Selective and Simultaneous Removal of Ni (II) and Cu (II) Ions from Industrial Wastewater Employing a Double Ni-Cu-Ion Imprinted Polymer

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Abstract— In this paper, a Ni-Cu ion imprinted polymer was synthesized and employed for the simultaneous removal of high levels of copper (II) and nickel (II) ions from wastewater. Bulk polymerization technique employing methacrylic acid, ethylene glycol dimethylacrylate, azobisisobutyronitrile as the functional monomer, cross linker and initiator respectively was used to synthesize the ionic imprinted polymer. Rigorous template removal was conducted employing increasing hydrochloric acid concentration ranging from 1.0 M to 10.0 M. The chemical characteristic of the prepared polymer was evaluated by employing Fourier Transform Infrared Spectroscopy. Adsorption parameters including contact time, pH and prepared polymer dosage were investigated and found to be 12 min, 7.0 and 665.5 mg/L respectively. The prepared Ni-Cu ions imprinted polymer showed excellent copper (II) and nickel (II) ions removal efficiency from wastewater as indicated by the 89.1% and 83.2% at n = 3 removal of total copper (II) and nickel (II) ions in the wastewater sample.

Keywords— Nickel, Copper, ion imprinting, imprinted polymer and adsorption.

I. INTRODUCTION

In recent years, researchers have devoted more time and resources investigating ways to solve the crisis of fresh water scarcity(Garcia & Pargament, 2015). Some of these studies have led to wastewater being recycled and reused(Amin, Alazba, & Manzoor, 2014). Wastewater treatment plants have been setup in most countries worldwide to treat and recycle wastewater. However, the effluents from these plants often contain excess toxic heavy metal ions that are detrimental to the environment(Barakat, 2011).

Human activities such as agriculture, irrigation, industrialization, urbanization and technological activities often release high levels (toxic) of heavy metal ions in the aquatic environment posing serious health hazard to the environment(Musyoka, Ngila, & Mamba, 2013).Usually, these toxic ions are stable under ambient conditions. They are not biodegradable and hence accumulate over time(Anuja Ashok Bhatt, 2015).

Although some of these ions are essential to life, their presence in high concentrations often results in serious health issues to the environment(National Research Council, 2000). Therefore, it is important that the level of heavy metal ions in the environment remain within acceptable levels as set out international monitoring bodies(Welna, Szymczycha-madeja, & Pohl, 2011).

Several methods and techniques have been employed by researchers to remove heavy metal ions from wastewater. For example, membrane assisted liquid extraction (MALE)(Boeva & Sergeyev, 2014), liquid–liquid extraction(Rao, Kala, & Daniel, 2006)(Shirkhanloo, Mousavi, & Rouhollahi, 2011), membrane filtration(Barakat, 2011); ion exchange(Ozcan, Satiroglu, & Soylak, 2010), biosorbents(Maina, Obuseng, & Nareetsile, 2016) have been employed to remove toxic heavy metal ionsfrom wastewater. As excellent as these methods have proven to be, they have some limitations such as high cost of reagents and equipment, time consumption, high energy consumption and selectivity(Othman, Abd-Kadir, & Zayadi, 2016)(EL-Sharif, Phan, & Reddy, 2014). In the quest to address the challenges faced with the available methods/techniques often used to remove toxic heavy metal ions form wastewater, the development of new technology; molecular imprinting technology, which has proven to be selective, time efficient, low cost, less/no energy

consumption have been proposed. Imprinted polymers exhibit high and specific affinity for a target ion(s)(Yungerman & Srebnik, 2006). They are nano-porous, which upon removing the imprinted ion (template ion) will specifically rebind to that ion based on size, shape and charge of the template ion.

In this paper, Ni-Cu ion imprinted polymer was synthesized for the simultaneous and selective removal of nickel (II) and copper (II) ions from wastewater. There have been lots of works that have been done demonstrating the extraction of a single ion at a time by ion imprinted polymer (IIP). In the need to reduce time, in this case, a double ion imprinted polymer was synthesized.

