

Selective removal of copper and cobalt from aqueous environment using new Cu(II) and Co(II) imprinted polymer and their determination by flame atomic absorption spectrophotometry

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ABSTRACT

Imprinted polymers of Cu(II) and Co(II) were prepared for the removal of copper and cobalt ions from aqueous samples. Cu(II) and Co(II) ion-imprinted polymer were synthesized via precipitation polymerization method using functional monomer, 2-mercaptobenzimidazole, and divinylbenzene and 2-azobisisobutyronitrile as cross-linker and initiator, respectively. Non imprinted polymer was also synthesized in the same way except for the addition of template ions. It was found that ion-imprinted polymer shows greater affinity than the non-imprinted polymer. Various parameters were optimized for the preparation of Cu(II) and Co(II) ion-imprinted polymers such as pH and amount of crosslinker, monomer, and solvent. The polymers were characterized using scanning electron microscopy, Fourier transform infrared spectroscopy, and thermogravimetric analysis techniques. The kinetic and adsorption study shows that binding of Cu²⁺ and Co²⁺ follows pseudo-second-order kinetic and fitted best to the Freundlich isotherm respectively. The polymers were reused up to five cycles with RSD of 4.32% and 3.54% for Cu(II) and Co(II). Cu(II) and Co(II) ion-imprinted polymer were used for the removal of Cu²⁺ and Co²⁺ ions from various water samples.

Keywords: Ion imprinted polymers; Cu(II); Co(II); Divinyl benzene; 2-mercaptobenzimidazole

1. Introduction

Copper (II) is a common contaminant added to the environment by the industrial discharges [1]. According to the United States Environmental Protection Agency, the contamination level of copper in safe drinking water is 1.3 mg L⁻¹ [2]. Although biologically it is essential in small concentrations for humans, however, it is non-degradable and can accumulate in several living tissues and cause various diseases such as hypoglycemia, gastrointestinal, and Wilson diseases when present in high concentration [3,4].

In blood serum, its normal level is from 700–1,500 ng mL⁻¹, it plays an important role in energy generation, metabolism, phytoplankton in the ocean, and for proper growth of plants. In addition, free copper ion produces atomic oxygen; a reactive species, which can damage DNA, protein, and lipid in the human system [5].

Cobalt is another very essential metal needed by humans in a small amount but in higher concentrations, it becomes toxic and carcinogenic [6]. It is released as a result of anthropogenic activities like metal production, mining, and plating. Its exposure to humans can cause severe

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damage such as diseases of liver and kidney, anemia, brain dysfunction, and in extreme cases death may occur [7].

Different conventional methods used for removal of Cu(II) and Co(II) are ion exchange, adsorption, electrolysis, membrane filtration, chelate precipitation, biosorption, evaporation and reverse osmosis. Some of these methods have a high cost, low efficiency, and sometimes limited selectivity [8–11]. A variety of various analytical techniques have been investigated for the determination of these heavy metals like anodic stripping voltammetry, atomic absorption spectrometry, high-performance liquid chromatography, and electro gravimetry [12,13]. The traditional method of chemical precipitation and extraction has also been carried out for these metal ions from the aqueous system, however, it produces a greater quantity of sludge which requires further treatment [14,15].

Besides these methods, some electrochemical methods were regarded as well-controlled, rapid, required fewer chemicals, and produced a small amount of sludge but sometimes may lack specificity and selectivity for the target metal ions. Search for an inexpensive and highly selective analytical method is still needed to be evaluated and worked out [16,17]. Molecularly imprinted polymer (MIP) is a versatile, convenient, and powerful technique. These are tailor-made polymeric materials with specific recognition capability for template molecule [18,19], wherein the presence of target molecule, functional monomer and cross-linker are copolymerized by covalent or non-covalent or by semi covalent interaction between functional monomer and template molecule. Its imprint is similar to lock and key, like a biological system such as receptors and hormones, antigens and antibodies, substrates, and enzymes [20–26]. Ion-imprinted polymerization (IIP) is a major branch of imprinting. Its preparation is similar to MIP but differs only is that IIP recognizes metal ion (target) after imprinting [27–31]. IIPs are highly selective polymeric material synthesized by complexation of functional monomer and target ion in the presence of cross-linker [32]. It has excellent advantages like mechanical, thermal and chemical stability, easy preparation, predetermined selectivity, and low cost [33–35]. In recent years both IIP and MIP have received more attention in drug analysis, biosensors, chemosensors, and catalysis [36]. The promising application of IIP as SPE preconcentration and extraction of metal ion from coexisting metal ion, which is much difficult to carry out with other methods is explored in this research.

Ligands used for IIP, in general, include 1,10-phenanthroline for Ag(II), dithiocarbamate for Sr(II), vinyl benzyl iminodiacetic acid for Ni(II), 4-(2-thiazolylazo) resorcinol for Hg(II), N,N'-o-phenylene bis(salicylideneimine) and 8-hydroxy quinoline for Al(III) and 8-acryloyloxyquinoline for Zn(II) [37–42]. The chelating agents used for Cu(II) are 5-methyl-2-thiozymethacrylamide, oleic acid, 4-(2-Pyridylazo) resorcinol, vinylbenzyliminodiacetic acid, poly(4-vinylpyridine) and for Co(II) are vinylbenzyl iminodiacetate [43–45].

With our knowledge of the existing literature on IIP for Cu(II) and Co(II), 2-mercaptobenzimidazole had not been used in the preparation of Cu(II) and Co(II)-imprinted polymer.

The current method is based on the fact that the use of 2-mercaptobenzimidazole as a functionalizing agent in the

IIP offers control and selective extraction of Cu(II) and Co(II) under specified pH conditions as discussed later in this manuscript. The 2-mercaptobenzimidazole monomer forms a strong and thermally stable complex with Cu(II) and Co(II) ions.

The main objective of this work was to remove Cu(II) and Co(II) ions from an aqueous solution with an economical and a simple method.

The present research work is focused on the synthesis of IIPs for solid-phase extraction of Cu(II) and Co(II) from aqueous samples. For this purpose, a complex of copper and cobalt were prepared, which were further co-polymerized in an organic solvent dimethylformamide in the presence of divinylbenzene and 2-azobisisobutyronitrile as crosslinker and initiator. Optimization of different parameters like concentration of monomer, crosslinker, metal-ligand ratio, and volume of porogen and pH were studied. Finally the IIPs were used for selective removal of Cu(II) and Co(II) from various water samples.

2. Experimental

2.1. Instruments

For desorption of metal ion from the imprinted polymers, a sonicator (ks300 KUM SUNG, Korea) was used. For the heating purposes, an electrical thermostatic water bath (Model DSB-1000T, Taiwan) and for the binding of metal to the ion-imprinted polymer, an orbital shaker (model OS-340C, Taiwan) were used. Thermogravimetric analysis (TGA) (Perkin Elmer, USA), scanning electron microscopy (SEM) (JSM 5910, JEOL, Japan) and Fourier transform infrared spectroscopy (FTIR) (Perkin Elmer, USA, spectrum version 10.5.1) were used for the characterization of polymers. Atomic absorption spectrophotometer (Perkin Elmer, USA, Analyst 800 Atomic Absorption Spectrometer) was used for the determination of Cu(II) and Co(II).

