IIP in aqueous samples (n=3).

Type of water sample	^a Ni(II) conc. value in the sample (µg/mL) (digested)	^b Ni(II) conc. value got without digestion (µg/mL)	^c Ni(II) conc. value got when using Ni(II)-DMG IIP (µg/mL)	EF*	Ratio (b/a)
Sea	0.0220	0.0015	0.0265	18	0.07
Town River	0.041	0.0193	0.0546	3	0.47
Village River	0.1001	0.0112	0.1246	11	0.11
Treated sewage	0.1013	0.0181	0.1164	6	0.18
Untreated sewage	0.0339	0.0201	0.0408	2	0.59

*EF was calculated as; $\frac{c}{b}$.

The complexity of the water sample was estimated from the ratio of concentrations obtained with and without digestion. The recoveries were very good given the complexity of the matrices because the ratios of the Ni(II) concentration values in the sample obtained with digestion divided by the values of Ni(II) obtained without digestion was low. In all the water samples the concentrations of Cu(II) and Zn(II) were higher than that of Ni(II) (as shown in Table 12) but they did not interfere with the rebinding of Ni(II) on the Ni(II)-DMG IIP.

Table 12

Composition of the water samples (n=3).

Sample	Ni(II)	Co(II)	Cu(II)	Zn(II)	Na(I)	K(I)	Ca(II)	Mg(II)
	($\mu\text{g/mL}$)	($\mu\text{g/mL}$)	($\mu\text{g/mL}$)	($\mu\text{g/mL}$)	($\mu\text{g/mL}$)	($\mu\text{g/mL}$)	($\mu\text{g/mL}$)	($\mu\text{g/mL}$)
Sea	0.0087	0.0015	0.5337	1.145	1877	3617	2035	8319
Town River	0.0417	0.0021	0.4130	1.273	833.0	128.2	477.2	512.2
Village River	0.1001	0.0035	0.2971	1.237	268.3	8.154	110.3	55.85
Treated sewage	0.1013	0.0022	0.3111	1.465	591.5	212.0	485.6	278.6
Untreated sewage	0.033	0.0075	0.7000	1.979	677.7	245.0	487.5	278.6

Major elements found in water; Ca(II), Mg(II), Na(I) and K(I) also did not affect the recoveries of Ni(II) using the IIP.

7.12 Analysis of Soil samples

All soil samples were complex as estimated from the ratios evaluated with the digested and undigested samples (as shown in Tables 13 and 14). EF was found to range from 27 to 40.

Table 13

EFs of Ni(II)-DMG IIP in soil samples (n=3).

Type of soil sample	^a Ni(II) conc. value in the sample (µg/mL) (digested)	^b Ni(II) conc. value got without digestion (µg/mL)	^c Ni(II) conc. value got when using Ni(II)-DMG-IIP (µg/mL)	EF*	Ratio (b/a)
Loam A	0.3909	0.0156	0.4286	27	0.04
Loam B	0.4571	0.0183	0.5178	28	0.04
Sand	0.0342	0.0010	0.0402	40	0.03

*EF was calculated as; $\frac{c}{b}$.

Table 14

Composition of the soil samples (n=3).

Sample	Ni(II) (µg/mL)	Co(II) (µg/mL)	Cu(II) (µg/mL)	Zn(II) (µg/mL)	Na(I) (µg/mL)	K(I) (µg/mL)	Ca(II) (µg/mL)	Mg(II) (µg/mL)
Loam A	0.1076	0.0625	0.0770	3.432	8.899	90.68	399.0	54.20
Loam B	0.0964	0.0915	0.0770	4.820	9.332	92.95	280.6	59.04
Sand	0.033	0.0074	0.8033	3.113	30.25	17.43	5316	86.52

Sand was less complex than loam soils A and B but had high concentrations of Cu(II) than Ni(II) however the recovery of Ni(II) was still high; 98 and 99% for spiking at 5 and 10 µg/mL respectively. The soil samples had higher concentrations of Zn(II) than Ni(II) and loam soil B had the same concentration of Ni(II) as that of Co(II) but the recoveries of the Ni(II)-DMG IIP was 100%.

