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Research Article

Removal of Ni(II) Ions from Aqueous Solutions Using Ion Imprinted Polymer Prepared from Dual Vinyl Monomers

¹Vusumzi Emmanuel Pakade, ¹Solomon Motsisi Monageng and ²Nikita Tawanda Tavengwa

¹Department of Chemistry, Vaal University of Technology, Private Bag X 021, 1900 Vanderbijlpark, South Africa

²Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, Private Bag 3, Johannesburg 2050, South Africa

Abstract

Objective: The aim of the study was to selectively remove and pre-concentrate nickel(II) ions from aqueous solutions using ion imprinted polymers. **Methodology:** Ion imprinted polymers (IIPs) were prepared by forming a ternary complex of nickel(II) ion with acrylamide and 1-vinylimidazole as co-monomers in porogenic methanol. Polymerization was then effected by addition of ethylene glycol dimethacrylate as a cross-linker and 1,1-azobis(cyclohexanecarbonitrile) as initiator. About 5 M HCl solution was used as a leachant for the removal of the nickel(II) ion template from the IIP particles. Similarly, control polymer (CP) material was prepared but the template inclusion was omitted. The synthesized polymer particles were characterized by Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscope (SEM) and Brunauer Emmett Teller (BET) analysis. **Results:** The optimum pH for quantitative removal was 4, mass of the IIP sorbent was 40 mg, contact time was 10 min and the optimum concentration was 20 mg L⁻¹. The pseudo-second-order rate modelled the kinetic data better implying a chemisorption type of interaction between the imprinted polymer and Ni(II) ion. Based on the correlation of determination (R²>0.9), the Langmuir isotherm model, which implies monolayer mechanism was the best. **Conclusion:** The prepared IIP demonstrated superior potential on removal of Ni(II) ions from aqueous solutions compared to its corresponding CP.

Key words: Ion imprinted polymer, Ni(II) pre-concentration, selectivity, adsorption, removal, aqueous solution, isotherms, kinetic model, vinyl monomers, enrichment factor

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Corresponding Author: Vusumzi Emmanuel Pakade, Department of Chemistry, Vaal University of Technology, Private Bag X 021, 1900 Vanderbijlpark, South Africa Tel: +27 16 950 6629

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Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Nickel is used by a wide variety of industries including plating and cadmium-nickel battery, phosphate fertilizers, mining, pigments, stabilizers, alloys and it finds its way to the aquatic environment through wastewater discharged from these industries¹. In its trace levels, nickel is an essential element needed by the body to enhance insulin activity, among other functions, through enzyme activation². However, exposure to higher concentrations of nickel can have detrimental effects to the organisms and human health due to its known toxicity and carcinogenicity^{3,4}. Skin-eczema in women is one such detrimental disorder caused by excessive amounts of nickel in the body^{3,4}. Of concern are the recent discoveries of presence of nickel in living organisms⁵ as well as foodstuffs such as eggs and vegetables⁵. Hence, calling for a development of more precise analytical tools and selective adsorbents to determine nickel ion from various samples.

The determination of trace nickel ion concentrations in the environment is encountered with difficulties such as sample matrix problems owing to complexity of such samples⁶. Therefore, selective pre-concentration, determination and removal of nickel ion from complex samples require special attention⁷. Ionic imprinted polymeric sorbents have received wide attention over the past decades due to their high selectivity and pre-concentration properties^{3,8,9}.

Ion imprinted polymers (IIPs) arise because the polymer is synthesized in the presence of the template ion which upon its removal, pores complementary to the size, charge and shape of the ion template are generated¹⁰ which helps in the selective rebinding of target ions¹¹. Therefore, the selective recognition sites generated could preferentially rebind the template ion even in the presence of competing ions in complex matrix. The IIPs have been used for the removal of various metal ions from different sample matrices, for example U(VI)^{8,12,13}, Cd(II)¹⁴, Ni(II)¹⁵, Zn(II)¹⁶ and Pd(II)¹⁷.

The use of IIPs for the pre-concentration of metal ions from aqueous samples has shown superior advantages compared to traditional methods such as liquid-liquid extraction¹⁸, co-precipitation¹⁹, ion exchange²⁰, cloud point extraction²¹ and solid phase extraction²². The mentioned methods lack the required selectivity shown by IIPs of selectively pre-concentrating analyte metal ions without simultaneous extraction of contaminants, thus compromising recovery of the desired analytes. For the low concentration problem, high sensitive instruments than Atomic Absorption

Spectroscopy (AAS) have been suggested by Abbasi *et al.*¹⁵, but with the same instrument, detection of trace Ni(II) ions is possible following pre-concentration with IIPs.

The selectivity of IIPs is highly dependent on the strength of interactions between metal ion and the ligand used. Hence, research has focused on using different ligands (functional monomers) to improve the selectivity of nickel ions. These include morin and methacrylic acid⁹, aniline and formaldehyde⁶, dithizone and vinylpyridine²³, 2-hydroxyethyl methacrylate and vinylbenzoate²⁴, 4-vinylpyridine and 2-(diethylamino)ethylmethacrylate²⁵. In some of the mentioned studies, ligands that were not covalently bonded to the polymer matrix were used and these ligands maybe leached out during IIP regeneration studies.

In the present study, the combination of two functional monomers acrylamide-vinylimidazole covalently bonded to the polymer matrix was used. This combination proved to be selective for the nickel ions. Another challenge for the applying IIPs for the removal of Ni(II) ions are the low adsorption capacities^{23,25,26} reported, 1.3, 3.26 and 5.44 mg g⁻¹. This could be a limitation, particularly if the IIP is used at high concentration environment of nickel ion. Mainly, because adsorption sites at higher concentrations would be much lesser compared to the available pollutant ions, hence, the performance of the adsorbent will be affected by the initial concentration of metal ion²⁷. However, at low concentration the adsorption is not reliant on initial metal concentration because the number of available adsorption sites is greater than the adsorbate ions²⁷. Therefore, the present study attempts to synthesis Ni(II) ion IIPs with high selectivity and adsorption capacity. Factors which affect the sorption of the Ni(II) ions such as sample pH, contact time, initial concentration were investigated. To the best of our knowledge no study has reported on the use of acrylamide and vinylimidazole co-monomers for the synthesis of nickel ion imprinted polymers.