II. MATERIALS AND INSTRUMENTS

Reagents used were: analytical grade HCl (32%) acetonitrile (99.9%), Nickel (II) Nitrate Hexahydrate (97.0%), Copper (II) Nitrate Trihydrate ($\geq$ 98.0 %) purchased from ACE (Johannesburg, South Africa), Ethanol (99.9%) purchased from Skylabs (Johannesburg, South Africa), analytical grade Methacrylic acid, MAA (99%), α,α′-Azoisobutyronitrile, AIBN (98%), analytical grade HNO3 (50%), 1,10-Phenanthroline (99%), analytical grade Ethylene glycol dimethacrylate (98%), ethylenediaminetetraacetic acid, EDTA (98%), Mercuric Nitrate monohydrate (95%), elemental standard solutions used (1000ppm – Fe, Ni, Cu, Pb, Zn & Hg), 0.45 µm pore sized Whatman filter papers (Hardened Ashless Circles 45 mm) that was used for all filtering processes purchased from Sigma-Aldrich (Johannesburg, South Africa), and NaOH (97%) pellets, purchased from Rochelle Chemicals (Johannesburg, South Africa). Laval stainless steel sieve (5 – 20 µm) was purchased from Laval Lab (Minnesota, USA) was used for sieving the IIPs and NIPs.

A Varian 220FS Atomic Absorption spectrometer (California, USA) operated with air/acetylene was employed for the analysis of metal ions. A Nicolet iS10 FTIR spectrometer purchased from Thermo Scientific (South Africa) was used for characterization of the washed and unwashed IIPs as well as the NIPs.

Synthesis of Double-templated Ion Imprinted Polymer and Non-imprinted Polymer and Optimal Template Removal

The double-templated Ni-Cu- IIP material was synthesized by firstly preparing the binary complex of 1 mmol of Ni(NO3)2·6H2O, 1 mmol of Cu(NO3) 2·3H2O, 1.1 g of 1,10-Phenanthroline as complexing agent and 1 mL of methacrylic acid (MAA) as the ligand. After forming the complex,11 mL of ethylenediaminetetraacetic acid

(EDGMA), 0.24 g α,α′-Azoisobutyronitrile (AIBN) and 40 mL of ethanol/acetonitrile (2:1 v/v) was added to the complex mixture and stirred at 900 rpm for 30 min, after which, the mixture was degassed using a sonicator for about 15 min. The bulk polymerization was preceded at 60 ℃ for 12 h under continuous stirring at 600 rpm until monolith was formed. The obtained monolith was pulverized, sieved and dried in a hot air oven at 60 ℃ for 3 h. Unreacted materials were removed by employing optimized template removal technique(Stevens & Batlokwa, 2017). A non-imprinted polymer was also synthesized employing the same procedure, but without template ions; as a control material.

The template ions (nickel and copper ions) and other unreacted reagents were exhaustively removed from the prepared materials in three (3) separate steps. Firstly, the unreacted reagents were removed by refluxing the prepared powder with 50 mL of deionized water for a total of 10 hours in a 2 hour cycles. At the end of every cycle the prepared powder was recovered by centrifugation and dried in a hot air oven for 5 hour. Secondly, the obtained material was refluxed at 60 ℃ with a mixture of a 1:1 v/v of 1.0 M HCl and ethylenediaminetetraacetic acid (EDTA) for a total of 24 hours of 8 hour cycles. At the end of every 8 hour cycle prepared powder was recovered by centrifugation and dried in a hot air oven for 5 hour. Finally, the obtained powder was refluxed at 60 ℃ with 10.0 M HCl for a total of 8 hours of 2 hour cycles (employing same procedures as in the second step). The eluents from every step was evaluated by employing atomic adsorption spectroscopy to evaluate the level of template ions removed from the washed material(Stevens & Batlokwa, 2017). The last three eluent contained none of the imprinted ions; thus, indicating complete removal of the template ions from the prepared material.

