Selective Separation of Cobalt Using a New Co(II)-Imprinted Polymer/Cryogel System

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Abstract. The aim of the present study was to investigate selective separation and preconcentration of Co(II) ions in aqueous solutions by ion imprinted technique. For this purpose, Co(II)-methacryloylhistidine((MAH)$_2$-Co(II)) complex monomer has been synthesized and polymerized with presence of 2-hydroxyethyl methacrylate (HEMA) followed by flushed out of bonded Co(II) ions from polymer with 5.0 mol*L^{-1} HNO$_3$. Thus, specific cavities for re-binding of target ions (Co(II)) have been created onto p-HEMA-MAH cryogel column. Prepared metal complex and Co-imprinted polymer/cryogel system have been characterized by FTIR and SEM. The effect of various parameters such as pH, initial concentration, flow rate, ionic strength have been investigated to determine optimal adsorption conditions. The maximum amount of adsorbed Co(II) has found as 106.0 mg*g^{-1} at pH 8.0 with flow rate of 1 mL*min^{-1}. For selectivity experiments, binding studies were carried out presence of Cu(II) and Ni(II). The k (selectivity coefficient) values have found as 8.9 and 3.8 for Co(II)/Cu(II) and Co(II)/Ni(II) binary mixture, respectively. The reuse of column also has been investigated and there was no significant decrease at adsorption capacity even in consecutive eleven experiments.

Keywords: Ion Imprinted polymer, cryogel, cobalt, selective recognition.

Yeni Bir Co(II)-Baskılı Polimer/Kriyojel Sistem Kullanılarak Kobalt(II)'ın Seçici Olarak Ayrılması

Özet. Bu çalışmanın amacı, iyon baskılama tekniği ile sulu çözeltilerden Co(II) iyonunun seçici olarak ayrılmasını ve ön derişimini araştırmaktı. Bu amaçla, Co(II)-metakriloilhistidin ((MAH)$_2$-Co(II)) kompleks monomer sentezlendi ve 2-hidroksietil metakrilat (HEMA) varlığında polimerleştirildi. Ardından, 5.0 mol*L^{-1} HNO$_3$ ile bağlı Co(II) iyonları polimerden söküldü. Böylece, hedef iyonun (Co(II)), p-HEMA-MAH kriyojel kolonuna tekrardan bağlanması için spesifik boşluklar oluşturuldu. Hazırlanan metal kompleks ve baskılı-kriyojel FTIR ve SEM ile karakterize edilmiştir. Optimum adsorpsiyon koşullarını belirlemek için, pH, başlangıç konsantrasyonu, akış hızı, iyonik şiddet gibi çeşitli parametrelerin etkisi araştırılmıştır. Maksimum adsorbe edilen Co(II) miktarı, pH 8.0'de 1 mL*dk^{-1} akış hızında 106.0 mg*g^{-1} olarak tespit edilmiştir. Seçicilik deneyleri için, bağlanma çalışmaları Cu(II) ve Ni(II) varlığında gerçekleştirilmiş olup k (seçicilik katsayısı) değerleri sırasıyla Co(II)/Cu(II) ve Co(II)/Ni(II) ikili karışımı için 8.9 ve 3.8 olarak bulunmuştur. Kolonun tekrar kullanımı araştırılmış ve ardışık on bir deneyde bile adsorpsiyon kapasitesinde önemli bir azalma olmadığı tespit edilmiştir.

Anahtar Kelimeler: İyon Baskılı Polimer, kriyojel, kobalt, seçici tanıma.

1. INTRODUCTION

Heavy metals which defined as metals with high specific gravity (≥5), especially, are noted for their potential human or environmental toxicity. Heavy metals such as Cd, Ni, Hg, Cr, Ag, Co, Sn, Cu, Zn and Pb are observed as most polluting effect on environmental [1]. Thus, separation of heavy metals is important for environmental protection and public health. Cobalt (Co) is an essential part

of our diet at low levels, however, high levels exposure can be toxic and cause health effects such as asthma, pneumonia and wheezing [2]. Various techniques have been used for separation and preconcentration for cobalt such as solvent extraction [3], precipitation and co-precipitation [4], ion-exchange [5], cloud-point extraction [6] and solid phase extraction [7].