MATERIALS AND METHODS

Materials: Acrylamide, 1-vinylimidazole, ethylene glycol dimethacrylate (EGDMA) and 1,1'-azobis (cyclohexanecarbonitrile) (ACCN) were purchased from Sigma Aldrich (Johannesburg, South Africa), Ni(NO₃)₂•6H₂O, HCl and NaOH were purchased from Merck Chemical Co (Johannesburg, South Africa).

Atomic absorption spectrophotometer AA-7000 from Shimadzu (Kyoto, Japan) was used for measuring metal ion concentration in solutions. A Perkin Elmer Spectrum 400

FT-IR/FT-NIR spectrometer (Waltham, USA) was used to obtain the FTIR spectra of the synthesized polymers. Surface morphological information of the sorbent material was investigated using a FEI Quanta 200 SEM (FEI, Hillsboro, OR, USA). A Brunauer Emmett Teller (BET) instrument was used for surface area determination. The solution pH was measured by a 766 calimatic pH meter equipped with a Shott N61 pH electrode from Knick (Berlin, Germany). Ultrapure water obtained from LaboStar equipment by Siemens (Warrendale, Pennsylvania, USA) was used for preparing all solutions.

Preparation of stock solution: A stock solution of 1000 mg L⁻¹ Ni(II) was prepared from Ni(NO₃)₂•6H₂O. Standard stock solutions (1000 mg L⁻¹) of Cu(II), Cd(II), Mn(II), Pb(II), Cr(III), Co(II), Fe(II), Zn(II) and Cu(II) were prepared in 2% v/v HNO₃. Working stock and standard solutions were prepared from serial dilutions of stock solutions with ultrapure water. Solutions were stored in the fridge when not in use.

Preparation of Ni(II) IIP and NIP: The Ni(NO₃)₂•6H₂O (0.291 g, 1 mmol) was reacted with acrylamide (5 mmol) and 1-vinylimidazole (5 mmol) in 40 mL methanol for 30 min at room temperature. The EGDMA (18 mmol) and 100 mg of ACCN were added while the reaction vessel was kept on ice and purged with N₂ for 10 min. Polymerization was initiated by heating the reaction vessel contents in an oil bath at 80°C for 8 h. After polymerization, the solid product was crushed, ground and sieved between 45 and 90 µm screens. Unreacted monomers were removed by stirring the particles in methanol. Non-imprinted polymer (NIP) or control polymer (CP) was prepared following exactly the same procedure but the template was omitted. Once the IIP was prepared, the template Ni(II) was removed from polymer particles by successive stirring in 5 M HCl leaving free cavities complementary in size, shape and charge of the template.

Sorption studies: The effects of various parameters influencing adsorption of Ni(II) onto IIP and NIP were studied. Parameters investigated were the effect of pH (2-12), sorbent mass (10-100 mg), contact time (5-90 min) and initial concentration (5-25 mg L⁻¹). Briefly, 30 mL portions of 20 mg L⁻¹ Ni(II) solutions were prepared and the pH was adjusted from 2-12 using hydrochloric acid (0.1 M) and sodium hydroxide (0.1 M). Then 40 mg of Ni(II) IIP or NIP was added into each solution and stirred for 30 min. After the contact time elapsed, the contents in the reaction flask were filtered through a 0.45 µm membrane filter paper and the filtrate was analyzed for nickel concentration using atomic absorption

spectrometer. All experiments were conducted in duplicate. The extraction efficiency (E%) or removal efficiency (R%) was calculated using Eq. 1 where Ni(II) (enriched) and Ni(II) (initial) are the pre-concentrated and the initial Ni(II) concentration, respectively.

$$E (\%) = \frac{\text{Ni(II)(enriched)}}{\text{Ni(II)(initial)}} \times 100\% \quad (1)$$

RESULTS AND DISCUSSION

Synthesis and characterization of the polymer sorbents:

Figure 1 shows the synthetic scheme for Ni(II) imprinting process, where nickel ion was first reacted with two functional monomers (acrylamide and 1-vinylimidazole) in methanol porogen to produce a pre-polymerization ternary complex. The cross-linker and initiator were added and polymerization occurred as the contents were heated in an oil bath at 80°C to produce the unleached IIP. From Fig. 1, it was proposed that the ternary complex was formed by coordination bonding involving lone pairs of electrons from the oxygen and nitrogen atoms of the functional monomers (acrylamide and vinylimidazole). Following crushing and leaching of nickel ions from unleached IIP, leached IIP were produced and were used for studying the effects of adsorption. Several other studies in literature have followed the same synthesis protocol of bulk polymerization with some modifications^{23,24,28,29}.

Washing of template from the IIP was quantitatively monitored. The Ni(II) template was successively leached from the IIP particles with 40 mL of 5 M HCl and >98% of the template was removed. A fresh volume of 5 M HCl was used in each washing cycle. The amount of Ni(II) detected in each washing solution was less than the previous. The last washing at the 14th cycle had a <0.2 mg L⁻¹ Ni(II) detected and further leaching was stopped as long washing times are known to rapture the polymer matrix and thereby deforming the fabricated adsorption cavities³⁰.