2.2. Chemical and reagents

Cobalt acetate (Sigma-Aldrich, China), copper sulfate pentahydrate (Sigma-Aldrich, China), 2-mercaptobenzimidazole (MBI) (Alfa Aesar company, Seol, South Korea), 2-azobisisobutyronitrile (AIBN) (Sigma-Aldrich, China), divinylbenzene (DVB) (Sigma-Aldrich, China), ethylene glycol dimethacrylate (EGDMA) (Sigma-Aldrich, China), dimethylformamide (DMF) (Sigma-Aldrich, China), nitric acid (Reidel de Haen, Germany), phosphoric acid (Riedel-de Haen), ammonia (Sigma-Aldrich, China), hydrochloric acid (Riedel-de Haen) and ethylenediamine tetraacetic acid (EDTA) (Fisher) were used, in this research work.

2.3. Preparation of standard solution

Stock solution (1,000 mg L⁻¹) of cobalt acetate and copper sulfate pentahydrate were prepared. For polymers washing, 0.1 N hydrochloric acid (36.46 M) was used. Britton Robinson buffer (BR) was prepared from phosphoric acid, boric acid, and acetic acid (0.04 M), and adjusted its pH with sodium hydroxide (0.2 M). Ammonia buffer was prepared by dissolving 7.1 g ammonium chloride and

57 mL ammonia in 100 mL flask and diluted with distilled water.

2.4. Preparation of Cu(II)-IIP and Co(II)-IIP polymer via precipitation polymerization

Preparation of imprinted polymers of Cu(II) and Co(II) was carried out in steps. A complex of Cu(II)-MBI and Co(II)-MBI was prepared. Copper sulfate (0.5 mmol) was dissolved in dimethylformamide (10 mL) through heating for 5 min and then MBI (0.5 mmol) was added to it as a functional monomer and the same procedure was repeated for cobalt acetate and MBI. The resulted in dark green color (copper complex) and blue color (cobalt complex) crystals were obtained and then used for the preparation of Cu(II)-IIP and Co(II)-IIP. In the second step, 40 mg AIBN (initiator) and 1.0 mmol DVB (cross-linker) were added to the complex solutions. To complete the polymerization process, the glass tubes (reaction tubes) were sealed and placed in a thermostatic water bath for 24 h at 70°C.

The prepared polymers were filtered and the template ion was leached out by extensive washing with HCl solution. The washing of the polymer was continued until the supernatant was found free of metal ions. The resulted polymer was dried, and used for further studies. The proposed schematic representation for the Cu(II)-IIP and Co(II)-IIP is shown in Fig. 1.

2.5. Procedure for binding study of Cu(II)-IIP and Co(II)-IIP

For the binding studies, 0.001 g of Cu(II)-IIP and NIP were taken in a plastic tube (15 mL), to this was added 10 $\mu\text{g mL}^{-1}$ of Cu^{2+} salt solution, stirred for 1 h and then filtered (performed in triplicate). Then by using the flame atomic absorption spectroscopy, the concentration of Cu^{2+} ion was determined. The concentration of metal ion bind to the IIP was calculated by Eq. (1). The same procedure was followed for Co(II)-IIP.

$$\% \text{ Binding} = \left[\frac{C_i - C_f}{C_i} \right] \times 100\% \quad (1)$$

where C_i = initial concentration of the Cu(II) and Co(II) solution (mg g^{-1}); C_f = Final concentration of the Cu(II) and Co(II) solution (mg g^{-1})

3. Results and discussions

3.1. Characterization of polymers (Cu(II)-IIP and Co(II)-IIP)

The prepared IIP of Cu^{2+} and Co^{2+} and NIP were characterized by FTIR, SEM, and TGA. A dried and powdered form of polymers were used for this purpose.

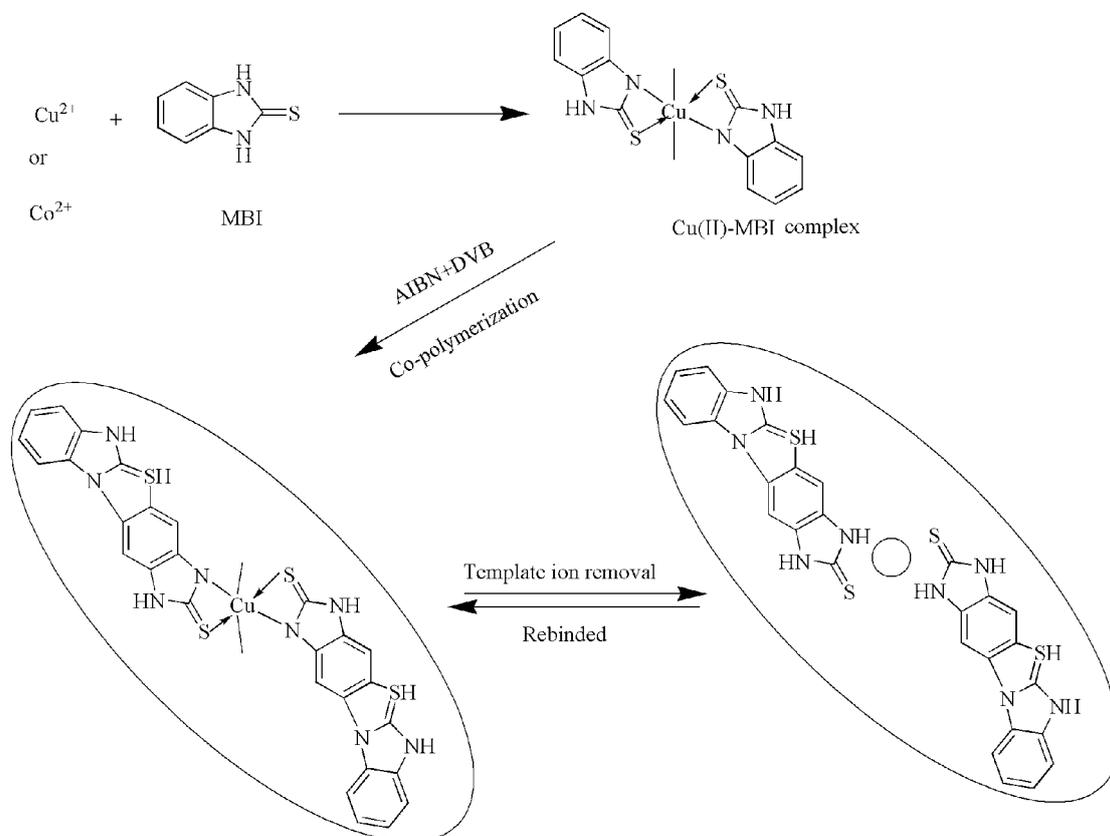


Fig. 1. Schematic representation of the proposed mechanism for the binding of Cu(II) and Co(II) to their respective ion-imprinted polymers.

The thermal stability of Cu(II)-IIP and Co(II)-IIP was evaluated using TGA (Fig. 2). The TGA plot of all polymers showed about 10% weight loss up to 300°C and then from 350°C to 800°C the polymeric chain was decomposed completely. Co(II)-IIP has a higher decomposition temperature than Cu(II)-IIP. Co(II)-IIP remained completely stable from 90°C to 350°C. The decomposition steps are 350°C, 416°C, and 484°C with 20%, 65%, and 99% weight loss respectively. The 20% and a further 45% weight loss at 350°C and 416°C may be due to the liberation of Co and Co-MBI complex respectively. Whereas the slow weight loss of Cu(II)-IIP from 300°C to 800°C in almost three steps (300°C, 366°C, and 550°C) may be attributed to the loss of metal ion alone then MBI and then DVB respectively.