After polymerization as described above, a forest greenish monolith (imprinted polymer) and a white monolith (non-imprinted polymer) were formed as showed in Figure 1 and 2 respectively.

Fig.1: Monolith of the Ni-Cu-IIP

Fig.2: Monolith of the non-imprinted polymer

Continuous washing of the greenish IIP powder resulted in the gradual colour change with each succeeding washing cycle. The loss of colour of the mixture to almost colourless from was an indication that indeed the template ions (print ions) were indeed washed off (removed) from the prepared Ni-Cu-IIP powder. The print ions, Ni(II) and Cu(II) are characterized by colour hence their removal by a successful template removal procedure must result in a product with less colour (colourless/white), thus the obtained product after filtering out the washing solvents was a whitish IIP powder as seen in Figure 3.
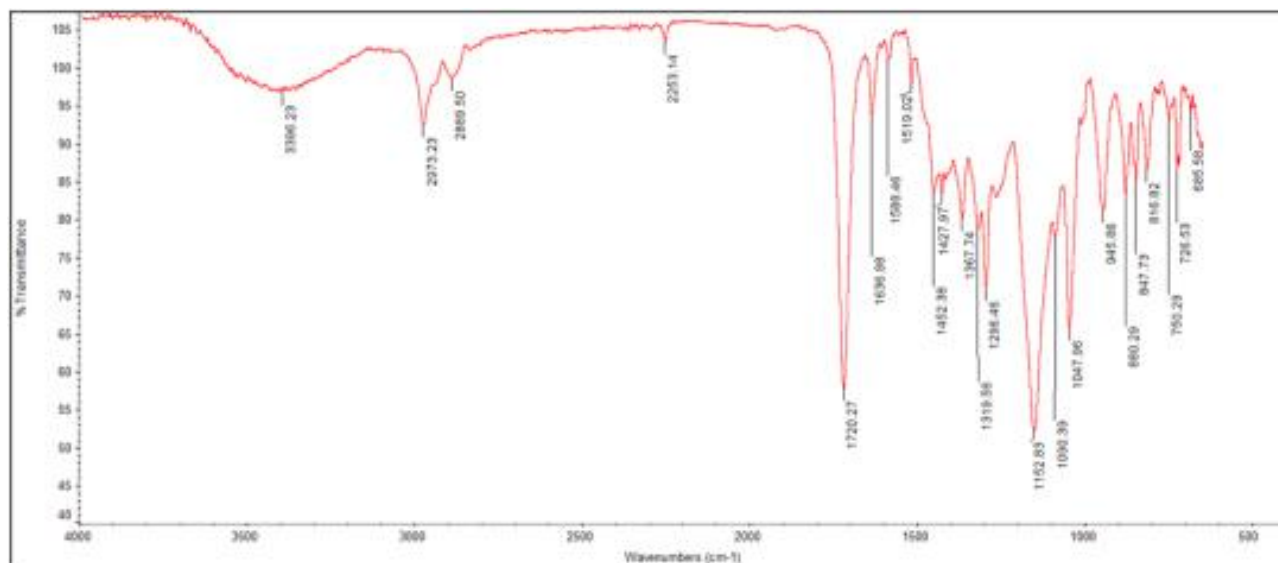