Scanning electron microscopy was used to investigate the surface features of the nickel(II) IIP and compared its morphology with the control polymer (Fig. 2). The surface of the leached IIP was rougher than that of the NIP. This behavior demonstrated that the presence of Ni(II) template during synthesis and its subsequent leaching promoted the formation of fabricated cavities within the polymer matrix. Roughness of the leached IIP promoted accumulation of nickel ions into the adsorption sites. The absence of the inclusion of Ni(II) ions during synthesis of the NIP resulted in a completely flat morphology.

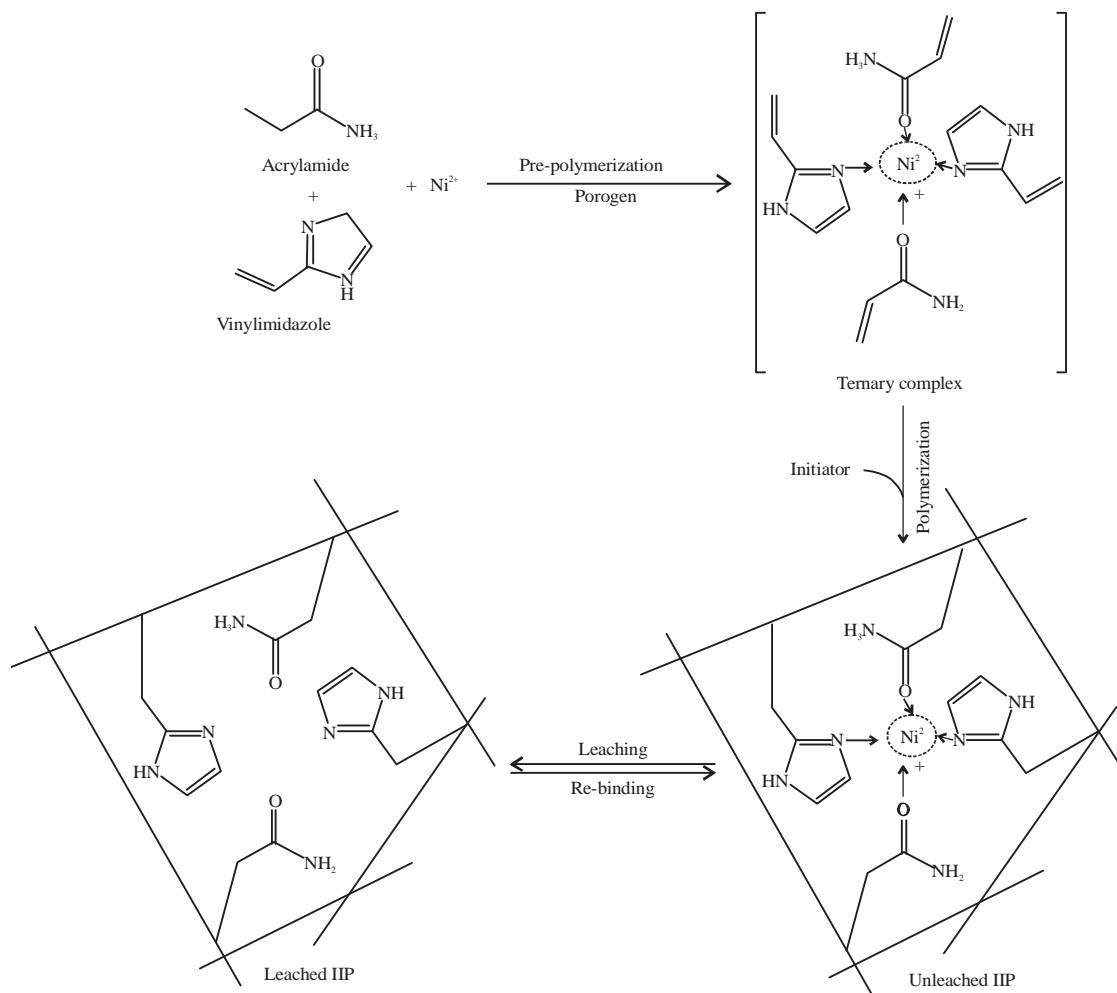


Fig. 1: Proposed schematic representative of the Ni(II) imprinting process

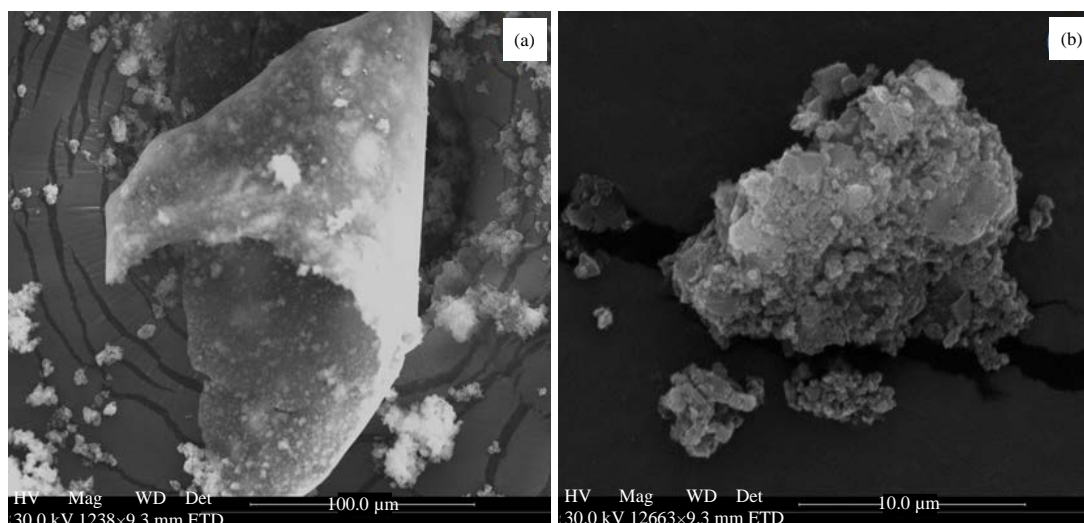


Fig. 2(a-b): SEM images of (a) NIP and (b) IIP

Energy dispersive x-ray spectroscopy (EDS) studies were carried out to determine the success of leaching of Ni(II) from the synthesized IIP. The EDS spectra of IIP material before (Fig. 3a) and after leaching (Fig. 3b) were obtained. Since the peaks for Ni at 0.8, 7.4 and 8.2 keV disappeared after leaching, it can be concluded that the template removal procedure was a success. The Ag and Au bands appeared in both spectra as these were used to coat the IIP particles mounted on an aluminum stub prior to analysis. In Fig. 3b, there were additional bands of Cl^- ions which were from HCl that was used for leaching out nickel from the polymer matrices.