The FTIR analysis of Cu(II)-IIP, Co(II)-IIP, and NIP were recorded by the KBr pellet method, respectively (Fig. 3). By comparing the IR spectra of IIP and NIP, a similar backbone was observed in the two sets of a polymer. In Cu(II)-IIP, Co(II)-IIP and NIP peaks ranging (700–1,500 cm^{-1}) were due to C–C vibration, with minor differences in % transmittance throughout the spectra (>95% for

IIP and <85% for NIP) due to the presence of metal ion in IIP. In both Cu(II)-IIP, Co(II)-IIP spectra, peaks in the range of 1,440.3 and 1,449.2 correspond to aromatic C–C bond. Peaks at 1,619 cm^{-1} and 1,651.5 cm^{-1} are the stretching vibrations of C=N, which is due to the presence of MBI. A peak at 3,076.3 cm^{-1} is due to the interaction of Cu^{2+} with MBI. The peaks at 2,925.7 and 2,923.02 cm^{-1} are due to the stretching vibration of $-\text{CH}_2$, representing the presence of DVB. The morphology of IIPs and NIP seem quite different from one another as shown in SEM (Fig. 3). The NIP is a visible threaded structure with uniform channels (cavities). Whereas, the morphology of Co(II)-IIP and Cu-IIP (Figs. 3a and b) shows nano-size particles arranged in an aggregated patterns.

3.2. Optimization of various parameters for the preparation of Cu(II)-IIP and Co(II)-IIP

MBI forms a complex with Cu^{2+} and Co^{2+} in DMF. The amount of MBI was investigated in the range of 0.5–2 mmol. It was concluded from the binding experiments

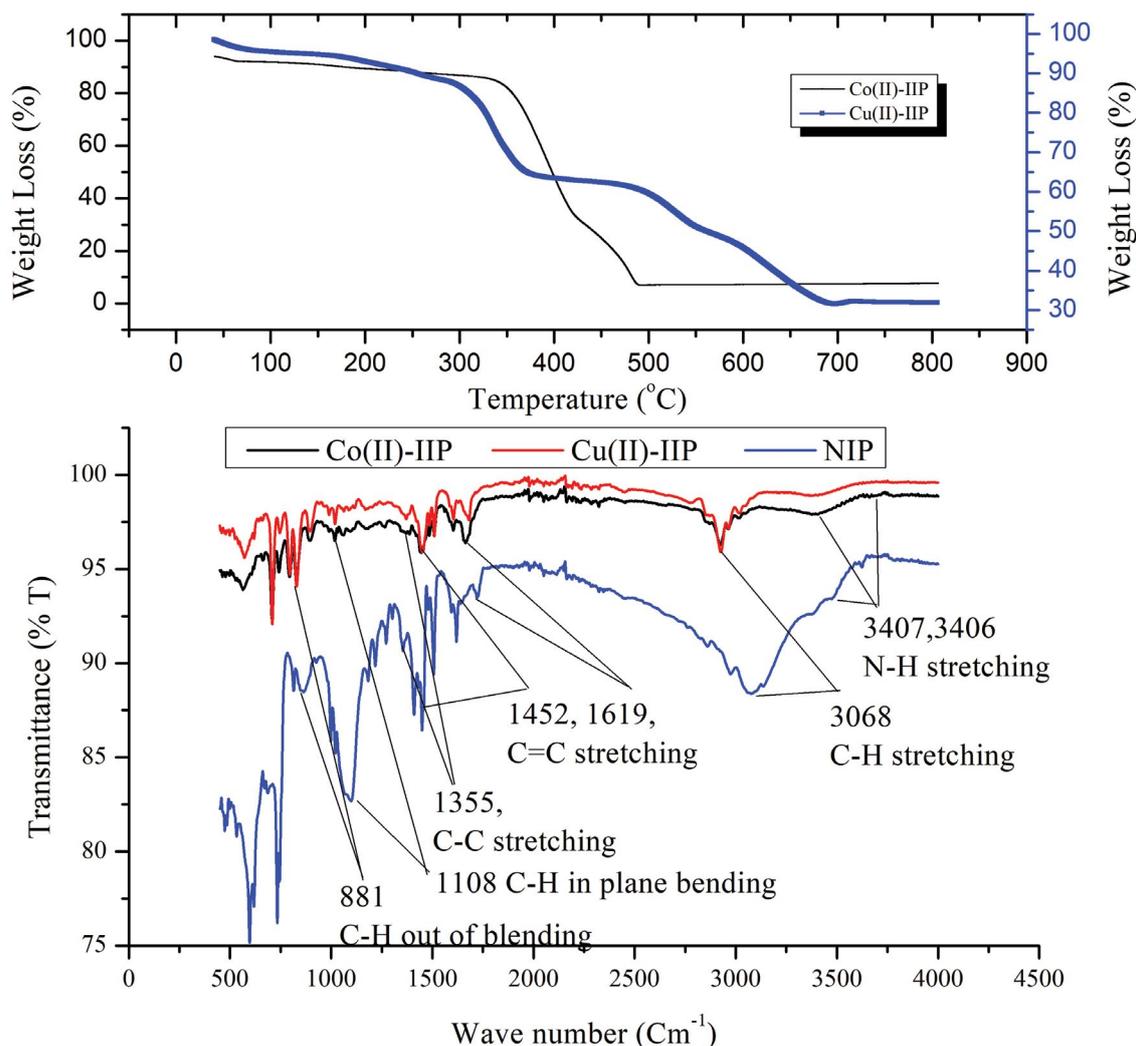


Fig. 2. TGA and FTIR of Cu(II)-IIP and Co(II)-IIP.

