

**ARASTIRMA MAKALESİ /RESEARCH ARTICLE**

**MAGNETIC ION-IMPRINTED BEADS FOR CADMIUM REMOVAL FROM  
AQUEOUS SOLUTIONS**

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**ABSTRACT**

In this study, magnetic ion-imprinted polymers were prepared that can be used for the selective removal of cadmium ions ( $Cd^{2+}$ ) from aqueous solutions in a batch system. N-methacryloyl-(L)-cysteine (MAC) was chosen as the complexing monomer. The MAC monomer was complexed with  $Cd^{2+}$  and the  $Cd^{2+}$ -imprinted magnetic poly(hydroxyethyl methacrylate-N-methacryloyl-(L)-cysteine) (mag-MIP) beads were synthesized in the presence of  $Fe_3O_4$  by suspension polymerization. The template ions ( $Cd^{2+}$ ) were removed by thiourea (0.5 % v/v) in 0.05 M HCl solution. The non-imprinted control beads (NIP) were prepared in the same conditions without using the template. The specific surface area of the mag-MIP beads was found to be 24.7  $m^2/g$  with a size range of 63-140  $\mu m$  in diameter. The swelling ratio of mag-MIP beads was 70%. According to the elemental analysis results, the mag-MIP beads contained 41.8  $\mu mol$  MAC/g polymer. The maximum adsorption capacity was 28.45  $\mu mol$   $Cd^{2+}/g$  polymer. The relative selectivity coefficients of mag-MIP beads for  $Cd^{2+}/Pb^{2+}$ ,  $Cd^{2+}/Zn^{2+}$  were 28.65 and 117.5 times greater than the non-imprinted (NIP) matrix, respectively. The mag-MIP beads could be used many times without decreasing in their adsorption capacities significantly.

**Keywords:** Molecular imprinting, Cadmium removal, Magnetic beads, Affinity binding.

**SULU ÇÖZELTİLERDEN MANYETİK İYON-BASKILI KÜRELERLE KADMİYUM  
UZAKLAŞTIRILMASI**

**ÖZ**

Bu çalışmada, kesikli sistemde sulu çözeltilerden  $Cd^{2+}$  iyonlarının seçici olarak uzaklaştırılması için manyetik iyon-baskılı polimerler sentezlenmiştir. N-metaroil-(L)-sistein (MAC) kompleksleştirici monomer olarak seçilmiştir. MAC monomeri  $Cd^{2+}$  iyonu ile kompleksleştirilmiş ve  $Cd^{2+}$ -baskılı manyetik poli(hidroksietil metakrilat-N-metaroil-(L)-sistein) (mag-MIP) küreleri  $Fe_3O_4$  varlığında süspan-siyon polimerizasyonu ile sentezlenmiştir. Kalıp iyonu ( $Cd^{2+}$ ) 0,05 M HCl de (0,5 % v/v) tiyoüre ile uzaklaştırılmıştır. Baskılı-olmayan polimerler (NIP) aynı şartlarda kalıp olmaksızın sentezlenmiştir. mag-MIP küreleri 24,7  $m^2/g$  spesifik yüzey alanına sahip, 63-140  $\mu m$  çapında ve şişme oranları % 70 di. Elementel analiz sonuçlarına göre mag-MIP küreleri 41,8  $\mu mol$  MAC/g polimer içermektedir. Maksimum adsorpsiyon kapasitesi 28,45  $\mu mol$   $Cd^{2+}/g$  olarak bulunmuştur.  $Cd^{2+}/Pb^{2+}$  ve  $Cd^{2+}/Zn^{2+}$  için baskılanmış mikrokürelerin bağıl seçicilikleri baskılanmamış mikrokürelere kıyasla sırasıyla 28,65 ve 117,5 kat daha fazladır.  $Cd^{2+}$ -baskılanmış poli(HEMA-MAC) mikroküreleri adsorpsiyon kapasitele-rinde önemli bir azalma olmaksızın defalarca kullanılabilir.