Molecular imprinting that first described in 1972 [8] is a rapidly developing technique and has been attracted the attention of researchers for preparing polymeric sorbents for selective separation and preconcentration. Molecularly imprinted polymers (MIPs) allows selective recognition and binding of chosen target molecule by leaving artificial cavities in polymeric materials that provide high affinity to target in preference of analog molecules [9]. The process of preparation molecularly imprinted polymer begins with complexing of the template molecule with functional monomers. The second step involves the polymerization of template-monomer complex and cross-linker reagents. Consequently, after flushed out of bonded template molecule with suitable elution agent, the rigid polymer matrix with three dimensional (3D) imprinted sites that complementary to the templates is obtained. MIPs are used particularly as stationary phases for pretreatment or chromatography applications of aminoacids [10], proteins [11,12], enzymes [13], DNA [14], drugs [15, 16] metals [17-19] as well as many other chemical or biological molecules in enviromental [19] and biological [16, 19, 21, 22] complex matrixes. Similar to MIPs, ion-imprinted polymers (IIPs) have been also used effective recognition and separation of metal ions. But when the metal ion itself used as an imprinting template, low selectivity occurs at IIPs versus template ion since same properties (similar ionic radii, same charges) of ions [23]. Now, the method of using pre-complex of metal ion and suitable ligand is a new trend in ion-imprinting that has been used in many studies [22, 24-27] and also in our study.

In this study, a new Co(II)-imprinted p(HEMA-(MAH) cryogel has been synthesized by radical polymerization. N-methacryloyl-L-histidine (MAH) was used as metal-complexing monomer (ligand) to obtain specific metal ion binding. After flushed out of Co(II) ions, imprinted polymer was described how pH, initial concentration, flow rate, ionic strength affect the binding capacity. Selectivity studies were also reported versus Cu and Ni as interfering metal ion. Finally, the study was terminated by preconcentration study.

2. MATERIAL AND METHODS

2.1. Reagents and Materials

Cobalt(II) nitrate hexahydrate ($Co(NO_3)_2.6H_2O$) ($\geq 97\%$), Copper(II) nitrate trihydrate ($Cu(NO_3)_2.3H_2O$) ($\geq 98\%$), Nickel(II) nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$) ($\geq 97\%$), were supplied from Sigma-Aldrich (St. Louis, MO, USA). 2-Hydroxyethyl methacrylate (HEMA) (97%), crosslinker N-N-methylenbisacrilamid (MBAAm) (99%), polymerization initiators N,N,N,N-tetramethylene diamine (TEMED) (99%) and Ammonium Persulfate (APS) ($\geq 98\%$) were provided from Sigma-Aldrich (Steinheim, Germany). The functional monomer, N-methacryloyl-L-histidine (MAH) was supplied from *Hür and coworkers [28]*. In pH studies, acetate buffer solutions CH_3COOH (Sigma-Aldrich, 100%)-$NaCH_3COOH$ (Sigma-Aldrich, $\geq 99\%$), phosphate buffer $NaH_2PO_4.2H_2O$ (Sigma-Aldrich, $\geq 98\%$)-Na_2HPO_4 (Merck, 99.5%) and Tris base (Sigma-Aldrich, 99.5%)-HCI (Merck, 37%) were used in the required compositional range. HNO_3 (Sigma-Aldrich, 70%) was used as a desorption agent. NaOH, NaCI were analytical grade and obtained from Merck A.G.