Fig.3: Washed Ni-Cu-IIP Powder
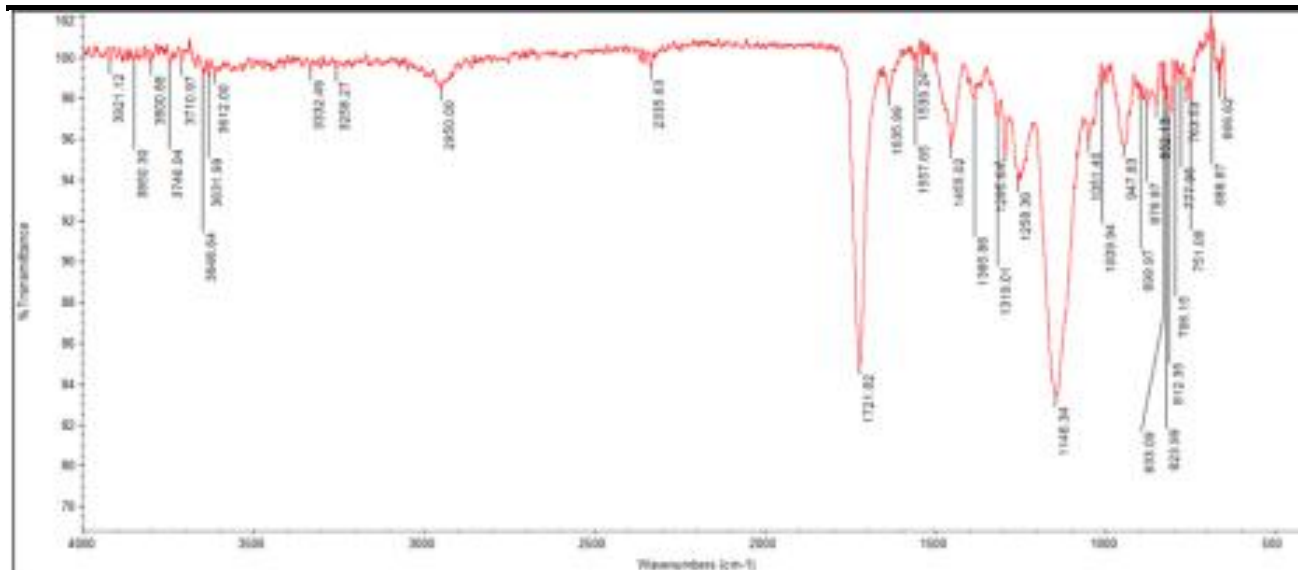

Fig.4: FT-IR of the unwashed Ni-Cu-IIP

Fig.5: FT-IR of the washed Ni-Cu-IIP

FT-IR Analysis

Fourier transform infrared (FTIR) spectroscopy was used to identify the functional groups (responsible for the metal uptake and bonding) possessed on the surface of the washed and unwashed IIP as well as the NIP. The FTIR spectra were recorded in the wavenumber range 500- 4000 cm^{-1} on a Nicolet iS10 Thermo Scientific FTIR. The data were collected at 2.0 cm^{-1} resolution, and each spectrum was a result of 256 scans(Rao et al., 2006).

Analysis using FT-IR enabled better understanding of the surface features of the powder and the evaluation of the optimal removal of template and unreacted materials as shown in Figure 4 and 5. Figure 4, shows the FTIR of the Unwashed Multi-templated Cu-Ni IIP powder. The band around 3400 cm^{-1} is very broad, indicating the presence OH groups from the likelihood of incomplete drying hence the presence of OH groups from water molecules within the structure. The two peaks at 2973 cm^{-1} and 2890 cm^{-1} are C-H stretch frequencies that belong to CH3 or CH2 groups from the backbone structure of the monomers. The large peak at 1720 cm^{-1} is the stretch frequency of a carbonyl group. There is a similar strong peak at 1153 cm^{-1}, which, together with the peaks at 3396 cm^{-1} and 1720 cm^{-1} evidence the presence of an ester. The minor peaks below 900 cm-1 are the finger print region.

Rebinding Studies

Contact Time

30 mg of the prepared Ni-Cu-IIP was put into 7 separate conical flasks and then 30 mL (5 mg/L equimolar) mixed standard solution of Ni (II) and Cu(II) was added. The mixture was shaken for 90 min, varying from 1 min, 10 min, 15 min, 30 min, 60 min, 90 min and 120 min after which the mixture was filtered using a 0.45 μm pore size Whatman 45 mm filter paper. The filtrate was then analyzed employing AAS.