The FTIR spectra of unleached IIP, leached IIP and NIP are shown in Fig. 4. It can be observed that all polymers displayed a similar backbone indicative of high levels of the EGDMA cross-linking reagent used³¹. In addition, the similarities in structural backbone of polymers implied that the leaching did not affect the polymeric network³², similar spectra of Fig. 4a and b. The Ni(II) bound to nitrogen atoms is evidenced by the presence of C=N stretching frequency at wave number 1636 cm^{-1} . Similar observations were found by Rammika *et al.*³³ from around 1638 cm^{-1} . The diminished nature of the band at 1638 cm^{-1} normally attributable to the

OH deformation (water) or C=C stretching from vinyl groups³⁴ could indicate that polymerization process was complete. It can also be seen that the presence of Ni(II) in the unleached polymers caused the appearance of a peak at 1500 cm^{-1} attributed to C=C/C=N stretching deformation³⁴. This was in contrast to the observation made by Tarley *et al.*³⁵ who observed a peak at 1487 cm^{-1} only after leaching the Pb^{2+} ions from IIP. The new peak was attributed to decreased rigidity of the imidazole ring resulting from leaching of Pb^{2+} ions³⁵. Nickel and lead interact with the imidazole ring differently. Furthermore, after leaching of the Ni(II) template from the polymer matrix with 5 M HCl, both bands at 1493 and 1638 cm^{-1} were absent. The similarity of the spectra of the leached IIP and the NIP (Fig. 4b, c) was indicative of the success of leaching out of the Ni(II) ion.

Effect of pH: Due to the presence of nitrogen and oxygen donor atoms in the functional monomers, the complex formation with metal ion is highly dependent on the pH of solution. As such, the effect of sample pH on the uptake of Ni(II) ions by IIP and NIP was studied at different pH values from 2-12 (Fig. 5). It can be observed that the removal