2.2. Apparatus

Watson Marlow, 120S peristaltic pump was used in all experiments for adjusting flow rate. The HANNA HI 2211 pH/ORP meter was used for pH measurements. The determination of Co(II), Ni(II) and Cu(II) content in effluent and eluted solutions from the column was performed using the Perkin Elmer AAnalyst 700 Spectrophotometer with deuterium (D_2) background instrument. Complex monomer and imprinted polymer were characterized with Fourier transform infrared

spectroscopy (FTIR) and Scanning electron microscopy-energy dispersive X-ray (SEM-EDX) analysis; FTIR measurements were analyzed on a Perkin Elmer Laser model 400 spectrum. SEM-EDX analysis were performed with FEI Quanta FEG 250 SCE model instrument. The distilled water used in the experiment was also purified by using Millipore Milli-Q Plus Ultra-Pure system.

2.3. Synthesis of Co(II)-Methacryloylhistidine Complex Monomer

For the synthesis of complex monomer; $Co(NO_3)_2.6H_2O$ (0.291g, 1.0 mmol) was slowly added to N-methacryloyl-L-histidine (MAH) (0.446g, 2 mmol) solution into distilled water (10 mL), followed by stirring overnight at room temperature. Finally, the complex monomer was filtered off, washed and dried.

2.4. Preparation of Co(II) Imprinted Cryogel

The Co(II) imprinted cryogel was prepared with minor modification of the method reported in the literature [11]. For this purpose; fistly, 0.283 g MBAAm in distilled water (5 mL) was added to a mixed solution composed of HEMA (1.3 mL) and (MAH)$_2$-Co(II) (1 mL), followed by stirring magnetically for 2 min. After adding APS (20 mg) reaction mixture was cooled in an ice bath and TEMED (50 μL) was added under stirring for one min. followed by pouring into a plastic syringe (5 mL) with closed outlet at the bottom and frozen at 20 °C for 24 h. After the radical polymerization was over (24 h.), the column was then thawed to room temperature and washed with water to remove undesired impurities. As a final stage, the template Co(II) was removed from the p-HEMA-MAH-Co(II) cryogel column by washing with 5.0 mol*L^{-1} HNO$_3$ as the desorption agent for several times until no cobalt was detected in the washing solution to obtain cavities for re-binding of template. Prepared MIP composite cryogel was stored at 4 °C until use.

2.5. Binding Studies of Co(II) on MIP

For the binding of Co(II) to Co-imprinted cryogel, continuous column system was used and all experiments were briefly consisted three steps: equilibrium, binding and elution. Firstly, ten milliliters of Co(II) at 10 ppm concentration prepared with the appropriate buffer was pumped through the 0.2 g of cryogel column at flow rate 1.0 mL*min^{-1} for 1h after equilibration step. Right after, as a elution agent 5.0 mol*L^{-1} HNO$_3$ (10 mL) was passed to elute bonded Co(II) followed by washing with water. The content of Co(II) in effluent and eluted solutions from the column was determined by AAS. The effect of different factors such as pH (4-8), flow rate (1.0–4.0 mL*min^{-1}), initial Co(II) concentration (100-4000 mg*L^{-1}) and ionic strength (0.25-1.0 mol*L^{-1} NaCl) on binding capacity were investigated.

2.6. Selectivity, Reusability and Preconcentration Studies

The selectivity of Co(II)-imprinted polymer/cryogel was carried out in the presence of Co(II)-Cu(II) and Co(II)-Ni(II) ion pairs. For this purpose 10 mL of 10 ppm binary mixtures in Tris buffer (pH 8.0) were passed from column with flow rate of 1 mL*min^{-1} at room temperature. Selectivity coefficient (k) of prepared column was determined as the ratio of the distribution constant (K$_d$) of the two ions that was calculated according to follows:

$$K_d = \frac{C_i - C_f}{C_f} \times \frac{V}{m}$$

$$k = K_{d\,Template}/K_{d\,Interfering\,ion}$$

where K_d is the distribution coefficient, C$_i$ and C$_f$ are the initial and final concenrations, respectively, V is the volume of solution (mL) and m is the mass IIP (g).

For the reusability studies of imprinted cryogel, loading-elution studies were repeated eleven times (other binding studies not included) using same IIP. After each step, adsorbed metal ions were eluted with 5 mol*L^{-1}HNO$_3$ and washed with distilled water.