The percentage removal of Ni (II) and Cu (II) ions by the prepared Ni-Cu-IIP increased with increase in contact time**.** When the washed Ni-Cu-IIP was applied as described, the optimal removal efficiency of the Ni-Cu-IIP was obtained within 12 minutes. Further increase in contact time did not show any further significant increase in the prepared material efficiency. The optimum time was as such, investigated to be 12 minutes as shown in Figure 6. Consequently, subsequent experiments employing the washed Ni-Cu-IIP were performed within 12 minutes of contact time.
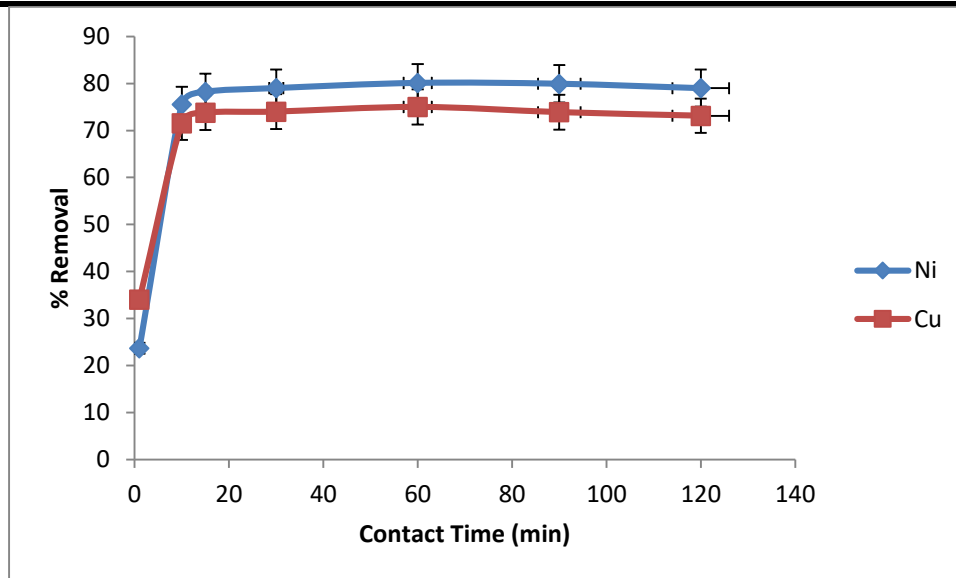
Fig.6: Optimization of contact time

pH

To evaluate the optimal pH require for optimal Ni (II) and Cu (II) removal by the prepared Ni-Cu-IIP, 30 mL of the 5 mg/L equimolar mixed standard solution was put into 7 different 100 mL conical flasks and the pH was adjusted to pH 2, 4, 6.5, 7.5, 8, 9, 10 respectively using 0.1 M HCl and 0.1 M NaOH. After which, 30 mg of the prepared Ni-Cu-IIP was added into each flask. The mixture was shaken for 12 min, then filtered with 0.45 μm pore size Whatman 45 mm filter paper. The filtrate was then analyzed employing AAS.