**Anahtar kelimeler:** Moleküler baskılama, Kadmiyum uzaklaştırılması, Manyetik küreler, Afinite bağlanması.

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## 1. INTRODUCTION

Cadmium is a toxic transition heavy metal of continuing occupational and environmental concern with a wide variety of adverse effects (Stokinger, 1981). General sources of exposure to cadmium include air, water and food. Waterborne cadmium is probably the largest problem because it is common in the aquatic environment. Many cadmium-containing wastes end up in lakes and marine water. Cadmium has an extremely long biological half-life that essentially makes it a cumulative toxin. The chronic toxicity of cadmium compounds includes kidney damage with proteinuria of low-molecular-weight molecules. An epidemic of Japanese itai-itai disease also believed to be the result of chronic ingestion of Cd (II) (via environmental pollution), with altered renal tubular function, impaired regulation of calcium and phosphorus, manifesting bone demineralization, osteomalacia, and pathological fractures (Friberg and Elinder, 1985). Many methods of treatment for industrial wastewaters have been reported in the literature, such as neutralization, precipitation, ion-exchange, biosorption and adsorption (Friberg et al. 1974; Say et al. 2001; Karabulut et al. 2001; Say et al. 2002; Reed et al. 1997; Yalcinkaya et al. 2002). The selective removal of cadmium ions have been extensively investigated by applying several techniques (Wang et al. 2001; Kantipuly et al. 1990; Chanda and Rempel, 1997; Denizli et al. 2000; Arvanitoyannis et al. 1995; Vijayalakshmi, 1998; Denizli et al. 2003).

Among them, the use of molecularly imprinted polymers has been considered as one of the most promising techniques (Say et al. 2003; Say et al. 2003; Yoshida et al. 1999; Andac et al. 2004; Aşır et al. 2005; Hart, 2001). Molecular recognition-based separation techniques have received much attention in various fields because of their high selectivity for target molecules. Molecular imprinting technology creates recognition sites in a macromolecular matrix using a molecular template (Ramstrom et al. 1999; Ramstrom et al. 1999). Molecularly imprinted polymers (mag-MIPs) are easy to prepare, stable, inexpensive and capable of molecular recognition. Three steps are involved in ion-imprinting process: (i) complexation of template (i.e. metal ions) to a polymerizable ligand, (ii) polymerization of this complex, and (iii) removal of template after polymerization. In the ion imprinting process, the selectivity of a polymeric adsorbent is based

on the specificity of the ligand, on the coordination geometry and coordination number of the ions, on their charges and sizes (Yoshikawa, 2002; Haginaka, 2002; Mosbach, 2001; Zhang et al. 2003, Nicholl, 2002).

In this study, mMIP beads were prepared for the selective removal of  $\text{Cd}^{2+}$  ions from aqueous solutions. N-methacryloyl-(L)-cysteinemethylester (MAC) was used as the metal complexing monomer. Usually, MIPs are prepared by the bulk polymerization. The disadvantage of this method is that the obtained block polymer should be crushed, ground and sieved to obtain packing materials. Here,  $\text{Cd}^{2+}$ -imprinted poly(hydroxy ethyl methacrylate-N-methacryloyl-(L)-cysteinemethylester) beads were prepared by suspension polymerization. After removal of  $\text{Cd}^{2+}$  ions, mag-MIP beads were used for the separation of  $\text{Cd}^{2+}$  ions from aqueous solutions. The effects of pH, contact time and initial concentration of  $\text{Cd}^{2+}$  ions on the adsorption capacity were studied. Selectivity studies of cadmium versus other metal ions which are  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  are reported here. Finally, repeated use of the mag-MIP beads is also discussed.