For the preconcentration of Co(II) ions 250 mL of the aqueous solution containing 0.1 mg*L^{-1} Co(II) was pumped through the column at a flow rate of

1.0 mL*min^{-1} for 4h. After passage of solution, the bonded cobalt was eluted with 5 mL of elution agent.

3. RESULTS AND DISCUSSION

3.1. Characterization Studies

The complex formation of MAH with Co(II) was supported with FT-IR and EDX analyses. From the FT-IR spectrum, interaction between monomer and metal ion caused a shift in the complex spectrum. The spectral differences between monomer and complex is shown in Fig. 1 that the characteristic peak assigned to hydroxyl groups (OH streching)

at 3191 shifted to 3241 cm^{-1}. On the other hand one of the peaks corresponding to carbonyl (C=O) bonds of amid or carboxylic acid at 1724 cm^{-1} and 1696 cm^{-1}was disappeared in the (MAH)$_2$-Co(II) spectrum. And it was estimated that the peak at 677 cm^{-1} was resulted from Co-O vibration. This result indicated that template metal ion was complexed with MAH monomer. In addition, the amount of each element in weight for metal complex were determined as 50.98% C, 20.82% N, 24.73% O and 2.53% Co to support the complex formation by EDX analysis that is illustrated in Fig. 2.
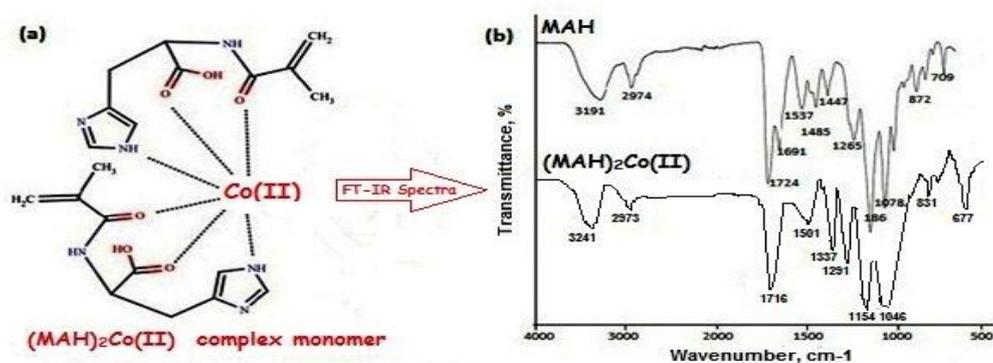
Figure 1. FT-IR spectrum of MAH and (MAH)$_2$Co(II) preorganized monomer.
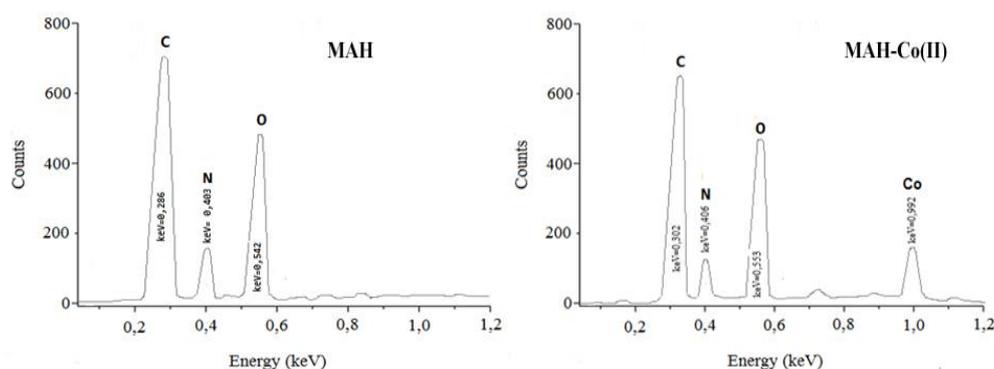
Figure 2. SEM-EDX spectra of MAH and (MAH)$_2$Co(II) complex.