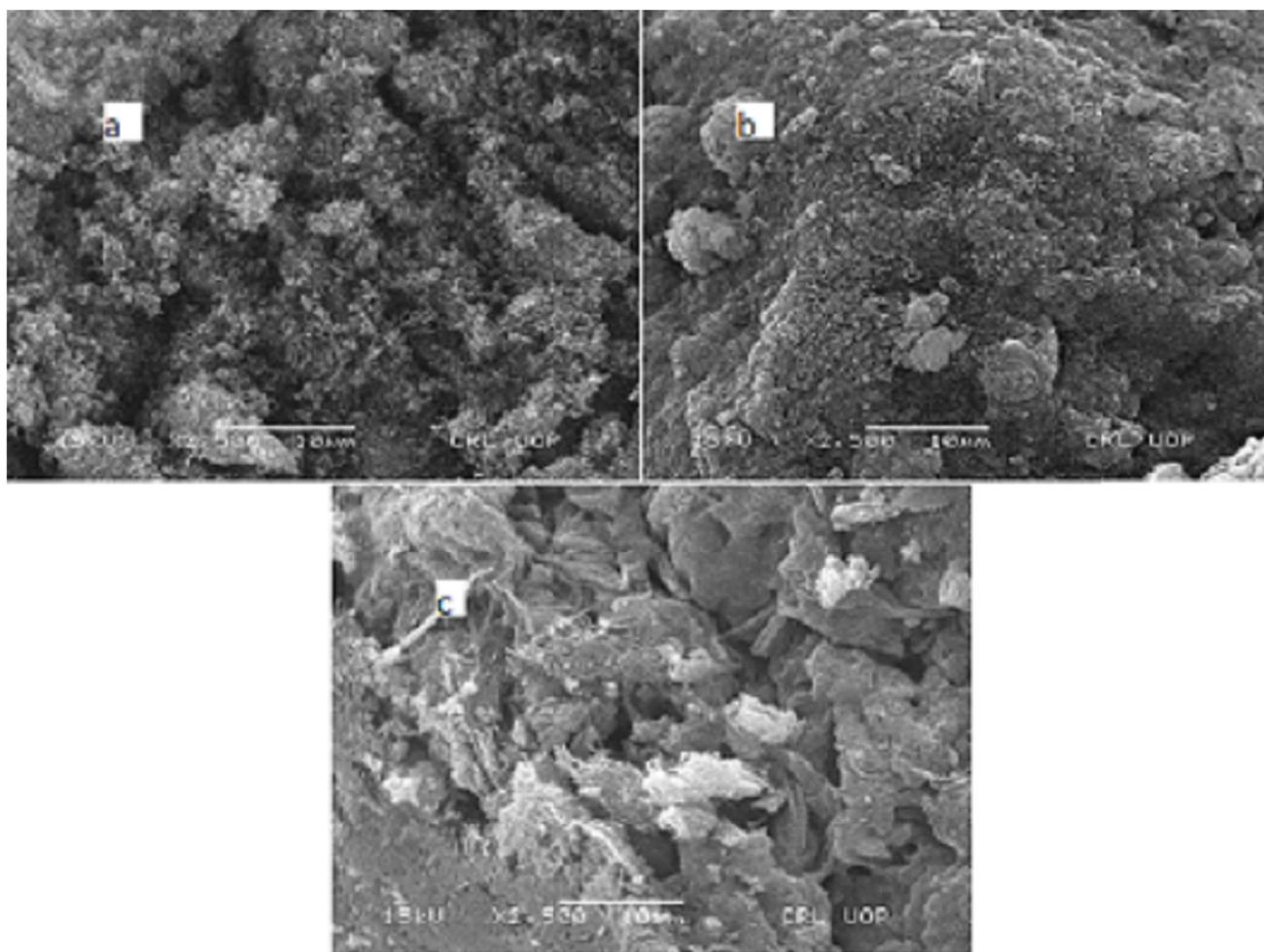


Fig. 3. SEM images of (a) Co(II)-IIP, (b) Cu(II)-IIP, and (c) NIP.

that 2 and 1.5 mmol were the optimized amounts for the preparation of IIP of Cu^{2+} and Co^{2+} respectively (Fig. 4) based on the difference in the binding capacity between the IIP and NIP.

Cross-linker amount was investigated in a range of 1 to 3 mmol, it was observed from the binding efficiency that 1 and 2 mmol were the optimized amount for Cu(II)-IIP and Co(II)-IIP preparation (Fig. 4). Crosslinkers such as ethylene glycol dimethacrylate, trimethylolpropane trimethacrylate, 1,6-hexanediol diacrylate, tripropylene glycol diacrylate, and divinylbenzene are reported for IIPs. The crosslinker, divinylbenzene was selected for this work based on its low polarity and interaction with the metal ions. Divinyl benzene has also been shown to have an increased loading capacity relative to ethylene glycol dimethacrylate, 1,6-Hexanediol diacrylate, trimethylolpropane triacrylate, and tripropylene glycol diacrylate. Polymers prepared using divinylbenzene as a crosslinker were shown to have a better binding of the analyte and lower non-specific binding than ethylene glycol dimethacrylate [46].

Solvent volume was investigated in the range of 5–15 mL. For the generation of cavities in the imprinted polymer, the solvent acts as a porogen. For the polymer formation, volume

less than 10 mL was insufficient for the adequate formation of cavities, in which the template cannot be attached properly due to the insufficient swelling of the polymer during its preparation, while volume greater than 10 mL was found enough for increased binding efficiency, and the maximum difference in % binding of IIP and NIP occurred, hence concluded that the optimized porogen volume was 12 and 15 mL for Cu^{2+} and Co^{2+} imprinted polymer respectively (Fig. 4).

Different metal to ligand (M:L) ratio of Cu^{2+} and Co^{2+} salts and MBI were investigated for the formation of Cu(II)-IIP, Co(II)-IIP and it was concluded from the binding experiment that 1:2 ratio of the M:L was the optimized ratio for the complex formation. MBI is ambidentate ligand having both nitrogen and sulfur groups. Both these groups are electron-donating groups, attached to Cu^{2+} and Co^{2+} ion from either side of attachment. Hence 1:2 ratio of M:L was optimized after performing the binding experiments (Fig. 4).

The effect of pH on the binding of Cu^{2+} and Co^{2+} to Cu(II)-IIP and Co(II)-IIP was investigated in the range from 2 to 10, and it was found that pH 8 resulted in maximum binding of Cu^{2+} and Co^{2+} (Fig. 5). Similar results were reported by Mosafiri et al. [47] where he described the maximum formation of a copper-MBI complex between pH 8–10.