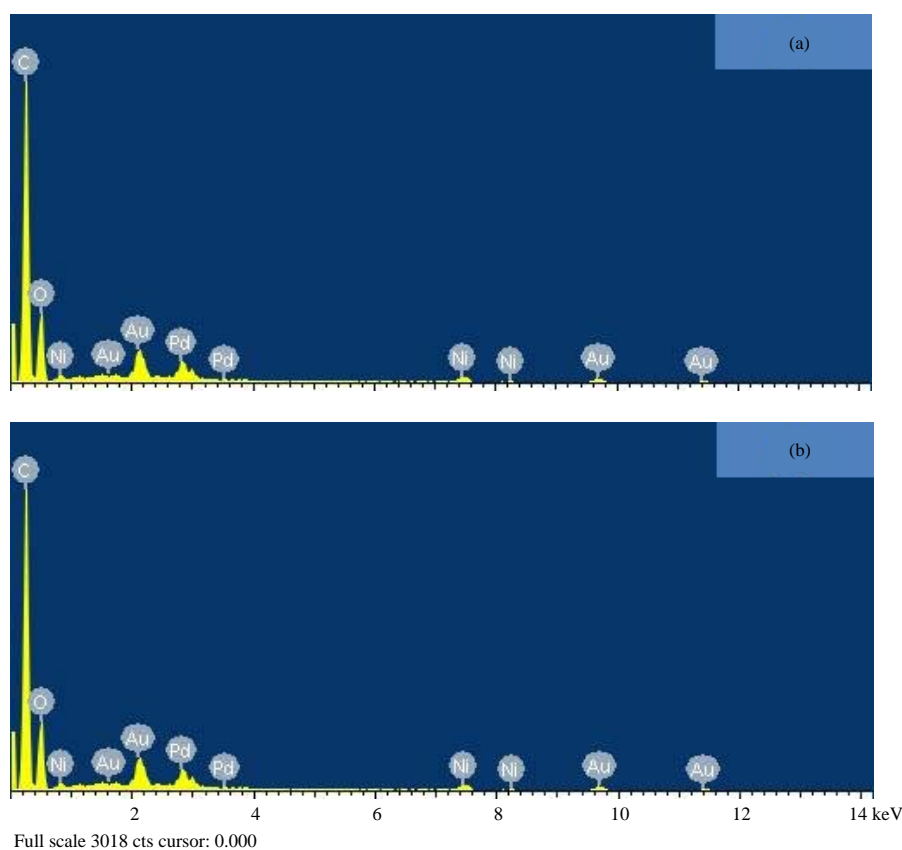


Fig. 3(a-b): EDS of (a) Unleached IIP and (b) Leached IIP

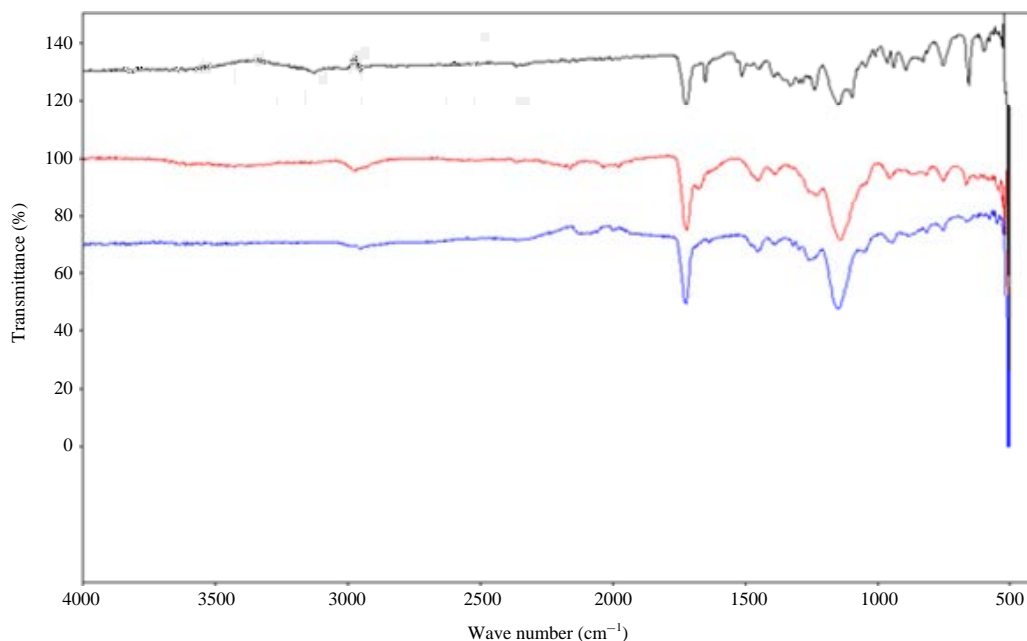


Fig. 4: FTIR of unbleached IIP, leached IIP and NIP

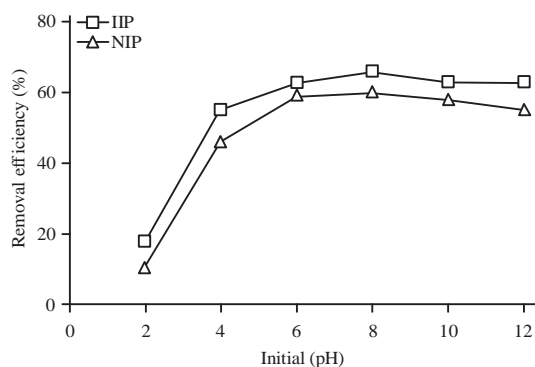


Fig. 5: Effect of initial sample pH on the uptake of Ni(II). Experimental conditions: Amount of IIP/CP 40 mg, initial concentration 20 mg L⁻¹, contact time 30 min and solution volume 30 mL

efficiency was low at acidic conditions, then increased as the pH was varied from pH 2-6. Maximal removal efficiency was reached at pH 6 and remained constant up until pH 12 an observation ascribed to the lesser concentration of H⁺ ions in solution. Singh and Mishra²⁴ also observed similar trend. Therefore, for subsequent experiments pH 6 was used. Even though there is a risk of nickel hydrolysis at high pH's, pH 8^{9,26} and pH 9^{15,36} have been used for the rebinding of Ni²⁺ ions by IIP. Both IIP and NIP showed similar trends but IIP removal efficiencies were much higher due to imprinting effects. Karimi *et al.*³⁷ pointed out that the acidity of the initial

solution in pre-concentration processes may have the following three effects on the metal ion adsorption by imprinted polymers: (a) Protonation of the binding sites by the hydrogen ions, (b) Competition for binding sites between H⁺ and metal ion and (c) The formation of hydroxide complexes or precipitates at basic conditions³⁸. In our case, it can be said that the lower removal efficiency at acidic pH was also attributed to the competition of binding sites by Ni²⁺ and H⁺ ions owing to the fact that H⁺ ions are more mobile than metal ions and are also present in higher concentration at low pH. There was also a possibility of the functional monomers (acrylamide and vinylimidazole) to be protonated resulting in a repulsion of Ni²⁺ ion by the positively charged surface.

Optimization of polymer mass: Figure 6 shows the results of the effect of varying the mass of the IIP and the corresponding NIP. Interesting to note that at lower masses of the polymers, there was roughly a linear dependency of the amount of Ni(II) adsorbed up until 40 mg. This could have been attributed to the availability of larger surface areas, in terms of the number of adsorption sites. However, after about 40 mg, the amount of Ni(II) adsorbed did not vary much. Possible explanations for this could have been the aggregation of the polymers as the mass was increased or that the ratio of adsorption sites to the metal ion concentration was higher. Therefore, 40 mg was found to be optimum and was used in subsequent experiments. Similar observations were made elsewhere⁹.

Optimization of time and kinetic modeling: In rebinding of metal ions by IIP, it is important that sufficient time be allowed because the binding sites are sometimes not on the surface of the sorbent^{39,40} but deep embedded on the polymer matrix. Therefore, it is vital that metal ions are given enough time to diffuse through the pores of the sorbent to the binding sites. To evaluate the effect of time on rebinding of Ni(II) ions onto IIP and NIP, solutions of Ni(II) ions (30 mL; 20 mg L⁻¹) at pH 6 were stirred in a batch mode for preset times (5-90 min). Optimum rebinding time was achieved after 10 min and this showed good accessibility (pores on the surface of the polymer as discussed for SEM) to the sorption sites as the sorption time was short (Fig. 7). The shorter contact times can also be explained by a known high affinity of Ni²⁺ ions for amino donors on acrylamide and vinylimidazole functional monomers. This has been the case with other nitrogen donor ligands used elsewhere for the adsorption of Ni(II)⁶. Sorption time as low as 2 min was reported by Panahi *et al.*⁶ when poly(aniline-formaldehyde) copolymer was used as a functional monomer for the nickel IIP preparation. For oxygen containing sorbents, sorption times as high as 30 min have been reported²⁴ but the combination of nitrogen and oxygen donors used in functional monomers has yielded¹⁵ shorter sorption time, 15 min. In this study, 10 min taken as the optimum and was used in subsequent experiments. With respect to other investigated imprinted polymer sorbents⁴¹, the IIP here was considered to have a fast mass transfer.