As seen in Fig. 3, it can be said that imprinted polymer exhibited similar spectral pattern with p-HEMA. The similarities between the FT-IR spectrum of HEMA and Co-imprinted p(HEMA-(MAH)$_2$-Co(II)) can be due to having the similarity of the polymer backbone structure. The surface

morphology of polymer was examined by SEM analysis. As showed in Fig. 4, SEM image shows that cryogel has pores with size of 50 µm.
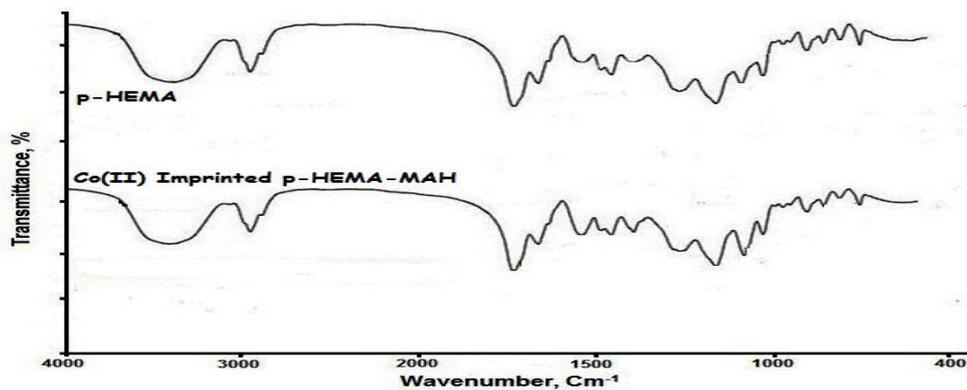
Figure 3. FT-IR Spectra p-HEMA and Co(II) imprinted p-HEMA-MAH.
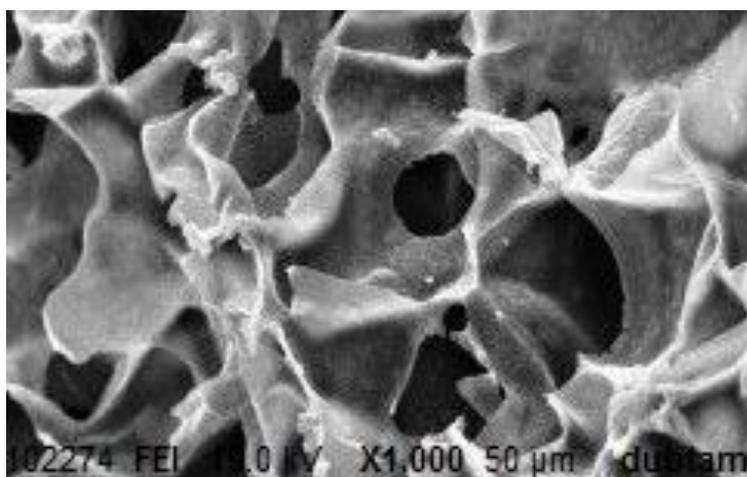
Figure 4. SEM image Co(II) imprinted p-HEMA-MAH.

3.2. Binding Studies

3.2.1. Effect of Medium pH on Binding

The high effect of pH on adsorption of metal ion onto sorbents is well known [29,30]. For this purpose, the binding of Co(II) onto MIP cryogel was studied in acetate (pH: 4.0-5.0), phosphate (pH: 6-7.0) and Tris-HCl (pH: 8-9.0) buffers systems. As shown in Fig. 5, the amount of binding of Co(II) increased with increasing pH. The low binding at acidic pH can be attributed to the protonation of functional groups of MAH monomer. Similar result was also reported for Ni(II) metal ion [27]. From the plot of % binding versus pH, the optimum binding was found to be at pH 8.
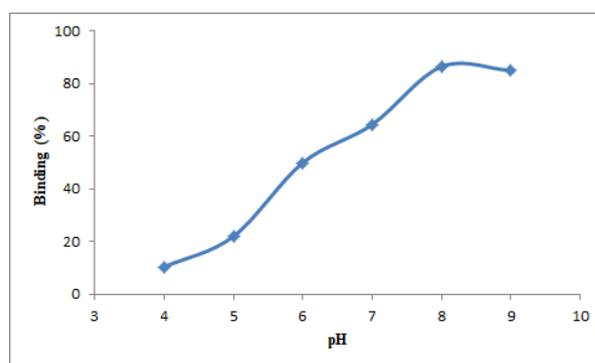
Figure 5. Effect of pH on Co(II) binding. (Conditions: C_i: 10 mg*L^{-1} in buffer, Flow rate: 1 mL*min^{-1}, t: 1 h).