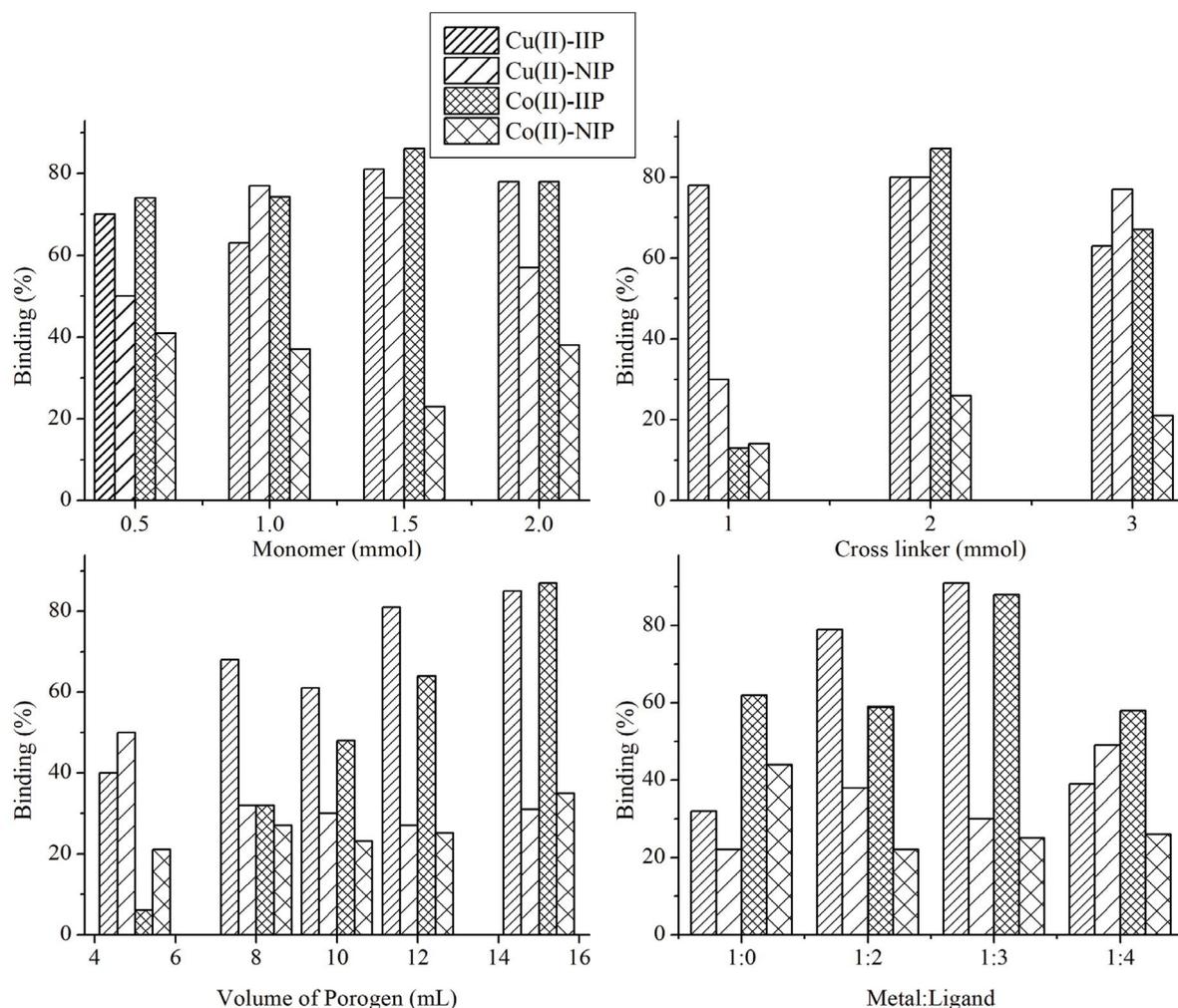


Fig. 4. Optimization of the amount of monomer, crosslinker, the volume of progen, and metal to ligand ratio for the preparation of Cu(II)-IIP and Co(II)-IIP and comparison of the IIP's with their respective NIP.

3.3. Amount of polymer

The amount of Polymer was investigated in the range of 5–16 mg. From the binding result, it was concluded that although both 5 and 10 mg showed maximum efficiency for binding at 5 mg, the binding capacity of Cu(II)-IIP and Co(II)-IIP was greater than their respective NIP (Fig. 5) possibly because the metal ion establishes an equilibrium with the occupied binding sites at these polymer amounts. At higher amounts of polymer, the adsorption–desorption becomes too rapid and results in decreased sorption/binding of the metal ion. Based on the maximum difference in the binding efficiency between IIP and NIP, 5 mg was selected as an optimum amount of polymer.

3.4. Binding study at various concentrations of metal ion solution

The binding behavior of Cu²⁺ and Co²⁺ on the polymer was investigated at a varying concentration of metal ion solution ranging from 25–200 mg L⁻¹, which illustrates that at all concentrations, the binding capacity of Cu²⁺ and Co²⁺ ions to IIPs was greater than its binding to NIP. Thus the

polymers can be used for binding of Cu²⁺ and Co²⁺ ions even at higher concentrations up to 200 mg L⁻¹(Fig. 5) establishing the fact that the available binding sites are sufficient for the metal ion in 5 mg of polymer. In addition, the sorption capacity may be due to disparity in cations radius and interaction enthalpy values.

3.5. Point of zero charge

The point of zero charge was investigated for Cu(II)-IIP, Co(II)-IIP, and NIP by observing the pH of the solution at the start of the experiment and then after 24 h. It was found that pH 5 and 4 are the point of zero charge for Cu(II)-IIP and Co(II)-IIP (Fig. 7). Beyond the point of zero charge of Cu(II)-IIP and Co(II)-IIP, the surfaces are negatively charged, and hence the binding of Cu²⁺ and Co²⁺ ions are by electrostatic attraction between the metal ions and the IIP's. The effect of initial solution pH on the metal ions sorption by the polymer was pH-dependent (Fig. 5). It was observed that the uptake of metal ions increased as the solution pH increased until the maximum uptakes were

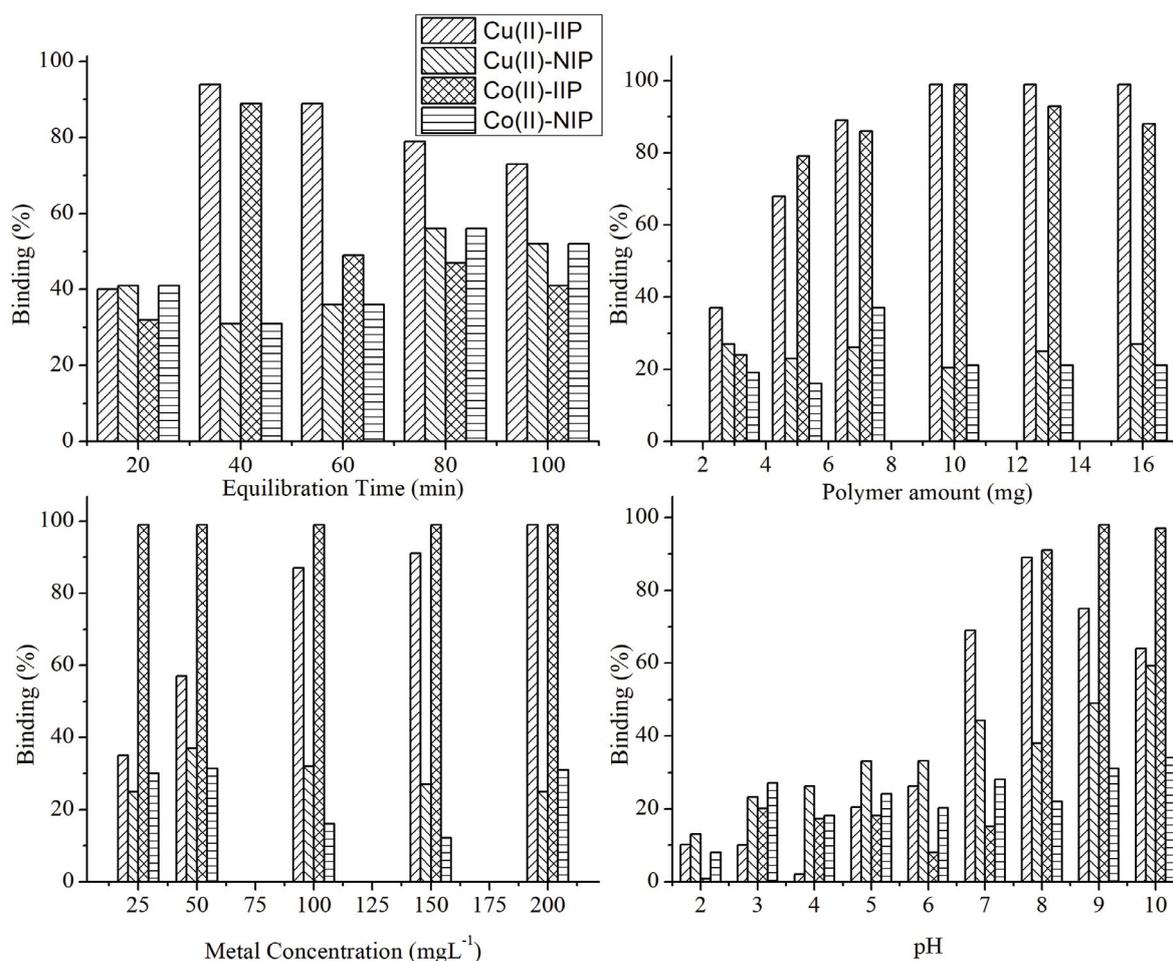


Fig. 5. Optimization of the amount of polymers, metal, equilibration time, and pH for the maximum binding of the Cu(II) and Co(II) to Cu(II)-IIP and Co(II)-IIP and comparison of the IIP's with their respective NIP.

noted at pH around 8. As the pH of the solution increased to approximately 9, precipitation begins in the form of insoluble hydroxide. Thus, it was supposed that the sorption process became concealed by precipitation and resulted in the increase of the sorption capacity of metal ions at pH around 9. Therefore, experiments were not performed above pH 8 to evade precipitation of metal ions.