Data from the effect of contact time was fitted in kinetic models to evaluate the process of adsorption. Two most commonly used rate models; pseudo-first-order and pseudo-second-order were used in their linearized form of, Eq. 2 and 3, respectively.

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

where, k_1 (min⁻¹) is the pseudo-first-order rate constant of the adsorption process and k_2 (g mg⁻¹ min⁻¹) is the pseudo-second-order rate constant, q_t (mg g⁻¹) is the amount of Ni²⁺ adsorbed at any time t . The values of q_e and k_1 are calculated from linearised form of Eq. 2. The slope and intercept from a graph of t/q_t vs t were used to calculate q_e and k_2 , respectively. According to coefficient of determination (R^2) values and correlation between q_t and q_e in Table 1, the IIP was best described by the pseudo-second-order rate model. Likewise, the NIP was also best described by

pseudo-second-order model. This implied that adsorption of Ni²⁺ by IIP and NIP was more of a chemisorption type. Wang and Li⁴² also observed that both the NIP and IIP followed the same kinetic pseudo-second order rate model.

Optimization of concentration and adsorption modeling:

The influence of initial nickel ion concentration on its removal

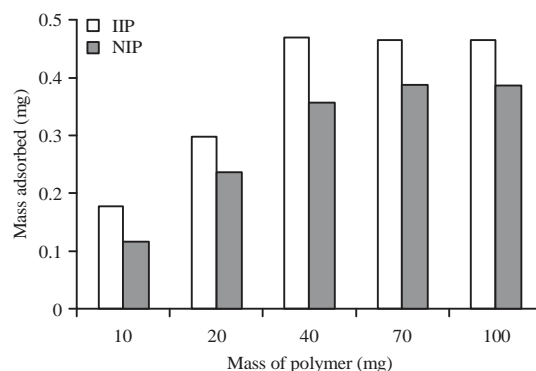


Fig. 6: Effect of polymer mass on the uptake of Ni(II). Experimental conditions: Solution pH 6, initial concentration 20 mg L⁻¹, contact time 30 min and solution volume 30 mL

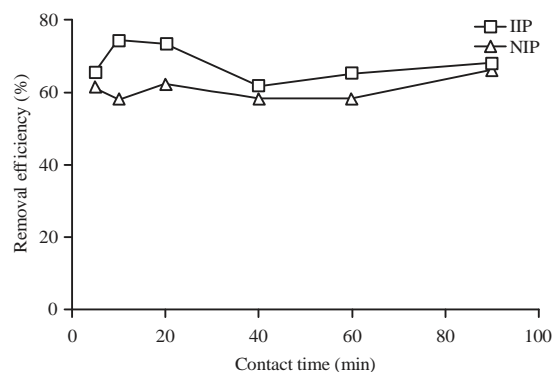


Fig. 7: Effect of contact time. Experimental conditions: Amount of IIP/CP 40 mg, initial concentration 20 mg L⁻¹, solution pH 6 and solution volume 30 mL

Table 1: Pseudo-first and second-order constants for adsorption of nickel onto the polymer sorbent

Kinetic model with parameters	IIP	NIP
Pseudo-first-order model		
k_1 (min ⁻¹)	0.026	0.056
q_e (mg g ⁻¹)	2.780	0.860
R^2	0.9833	0.6934
Pseudo-second-order model		
q_e (mg g ⁻¹)	5.010	1.800
k_2 (g mg ⁻¹ min ⁻¹)	0.219	0.066
R^2	0.985	0.981

IIP: Ion imprinted polymers, NIP: Non imprinted polymer

by IIP and NIP was studied by varying the concentration from 5-25 mg L⁻¹ while keeping solution volume (30 mL), pH 6 and contact time (10 min) constant (Fig. 8). At low concentrations, the removal efficiency for IIP was almost 100% but decreased as the concentration of Ni²⁺ ions in solution increased from 12-25 mg L⁻¹ due to the higher ratio of Ni²⁺ ions in solution to the number of adsorption sites on IIP surface. The same trend was observed for NIP but the removal efficiencies were much lower compared to IIP. The higher removal efficiencies demonstrated by IIP were attributable to the imprinting affect. The adsorption capacity (q_e) increased as the concentration was increased in both cases and the maximum adsorption capacity for IIP and NIP was 12.03 and 10.60 mg g⁻¹, respectively. Many studies have reported the same trend, where sorption capacity (mg g⁻¹) increases with increase in initial concentration while removal efficiency (%) decreases with increases in initial concentration^{6,15,23,41}.

In order to establish the interaction mechanism of nickel onto the polymer sorbent, the adsorption data was modeled

by two commonly used adsorption isotherms, the Freundlich and Langmuir models. The Langmuir considers a monolayer retention, while Freundlich considers sorption onto heterogeneous surfaces^{43,44}. The mathematical representations of these two models are given by Eq. 4 and 5, for the Freundlich and Langmuir, respectively. The Langmuir dimensionless separation factor (R_L), Eq. 6 was used to determine the favorability of the sorption process. The interpretation of R_L is as follows; $0 < R_L < 1$ favorable adsorption, $R_L > 1$ unfavorable, $R_L = 0$ irreversible and $R_L = 1$ linear adsorption⁴⁵. The constant n is the empirical parameter related to the intensity of adsorption, which varies with the heterogeneity of the material. When $1/n$ values are in the range $0.1 < 1/n < 1$, the adsorption process is favorable.