3.2.2. Effect of Flow Rate on Binding

In order to determine effect of flow rate on binding, flow rate values changed from 1 to 4 mL*min^{-1}. Fig. 6 illustrates the percent of binding of Co(II) at this flow rate range. As seen in Fig.6, the increase in flow rate through the column resulted decrease

in the binding of Co(II) from 86% to 70%. This can be explained by the insufficient contact time between the template molecule and cryogel at high flow rates. Similar comment was reported by Gedikli at al. [13]. Hereby, 1 mL*min^{-1} was selected as an optimum flow rate in the subsequent experiments.
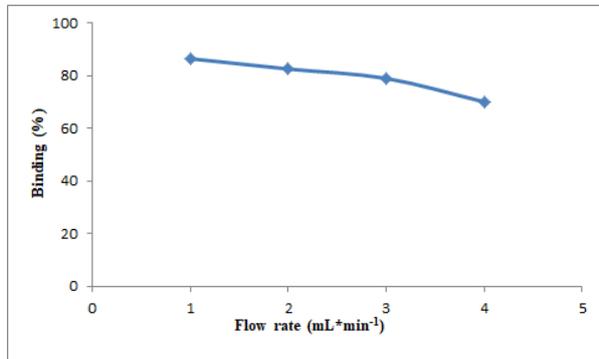
Figure 6. Effect of flow rate on Co(II) binding. (Conditions: C_i: 10 mg*L^{-1}, pH: 8, t: 1 h).

3.2.3. Effect of Initial Concentration on Binding

The effect of the initial Co(II) concentration on binding capacity was studied between 100.0 to 4000 mg*L^{-1} and the maximum binding capacity was found as 106.0 mg*g^{-1} within 2 h. As shown in Fig. 7, the amount of bonded Co(II) increases linearly with increasing initial concentration. But for higher than 3000 mg*L^{-1}, the rate of increase becomes insignificant that specified as saturation point. This is because at high concentration the binding sites of cryogel matrix becomes less and saturated.
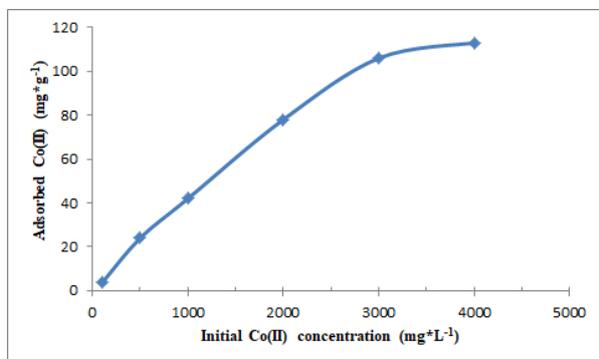
Figure 7. Effect of initial concentration on Co(II) binding. (Conditions: Flow rate: 1 mL*min^{-1}, pH: 8, t: 2 h).