The lower the pH of a solution, the higher the presence of hydrogen ions, there if there are cations ions (heavy metal ions) present in the same medium, both the hydrogen ions and the cations will compete for binding sites on the adsorbents, with the hydrogen ions most likely to bind due to their chemistry. Meanwhile, at higher pH; ≥ 8.5, cations (heavy metal ions) often form precipitates or oxide with the hydronium ions in the solution. These phenomena were observed during the optimization of pH applying the synthesized Ni-Cu-IIP. It was observed that at a pH of 7.0, the prepared polymer exhibited its highest nickel and copper ions removal efficiency as shown in Figure 7.
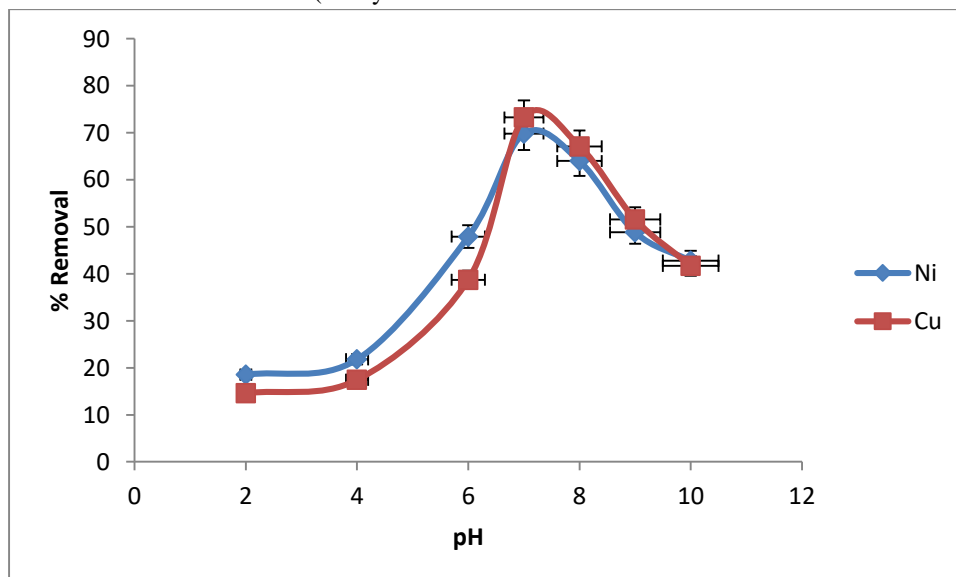

Fig.7: Optimization of pH

Consequently, subsequent experiments employing the washed Ni-Cu-IIP were performed at a pH of 7.

Ni-Cu-IIP Dosage

5 mg, 10 mg, 20 mg, 30 mg, 40 mg and 50 mg of the prepared Ni-Cu-IIPs powder were separately put into 6 different conical flasks. Then 30 mL of the 5 mg/L equimolar mixed standard solution at the obtained optimized pH was added to each flask and was shaken for the optimized time, and filtered off with a 0.45 µm pore size Whatman 45 mm filter paper. The filtrate was then analyzed employing AAS.

It was observed that by increasing the Ni-Cu-IIP dosage from 5 mg to 50 mg, the percentage removal of the selected ions was also increased. This was due to the adsorbent and selected ions concentration ratio. In other words, the more the Ni-Cu-IIP in the solution, the more binding sites present to allow the binding of the selected ions. With about 20 mg of the prepared material added, the highest optimal removal of the selected ions in the order of Cu > Ni was achieved as shown in Figure 8.
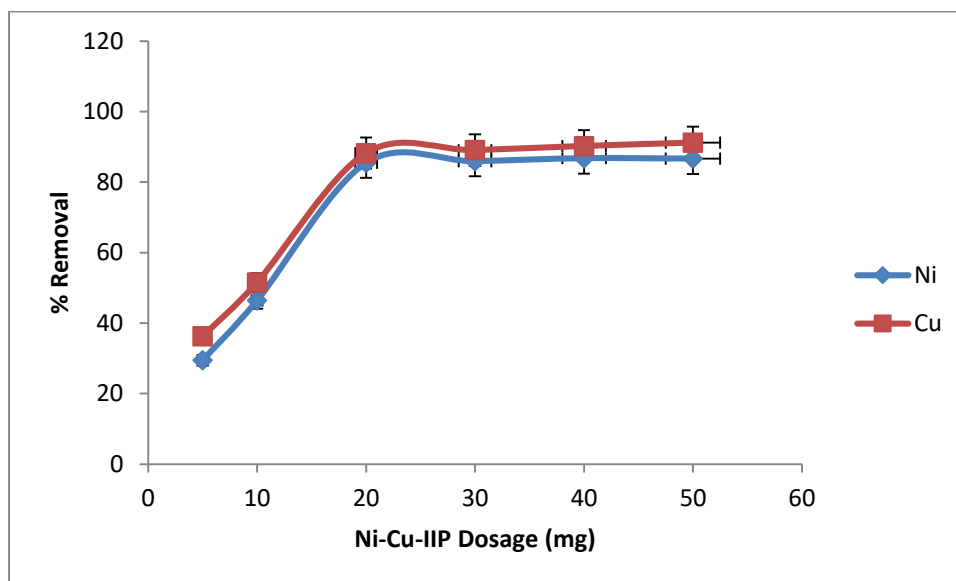

Fig.8: Optimization of Ni-Cu-IIP dosage

Consequently, subsequent experiments employing the washed Ni-Cu-IIP were performed employing 20 mg of the prepared Ni-Cu-IIP.