7.13 Analysis of mine tailing samples

The recoveries of Ni(II) from mine tailing samples were high (99%) considering the high background concentrations of Ca(II), Mg(II), K(I), Na(I), Cu(II) and Fe(II) that were present in the sample (Tables 15 and 16). This is especially for Fe(II) and Cu(II) which are also heavy metals. The matrix complexity of the mine tailings is simpler than that of soil samples as estimated from the ratio of Ni(II) concentration

values got with and without digestion. In addition, the amount of Co(II) which competes severely with Ni(II) is low [169,173-174]. Therefore this Ni(II)-DMG IIP can be successfully used to trap Ni(II) from mine tailings. EF was found to be 2.

Table 15

EF of Ni(II)-DMG IIP in mine tailing samples (n=3).

Type of sample	^a Ni(II) conc. value in the sample (µg/mL) (digested)	^b Ni(II) conc. value got without digestion (µg/mL)	^c Ni(II) conc. value got when using Ni(II)-DMG IIP (µg/mL)	EF*	Ratio (b/a)
Mine tailing	13.53	12.46	21.06	1.69	0.92

*EF was calculated as $\frac{c}{b}$.

Table 16

Composition of mine tailings (n=3).

Ca(II) (µg/mL)	Mg(II) (µg/mL)	K(I) (µg/mL)	Na(I) (µg/mL)	Co(II) (µg/mL)	Cu(II) (µg/mL)	Fe(II) (µg/mL)	Ni(II) (µg/mL)	Pd(II) (µg/mL)	Zn(II) (µg/mL)
12607	2595	612.6	442.9	0.837	10.12	246.28	13.53	1.75	1.08

CHAPTER 8

8.0 CONCLUSIONS AND FUTUTRE WORK

The synthesis of a Ni(II)-DMG IIP was carried out successfully as the polymer was optimised for pH, time and mass for the selective determination of Ni(II) from other closely related metal ions in complex matrices. The uniform design experimental method was successfully applied to optimise Ni(II)-DMG IIP in terms of the molar ratios of crosslinker to monomer, monomer to template, template to ligand and the amount of porogen with less number of experiments performed. Compared with the initiator that was optimised by the conventional method, the uniform design experimental method is efficient and effective. It is our observation that most imprinting studies do not report optimisation studies probably because of their long, tedious and time consuming nature. However, this study suggests that the uniform design experimental method is probably a more convenient and reliable method for optimising ion imprinting polymerisation process.

High Ni(II) recoveries with good % RSDs were obtained in the presence of closely related cations like Co(II), Cu(II), Zn(II), Pd(II) and Fe(II). Low LOQ and LOD, short contact time required for rebinding of the Ni(II), short time required for preparation of the IIP, lower volume/mass of reagents used to prepare the IIP, simplicity of the synthesis of the IIP which was done with cheap reagents, good EFs, very low interference from closely related metal ions and small polymer mass to solution volume required for optimal uptake of Ni(II) are some of the good characteristics that the polymer offered. The Ni(II)-DMG IIP was assessed by analysing aqueous and soil certified reference materials and the results were satisfactory. The Ni(II)-DMG IIP was used to determine Ni(II) in sea, river, sewage water and soil samples where good recoveries were also achieved considering the complexity of the matrices and concentrations of other metals. The Ni(II)-DMG IIP was then successfully used to trap Ni(II) ions from mine tailing samples and good recoveries were obtained. Though the matrix of the mine tailing samples were simpler than predicted, as estimated by high ratio of digested to undigested sample, the composition of different

metals showed the need of sample preconcentration methods such as the one offered by this method.

From the results presented in this thesis, the Ni(II)-DMG IIP offers a good opportunity to be used as sorbent in solid phase extraction of aqueous, soil and mine tailing samples. Özkütük et al. [117] and Kugimiya et al. [118] designed an ion imprinted polymer for the preconcentration of phosphate ion which is a major plant nutrient. This shows the important use of ion imprinted polymers in agriculture related applications. Therefore, more work should be done to use this Ni(II)-DMG IIP as a sorbent in SPE which is the next aim of the work. The performance of Ni(II)-DMG IIP can be further explored by electrospinning the polymer to see if the binding sites are available after the polymer has been electrospun. This will take advantage of the surface area to volume ratios that are offered by electrospun nanofibres.

CHAPTER 8

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