Table 2 revealed that the adsorption capacity of IIP, as measured by q_m was less than that of NIP. This difference could be attributed to the imprinting factor and pore blockages by un-extracted Ni²⁺ ions. The imprinting method creates pore sites, meaning that the nitrogen donor groups

Table 2: Constant parameters for the adsorption models for the adsorption of nickel onto polymer sorbent

Sorbent	Langmuir constants				Freundlich constants		
	q_m (mg g ⁻¹)	R_L	b (mg ⁻¹)	R^2	k_f (mg g ⁻¹)	n	R^2
IIP	13.6	0.0036	0.098	0.9080	5.12	2.75	0.9444
NIP	15.0	0.063	0.185	0.9996	2.91	1.75	0.9790

IIP: Ion imprinted polymers, NIP: Non imprinted polymer

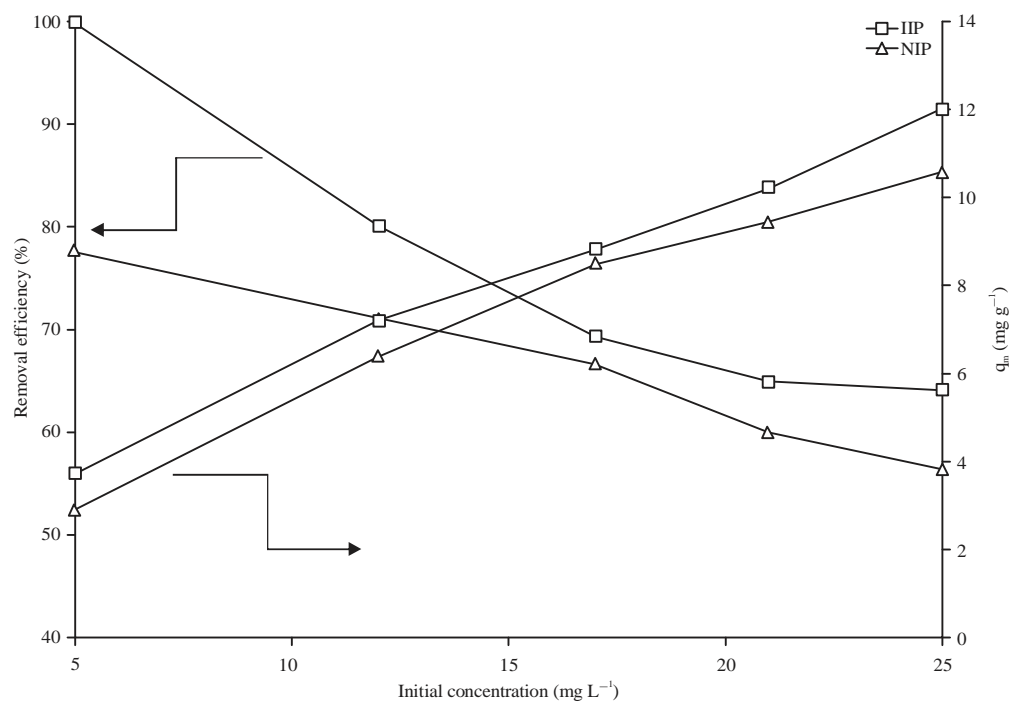


Fig. 8: Effect of initial concentration. Experimental conditions: Amount of IIP/CP 40 mg, solution pH 6, contact time 10 min and solution volume 30 mL

from the monomer are rearranged in a fixed direction toward the adsorption site. Whereas in the NIP, these nitrogen donors are freely available on the surface of the material and because of the high affinity of Ni^{2+} for nitrogen, many single point attachments can occur on the surface of NIP leading to higher adsorption capacity. The disadvantage is that, these are non-specific binding and in the presence of competing ions the adsorption of Ni^{2+} by NIP will be greatly affected. However, these values (13.6 and 15.0 mg g^{-1}) were close to the experimental values (Fig. 8) implying there was good modeling of the adsorption data by the Langmuir isotherm. The favorability of the model was further revealed by the R_L value of the IIP and NIP, 0.004 and 0.063, respectively. More so, the R^2 value of the NIP for the Langmuir was higher than that of the Freundlich isotherm (0.9996 vs 0.97). Though the R^2 value of the IIP for the Freundlich was higher than that of the Langmuir, it was observed that the k_f value was very low compared to that of the experimental (Fig. 8). Therefore, the sorption of $\text{Ni}(\text{II})$ ions by the synthesized polymers was modelled better with the Langmuir isotherm implying monolayer mechanism:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (4)$$

$$\frac{1}{q_e} = \frac{1}{q_m b C_e} + \frac{1}{q_m} \quad (5)$$

$$R_L = \frac{1}{1 + b C_0} \quad (6)$$

Selectivity studies: In order to investigate the effect of the presence of other cations, a selected multi-elemental solution of these interfering metal ions were added to 40 mL of solution containing 5 mg L^{-1} nickel ions. The competitors considered were $\text{Pb}(\text{II})$, $\text{Fe}(\text{II})$, $\text{U}(\text{VI})$, $\text{Co}(\text{II})$ and $\text{As}(\text{VI})$ with respective ionic radii of 87, 83.8, 109, 88 and 83 pm, respectively. Two closely related equations were used to explain the selectivity of the synthesized polymers. Equation 7 which gave the distribution coefficient (K_d) of a particular metal ion and Eq. 8 was used to calculate the selectivity (k) of the polymer towards Ni^{2+} in the presence of the competitor ion (M^{n+}). The extraction efficiency was calculated by using the previously defined Eq. 1. It was concluded that the prepared imprinted polymer had a high selectivity for $\text{Ni}(\text{II})$ ions. For the non-imprinted polymer, non-specific interactions were present and an indiscriminate uptake of the metal ions was observed. From the selectivity coefficients

obtained (Table 3) the quantitative selective removal of $\text{Ni}(\text{II})$ ions in the presence of the potential interfering ions was demonstrated. The selectivity of the imprinted polymers had strict configuration suitable for $\text{Ni}(\text{II})$ in terms of the nature, radius, charge and size of the template. The selectivity of IIP for $\text{Ni}(\text{II})$ ion was similar to other selectivity reported in literature^{9,15}.