3.6. Kinetics study

For the kinetics study, Cu(II)-IIP, Co(II)-IIP (0.005 g) was added to a plastic tube, 10 mL of standard Cu²⁺ and Co²⁺ salt solution was also added and were placed on the orbital shaker from 20–100 min and percent binding was determined. Equilibration between the bind and unbind amount of the metal ions was achieved in 40 min (Fig. 5) possibly because the rate of desorption becomes faster than the rate of adsorption after that. Initially the increase in the rate of ion removal can be due to the availability of the adsorbent/binding sites, whereas afterward, the ion removal rate by the polymer decreased considerably due to the decrease in adsorption sites.

The kinetics model for binding of Cu²⁺ and Co²⁺ ions on IIP was studied using Eqs. (2) and (3) as:

Pseudo-first-order kinetic equation is expressed as

$$\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303} \quad (2)$$

Pseudo-second-order equation as:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{K_2 q_e^2} \quad (3)$$

where q_e represents the amount of metal ions (Cu²⁺ and Co²⁺) bind (mgg⁻¹) at equilibrium and q_t is amount of metal ions bind (mg g⁻¹) at any given time (min), K_1 and K_2 is the pseudo-first-order and pseudo-second-order reaction constant rate constant for sorption of metal ions (min⁻¹).

The correlation values (0.9863 of pseudo-second-order kinetic vs. 0.8827 of pseudo-first-order for Cu(II)-IIP and 0.8331 of pseudo-second-order kinetic vs. 0.7902 of pseudo-first-order for Co(II)-IIP) in the plot shows that Cu²⁺ and Co²⁺ polymer followed pseudo-second-order, thus concluded that it was dependent on the amounts of metal ions and the polymers respectively. (Fig. 6, Table 1).

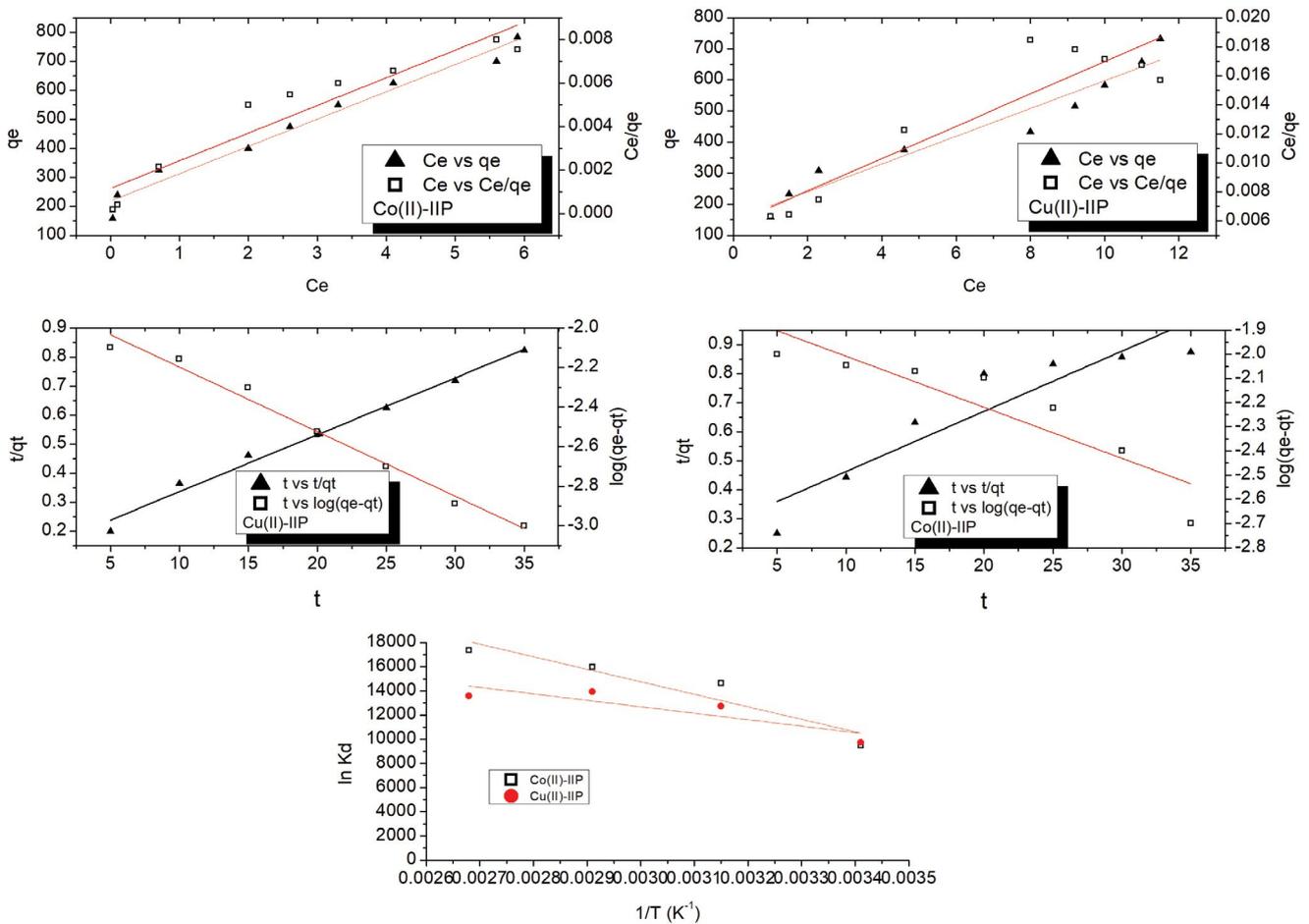


Fig. 6. Plot of C_e vs. q_e and C_e vs. C_e/q_e for Cu(II)-IIP and Co(II)-IIP. Plot of t vs. t/q_t and t vs. $\log(q_e - q_t)$ for Cu(II)-IIP and Co(II)-IIP. Plot of $1/T$ vs. $\ln K_d$ for Cu(II)-IIP and Co(II)-IIP.

3.7. Isotherm models

To evaluate the sorption of Cu^{2+} and Co^{2+} on their IIPs, Freundlich and Langmuir isotherm were examined to model the equilibrium binding data.

The Freundlich isotherm is used to describe sorption on heterogeneous surfaces and its expression is given as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{4}$$

where K_F is Freundlich isotherm constant (mg g^{-1}), q_e is amount of metal ion sorbed (mg g^{-1}) $1/n$ (g L^{-1}) is sorption intensity of polymer, and C_e is the equilibrium concentration ($\mu\text{g mL}^{-1}$).