Selectivity Studies

Selectivity of both the prepared Ni-Cu-IIPs and non-imprinted polymer were investigated by employing either of the materials to a mixture of Fe(III), Fe(II), Ni(II), Cu(II), Pb(II) and Zn(II). An optimal amount of each of the materials was separately added to a 30 mL of the 5 mg/L standard mixture solution containing all of the ions at optimal conditions and shaken for optimal time, after which they were filtered employing a 0.45 µm pore size Whatman 45 mm filter paper. The filtrate was then analyzed employing AAS.

Pb (II), Zn (II) and Hg (II) were chosen as the competitor ions, due to their similarities in their chemistry and the fact that most often these heavy metals exist in the environment together, especially in industrial wastewater. It was observed that the percent removal of Ni (II) and Cu (II) by the prepared Ni-Cu-IIP was higher than that of Pb (II), Zn (II) and Hg (II) as shown in Figure 9.
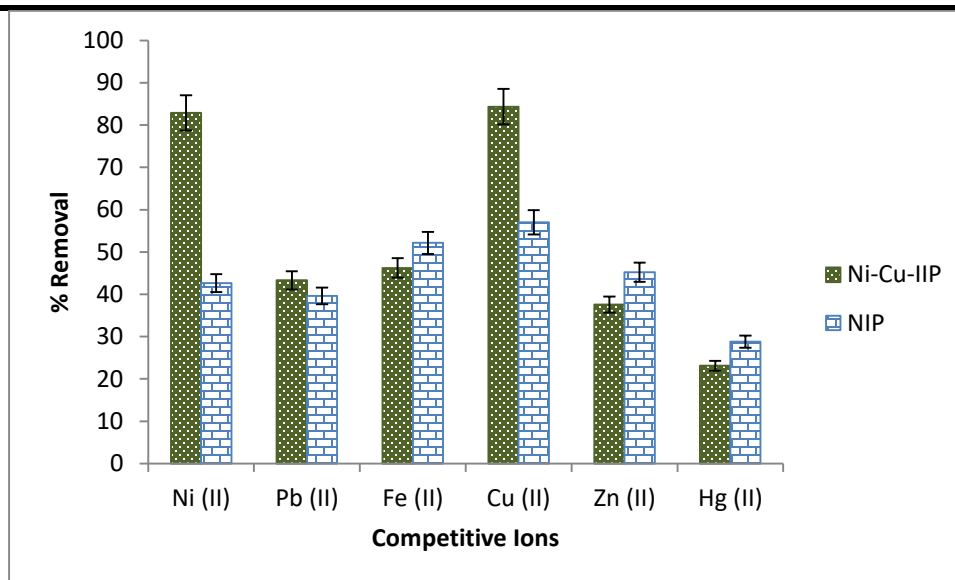
Fig.9: Selectivity studies

It was also observed that the NIP showed relatively similar removal percentage towards all of the ions. The non-selectivity of the NIP was due to the fact that it was not imprinted during the synthesis procedure. The selectivity of the Ni-Cu-IIP towards Ni (II) and Cu (II) was due to the imprinting of both ions on the polymer. By imprinting, one creates a binding site that will mostly rebind to an ion that is similar in shape, size and charge to the imprinted ion(s).