$$K_d = \frac{M^{n+}(\text{in solution})}{M^{n+}(\text{enriched})} \quad (7)$$

$$k = \frac{K_d(\text{Ni}^{2+})}{K_d(\text{M}^{n+})} \quad (8)$$

Reusability of the IIPs: In order to evaluate the reusability of the imprinted polymers, nine adsorption-desorption cycles were performed. Figure 9 shows that the imprinted polymers were stable for up to the ninth binding/regeneration cycle without observing any significant decrease in the removal efficiency. Only 3.4 and 6% loss of extraction efficiency were recorded for the IIP and NIP, respectively. These results

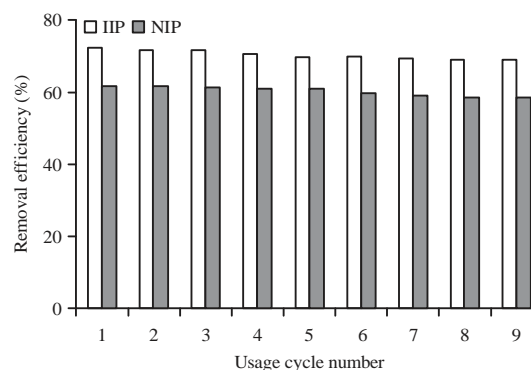


Fig. 9: Reusability of the imprinted polymers. Adsorption conditions: Amount of IIP/CP 40 mg, solution pH 6, contact time 10 min and solution volume 30 mL. Desorption conditions: Eluent 30 mL of 1 M HCl and contact time 5 min

Table 3: Extraction efficiency, distribution coefficient and selectivity of nickel and its competitor metal ions

Competitor ion	IIP			NIP		
	E (%)	K_d	$k \times 10^4$	E (%)	K_d	$k \times 10^4$
$\text{Ni}(\text{II})$	99.8	-	-	99.80	-	-
$\text{Pb}(\text{II})$	46.5	1.15	16	36.90	1.71	13
$\text{Fe}(\text{II})$	18.7	4.34	4	14.10	6.09	4
$\text{U}(\text{VI})$	6.7	13.90	1	2.53	38.50	0.6
$\text{Co}(\text{II})$	78.8	0.27	68	67.40	0.48	46
$\text{As}(\text{VI})$	98.3	0.02	1000	96.90	96.90	690

Table 4: Comparison of sorption capacities of different Ni (II)-IIPs

Functional monomer	q _m (mg g ⁻¹)	References
Dithizone and 4-vinylpyridine	1.30	Saraji and Yousefi ²³
Diphenylcarbazone and 2-vinylpyridine	3.26	Ashouri <i>et al.</i> ²⁶
2-aminoethyl-3-aminobutylmethyldimethoxysilane	5.44	Nacano <i>et al.</i> ²⁷
Dimethylglyoxime and 4-vinylpyridine	18.8 ⁸	Jiang and Kim ⁴¹
2-vinylpyridine and alizarin red S	73.20	Behbahani <i>et al.</i> ⁴⁶
Vinylbenzyliminodiacetic acid	12.00	Lenoble <i>et al.</i> ⁴⁷
N-(4-vinylbenzyl)-2-(aminomethyl)pyridine	4.90	Lenoble <i>et al.</i> ⁴⁸
Acrylamine and vinylimidazole	13.60	Present study

⁸Originally given as 320 mmol g⁻¹

indicated that the polymeric sorbents could be used repeatedly without incurring any significant loss in removal efficiency. Our results were similar to the nickel imprinted polymer prepared by Abbasi *et al.*¹⁵, that only had 4.9% lost in removal efficiency after 8 cycles of reusability.

Comparison studies: Table 4 shows that the sorption capacities obtained by different researchers varied widely. This can be attributed to the use of diverse functional monomers as shown in Table 4. There are also several factors that contributed to these differences like the synthetic approaches taken, porogenic solvents used, functional monomers, cross-linkers etc. However, the synthesized polymers had better Ni²⁺ uptake than other sorbents and can be used as an alternative sorbent. It can also be observed from recent literature^{47,48} that obtaining IIPs with higher sorption capacity (mg g⁻¹) is still a challenging task. Furthermore, the prepared IIP showed higher binding capacity when compared to recently published miscellaneous adsorbents such as polyacrylic acid hydrogel⁴⁹ (1.91 mg g⁻¹), *Moringa* pods⁵⁰ (5.53 mg g⁻¹) and water-cooled blast furnace slag⁵¹ (12.66 mg g⁻¹) for the removal of Ni²⁺ ion.

CONCLUSION

An ion imprinted polymer (IIP) for the removal of nickel(II) ions from aqueous solutions was successfully prepared with acrylamide and 1-vinylimidazole as co-monomers. It was concluded that 5 M HCl leachant exhaustively removed Ni(II) ions template from the polymer matrix. Influence of various parameters such as pH, contact time and concentration were studied and optimum values were used for the successive experiments. These results showed the produced IIP could be used for removal of nickel from aqueous solutions and its performance was superior to that of the control, NIP. For the kinetic and adsorption modeling, the pseudo-second-order rate and the Langmuir isotherm models were the best for modeling the kinetic and adsorption data, respectively. The adsorption capacity (13.6 mg g⁻¹) of the prepared IIP was

found to be higher than some of the adsorbents used in recent literature, suggesting that the produced IIP could be used in contaminated environments for prolonged times. Also, the prepared IIP showed superior selectivity towards Ni(II) ion from binary mixtures containing competitor ions like Pb(II), Co(II) and As(VI) ions.

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