The Langmuir isotherm is used to describe monolayer sorption on the homogenous surface, and expression is given as:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L C_e}{K_L} \tag{5}$$

where C_e ($\mu\text{g mL}^{-1}$) is the equilibrium concentration, q_e (mg g^{-1}) is amount of ion sorbed, K_L (L g^{-1}), and a_L (Lm g^{-1})

are the Langmuir sorption isotherm constants. The theoretical monolayer adsorption capacity is Q_0 and numerically equal to K_L/a_L .

According to the results of the binding experiments, it was concluded from the high regression coefficient value of Cu(II)-IIP (0.9919) and Co(II)-IIP (0.9919) that the sorption followed Freundlich isotherm (Fig. 6, Table 2). Hence multilayer sorption occurs. The value of n in Freundlich isotherm for both the metal ions is between 0–1, there might be some degree of non-linearity between the metal ion concentration and the binding sites of the polymer.

Based on the values of K_F in Table 2, which are 33 and 22 for Cu^{2+} and Co^{2+} respectively, indicates greater adsorption capacity. It can be concluded here that the studied metal ions binding has applicability of the Freundlich isotherm and shown that adsorption-complexation reactions may possibly take place in the adsorption process.

3.8. Thermodynamics study

The Cu (II)-IIP and Co (II)-IIP were used for investigation of the effect of temperature on the binding of Cu^{2+} and Co^{2+} . It was concluded from the binding experiments that sorption decreases with a gradual decrease in temperature from 70°C .

Table 1
Kinetic parameters for the binding of Cu(II) and Co(II) to their ion-imprinted polymer

Polymers	Pseudo-first-order			Pseudo-second-order				
	K_1 (min ⁻¹)	q_e (mg g ⁻¹)		R^2	K_2 (mg g ⁻¹ min ⁻¹)	q_e (mg g ⁻¹)		R^2
		Experimental	Calculated			Experimental	Calculated	
Cu(II)-IIP	0.0751	0.02167	0.0227	0.8827	9.0	0.0217	3.74	0.9863
Co(II)-IIP	0.04	0.0180	0.0173	0.7902	12.0	0.0180	3.91	0.8331

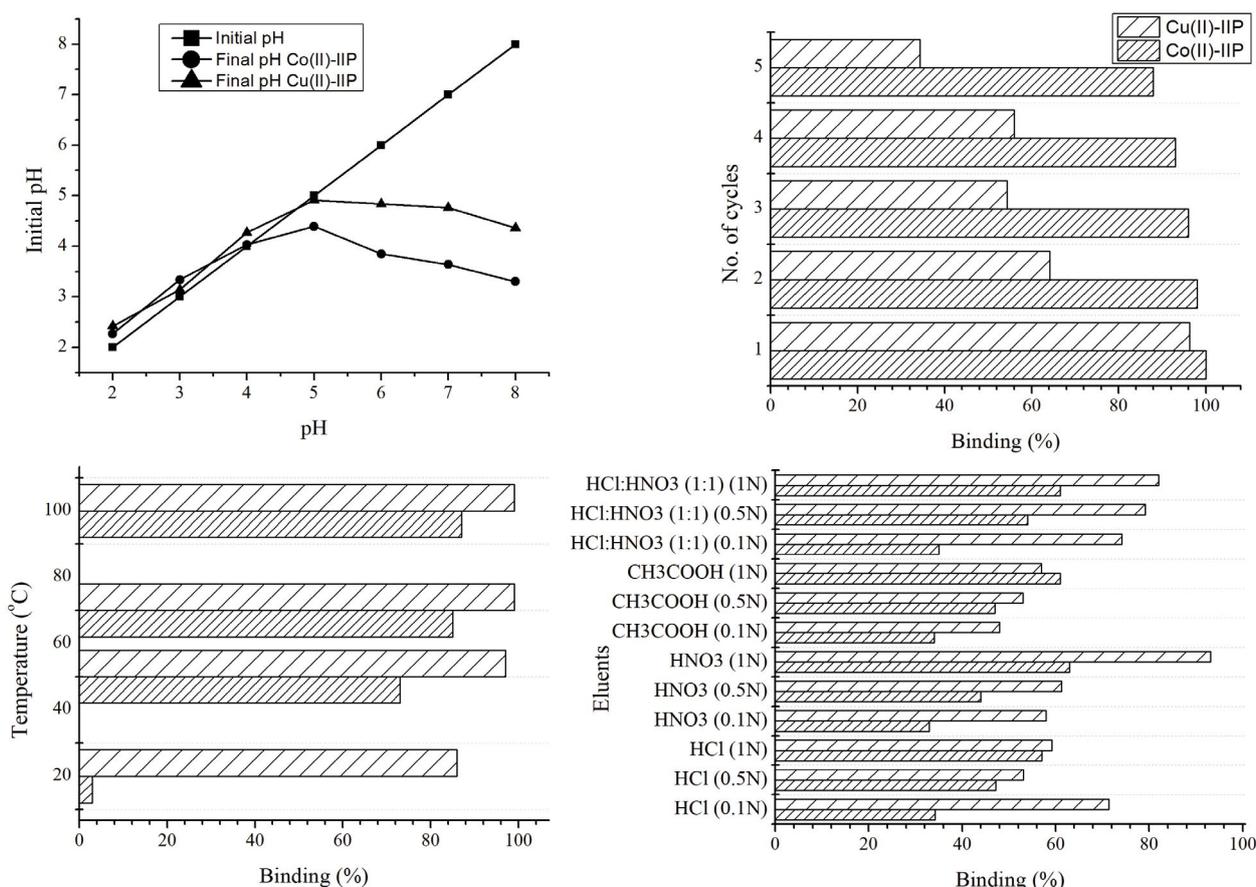


Fig. 7. Plot of initial pH vs. pH after 24 h for the determination of the point of zero charge for Cu(II)-IIP and Co(II)-IIP. Plot of the effect of temperature on the % binding of Cu(II) and Co(II) on Cu(II)-IIP and Co(II)-IIP. Plot of a number of cycles for which the Cu(II)-IIP and Co(II)-IIP is used with reasonable efficiency. Plot of the effect of various eluents of different concentrations on the leaching of Cu(II) and Co(II) from Cu(II)-IIP and Co(II)-IIP.

At 70°C and above up to 100°C, the binding capacity of IIP remained higher (Fig. 7). For the determination of sorption process, different thermodynamics parameters like entropy (ΔS°), enthalpy (ΔH°) and change in energy (ΔG°) were calculated, by using the Eqs. (6)–(8) given as under;

$$K_D = \frac{q_e}{C_e} \quad (6)$$

$$q_e = \left[\frac{C_i - C_e}{m} \right] \times V \quad (7)$$

$$\Delta G^\circ = -RT \ln K_D \quad (8)$$

where K_D is distribution constant, C_i is the initial concentration of metal ions (mg L⁻¹), C_e is the equilibrium concentration of Cu²⁺ and Co²⁺ ions (mg L⁻¹), q_e is sorption capacity, m is mass of the polymer (g), and V is the volume (mL).