Evaluation of Ni (II) and Cu (II) in the Raw Wastewater Sample

100 mL of wastewater was pulled in five 250 mL conical flasks. 3 mL of an aqua regia solution of HNO_3 and HCl was added to the flask. The mixture was heated until the initial volume was reduced to approximately 2 mL(Mitra & Brukh, 2003). The obtained mixture was then filtered into a 50 mL volumetric flask and filled to the mark with deionized water. The filtrate was then analyzed employing AAS to determine the concentration of nickel and copper.

The selected heavy metals ions concentrations in the wastewaters sample were observed to be lower than the toxic levels which are set by waste water specification-bobs

93:2012 in Botswana and US. Therefore, to test the full capability of the prepared Ni-Cu-IIP, the sample was spiked with 15 mg/L of each of the selected ions.

Application of the Prepared Ni-Cu-IIP to the Raw Wastewater Sample

The prepared double-templated Cu-Ni-IIP powder was applied to a raw wastewater samples under optimal conditions for the selective and simultaneous removal of Ni (II) and Cu (II) ions.The experiment was done in triplicate. Percentage removal of the selected ions from the raw wastewater sample was obtained by employing:

$$\% \, Removal = \frac{Initial \; ion \; concentration - final \; ion \; concentration}{Initial \; ion \; concentration} \, X \, 100\%$$

The obtained optimized parameters were applied to the spiked wastewater samples. The percentage removal of the selected ions was determined employing AAS and using the above formula to obtain the values. Figure 10, showed Ni recorded a low percentage removal (83.23%) as compare to Cu (89.14%) with highest percentage removal.
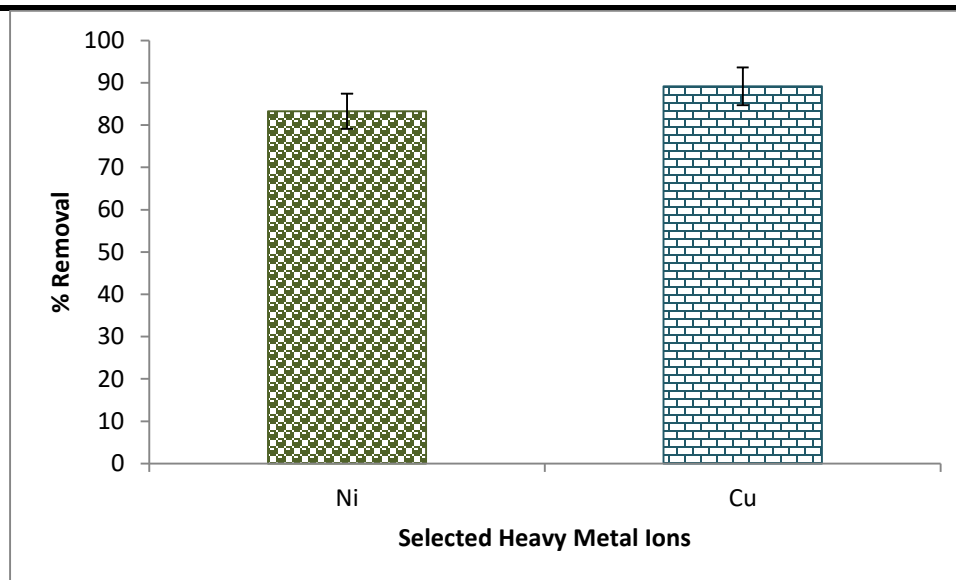
Fig.10: Ni-Cu-IIP percentage removal efficiency

III.   CONCLUSION

Double-templated ion imprinted polymers with Ni (II) and Cu (II) ions binding sites for the adsorptive removal of Ni (II) and Cu (II) from industrial wastewater was prepared in this study. The prepared Ni-Cu-IIP was synthesized using a non-covalent bulk polymerization approach and while it has demonstrated group selectivity towards two heavy metal ions; Ni (II) and Cu (II)), it also demonstrated the ability to differentiate between closely related structural analogues. The double-templated Ni-Cu-IIP was investigated for use as an extraction application as adsorbents and it was proved to be specific, selective and time efficient in recognizing and retaining the target ions.

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