3.2.4. Effect of Ionic Strength on Binding

The binding experiment was carried out with NaCl presence to investigate effect of ionic strength on binding capacity. For this purpose, 10 mg*L^{-1} Co(II) solution containing variable concentrations (0.25-1.0 mol*L^{-1}) of NaCl were pumped through column. Experimental results showed that binding of Co(II) was decreased from 85.8 to 58.0 with increasing of ionic strength (Fig. 8). This changes can be explained in this way: probably, the counter salt ions mask the binding sites via charge–charge interactions.
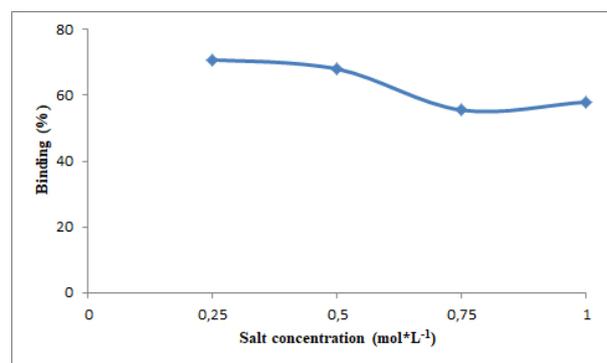
Figure 8. Effect of ionic strength of on binding. (Conditions: C_i: 10 mg*L^{-1}, pH: 8, Flow rate: 1 mL*min^{-1}, t: 1 h).

3.2.5. Reuse Performance

The reusability is reference factor of stabilization of sorbents. Loading-elution studies were performed consecutive eleven times at the optimum conditions to test the performance of reusing the MIP cryogel. The binding of Co(II) was found as 81% in the eleventh experiment, indicating no significant decrease for binding capacity.
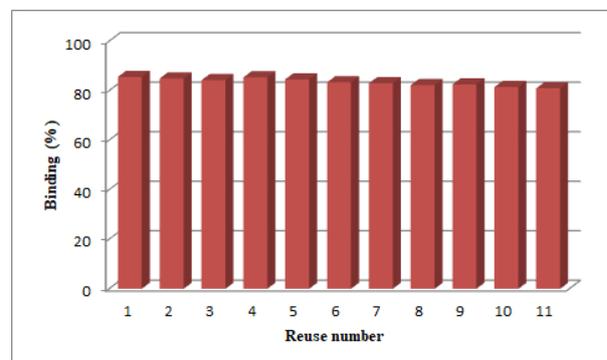
Figure 9. Reusability of the cryogel. (Conditions: C_i: 10 mg*L^{-1}, pH: 8, Flow rate: 1 mL*min^{-1}, t: 1 h).

3.2.6. Selectivity Experiments

Cu(II) and Ni(II) were chosen as competing metal ions to show the specificity of prepared Co(II)-imprinted cryogel toward to Co(II) ions. Despite

these ions are similar in ionic radii and charges, Co(II) imprinted cryogel exhibited higher selectivity toward Co(II) ions. Distribution (K_d) and selectivity coefficients (k) of each ion are summarized in Table 1.

Table 1. Competitive adsorption of Co(II), Cu(II) and Ni(II) on Co-Imprinted cryogel.

Binary mixtures (10 mg*L^{-1})	K_d			K	
	Co(II)	Cu(Il)	Ni(II)	Co/Cu	Co/Ni
Co(II)-Cu(II)	334.6	37.1	-	8.9	3.8
Co(II)-Ni(ll)	262.5	-	69.0		

3.2.7. Preconcentration of Co(II) in Aqueous Solution

Preconcentration of samples with low concentrations are especially important step. With this approach, concentration behavior of Co(II) ion was determined as term of preconcentration factor. Collection of the cobalt solution at 0.1 ppm concentration was achieved with 84% recovery and preconcentration factor was found to be 50.

4.   CONCLUSIONS

Current study has been on the selective recognition and separation of Co(II) metal ion through ion imprinted polymer (IIP) based cryogenic trap. For this purpose, Co(II) imprinted p-HEMA-MAH cryogel has been synthesized with radical polymerization for the first time. The simplicity, low cost and method specificity are the most important characteristics of the study. At the optimum binding condition (1 mL*min^{-1} flow rate, pH 8) maximum binding capacity has been found as 106.0 mg*g^{-1}. The selectivity of polymer has been evaluated through Cu(II) and Ni(II) separately in buffer solution and obtained binding percentages were as follows; Co>Ni>Cu. Based on the selectivity performance indicated in the this study, prepared imprinted polymer is a convenient candidate for selective isolation of Co(II) in environmental samples.

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