The negative value of ΔG° and ΔH° shows the feasibility, spontaneity, and the exothermic nature of the reaction. Positive values of ΔS° were obtained which support the exothermic spontaneous sorption of IIPs (Fig. 6, Table 3). The metal ion binding onto the polymer was conducted at temperatures of 293, 323, 343, and 373 K. From Fig. 6, it can

Table 2
Calculated values of isotherm parameters of Cu(II)-IIP and Co(II)-IIP

Polymers	Langmuir				Freundlich		
	K_L (L g ⁻¹)	a_L (Lm g ⁻¹)	Q_0 (mg g ⁻¹)	R^2	K_f	N	R^2
Cu(II)-IIP	1.8352	-555.2	3.3×10^{-3}	0.7354	33.17	6×10^{-4}	0.9919
Co(II)-IIP	5.6.18	-740.2	0.076	0.9726	21.52	6×10^{-4}	0.9919

Table 3
Calculated values for thermodynamics parameters studied for IIP of Cu(II) and Co(II)

Temperature (K)	ΔG° (KJ/mol)		ΔH° (KJ/mol)		ΔS° (KJ/mol)	
	Cu(II)-IIP	Co(II)-IIP	Cu(II)-IIP	Co(II)-IIP	Cu(II)-IIP	Co(II)-IIP
293	-9.7245	-9,500.30				
323	-12,728.90	-14,635.54				
343	-13,916.30	-15,969.53	3,574,055.7	83,140,000	1,21,916.5	3,80,914.22
373	-13,582.91	-17,366.28				

Table 4
Effect of the interfering ion on retention of Cu(II) and Co(II) on their respective IIP

Interfering ions	Concentrations (mg L ⁻¹)	Binding \pm standard deviation	
		Cu(II)-IIP	Co(II)-IIP
Cd ²⁺	100	99.63 \pm 0.0028	77.43 \pm 0.044
Pb ²⁺	100	99.62 \pm 0.0044	96.14 \pm 0.0213
Ca ²⁺	100	99.97 \pm 0.0071	80.55 \pm 0.0123
Mg ²⁺	100	99.99 \pm 0.0005	83.96 \pm 0.024
Zn ²⁺	100	99.87 \pm 0.0039	99.59 \pm 0.0342
Fe ²⁺	100	99.88 \pm 0.0004	99.87 \pm 0.0354
Ni ²⁺	100	99.31 \pm 0.0033	66.63 \pm 0.257
Co ²⁺	100	99.93 \pm 0.0078	97.14 \pm 0.0432

be seen that the metal ion adsorption has decreased with increasing the temperature possibly because the metal ions adsorbed on the IIP may be released into the aqueous solution because of the degree of saturation of the metal ion solution has decreased with heating due to desorption. The adsorption of metal ions was found to decrease with increasing temperature, indicating that metal adsorption was ideal at lower temperatures.

3.9. Interference study

Competitive binding of different divalent and monovalent common matrix ions such as Mg²⁺, Ni²⁺, Zn²⁺, Ca²⁺, K⁺, Fe²⁺, Pb²⁺, and Cd²⁺ were investigated for their effects on the binding of Cu²⁺ and Co²⁺ to the IIPs. From the binding experiment, it was concluded that no significant interference effect on the binding of Cu²⁺ and Co²⁺ ion was observed and their binding mechanism was unaffected by common matrix ions (Table 4). The IIP's are selective towards their respective metal ions based on the electrostatic force of attraction between the Cu²⁺ and Co²⁺ ions with the polymer surface and

also because of the stability of the Cu²⁺ and Co²⁺ metal ion complex with MBI. The arrangement of copper and cobalt with MBI enabled the binding sites to match the charge, size, and coordination number of these metal ions more than the interfering ions. Further, the geometry of the complex could be preserved through the linker and then the leaching of the IIPs, which created a favorable situation for the Cu²⁺ and Co²⁺ metal ion rebinding to the IIPs.

3.10. Desorption and reusability of Cu(II)-IIP and Co(II)-IIP

Prepared polymers were tested for several loading and elution cycles, which was performed to check the pre-concentration efficiency of IIPs without significant losses. For desorption of Cu²⁺ ions from their polymer that was loaded initially with Cu²⁺ salt solution, various eluents like HNO₃, HCl ranging from 0.1–1.0 N and their mixtures were used, it was concluded from the binding experiments that maximum desorption (93%) was observed with (10 mL) of 1.0 N HNO₃ solution possibly due to the electrostatic interaction competition established between the strong acid and the MBI for the metal ion. The reusability of the polymer was repeated for nine loading and elution cycles by using (1.0 N HNO₃).

Whereas for desorption of Co²⁺ ions from their polymer that was loaded initially with Co²⁺ salt solution, eluents like HNO₃, CH₃COOH, and HCl ranging from 0.1–0.2 N and mixture of HNO₃ and HCl were used (Fig. 7). Maximum desorption capacity was attained by HNO₃ (1.0 M), CH₃COOH (1 M), and a mixture of HNO₃ and HCl (1.0 M). To ensure 100% desorption of Co²⁺ ions, an imprinted polymer was washed in (2 times). The reusability of the polymer was repeated for five loading and elution cycles by using (1 M CH₃COOH) (Fig. 7).

The proton of the washing solvent in both cases replaces the metal ion and wash off the metal ion from the IIP. The proton regenerates the IIP for further use and repeated cycles.

Table 5
Binding of Cu(II) and Co(II) ions on Cu(II)-IIP and Co(II)-IIP in different water samples

Water sample	Amount of Cu(II) and Co(II) ions added (mg L ⁻¹)	Binding (%)	
		Cu(II)-IIP	Co(II)-IIP
Tap water	20	99.992	99.991
	40	99.993	99.995
	60	99.994	99.996
	80	99.995	99.998
	100	99.996	99.997
Well water	20	99.992	99.992
	40	99.995	99.996
	60	99.998	99.997
	80	99.994	99.997
	100	99.997	99.997
River water	20	99.995	99.997
	40	99.998	99.998
	60	99.996	99.998
	80	99.995	99.997
	100	99.992	99.997
Industrial effluents	20	99.995	99.978
	40	99.98	99.998
	60	99.998	99.997
	80	99.999	99.999
	100	99.997	99.999

3.11. Applications of Cu(II)-IIP and Co(II)-IIP

The prepared polymers were subjected to the analysis of several water samples. Different water samples were spiked with a known concentration of Cu²⁺ and Co²⁺ salt solution. It was found that the binding efficiency of all samples was greater than 99% which showed that the imprinted polymers of Cu²⁺ and Co²⁺ are versatile and can be used for a variety of aqueous samples (Table 5).

4. Conclusion

In the present work, imprinted polymers were prepared for Cu²⁺ and Co²⁺ for their removal from different samples of water. It was found that IIP shows greater affinity than NIP. By using different techniques such as SEM, FTIR, and TGA, the prepared polymers were characterized. The kinetics study showed that Cu²⁺ and Co²⁺ followed pseudo-second-order kinetic. The thermodynamics study shows that the reaction was exothermic and spontaneous. The maximum sorption behavior of Cu²⁺ and Co²⁺ ions showed that the binding of both metals follows Freundlich isotherm. There was no significant interference effect on the binding of Cu²⁺ and Co²⁺ ion, their binding mechanism was unaffected by common matrix ions. Nine binding and leaching cycles were repeated for desorption and reusability of polymers. Prepared Polymers were successfully tested for the removal of Cu²⁺ and Co²⁺ ions from various water samples with binding efficiency of 99.9%.

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