## 2. EXPERIMENTAL

### 2.1. Materials

The monomers, 2-hydroxyethyl methacrylate (HEMA) and ethylene glycol dimethacrylate (EGDMA) were obtained from Fluka A.G. (Buchs, Switzerland), distilled under reduced pressure in the presence of hydroquinone inhibitor and stored at 4°C until use. L-cysteine hydrochloride and methacryloyl chloride were purchased from Sigma (St. Louis, MO). 2,2'-azobis(izobutyronitril) (AIBN) was obtained from Fluka (Switzerland). Poly(vinyl alcohol) (PVAL; MW: 100.000, 98% hydrolyzed) was supplied from Aldrich Chem. Co. (USA). All other chemicals were of analytical grade and all solvents of HPLC grade and were purchased from Merck AG (Darmstadt, Germany). All water used in the adsorption experiments was purified using a Barnstead (Dubuque, IA) ROpure LP® reverse osmosis unit with a high flow cellulose acetate membrane (Barnstead D2731) followed by a Barnstead D3804 NANOpure® organic/colloid removal and ion exchange packed-bed system.

### 2.1.1. Preparation of Cd<sup>2+</sup>-Imprinted mag-p(HEMA-MAC) Beads

The synthesis of N-methacryloyl-(L)-cysteine (MAC) monomer was adapted from the procedure reported by elsewhere (Andac, 2004). In order to prepare MAC-Cd<sup>2+</sup> complex, solid MAC (2.0 mmol) was dissolved in 10 mL of methanol and then treated with Cd<sup>2+</sup> ions (1.0 mmol) solution at room temperature with continuous stirring for 3 h. The formed Cd<sup>2+</sup>-MAC complex was filtered, washed with 96% ethanol, and dried in a vacuum oven. HEMA (8.0 ml) and MAC-Cd<sup>2+</sup> complex monomer (680 mg) were polymerized in suspension medium using AIBN (100 mg) and poly(vinyl alcohol) (200 mg) as the initiator and the stabilizer, respectively. Toluene (6.0 ml), EGDMA (4.0 ml) and Fe<sub>3</sub>O<sub>4</sub> (0.5 g) were included as the diluent (as a pore former), crosslinker and magnetite particles, respectively. The non-imprinted mag-p(HEMA-MAC) [mag-NIP] beads were synthesized by the same method without template ions. After the polymerization reaction, soluble components were removed from the polymer by repeated decantation with water and ethyl alcohol. In order to remove unreacted monomers and other ingredients, the beads were extensively washed with methanol/water solution (60/40 v/v) for 24 h at room temperature. After cleaning procedure, the template was removed by using 0.5% thiourea in 0.05 M HCl solution for 48 h at room temperature. The template free beads were cleaned with 0.1 M HNO<sub>3</sub> in a magnetic stirrer for 3 h. When not in use, the resulting beads were kept under refrigeration in 0.02% NaN<sub>3</sub> solution for preventing of microbial contamination.

### 2.1.2. Characterization of Beads

The average size and size distribution of the mag-MIP and mag-NIP beads were determined by screen analysis performed by using Standard Test Sieves (Retsch GmbH & Co., Germany). The specific surface area of the beads was measured by Brunauer-Emmett-Teller (BET) model using single point analysis and a Flowsorb II 2300 from Micromeritics Instrument Corporation (Norcross, USA). Water uptake ratios of mag-MIP and mag-NIP beads were determined in deionized water. The weight ratio of dry and wet samples was recorded. The water content of mag-MIP and mag-NIP beads was calculated using the weights of beads before and after uptake of water. The surface

morphology of the polymeric beads was examined using scanning electron microscopy (SEM) (JEOL, JEM 1200 EX, Tokyo, Japan). The surface of the sample was scanned at the desired magnification to study the morphology of the mag-MIP beads. To evaluate the degree of MAC incorporation both mag-MIP and mag-NIP beads were subjected to elemental analysis using a Leco Elemental Analyzer (Model CHNS-932). FTIR spectroscopy was used in the range 4000–400 cm<sup>-1</sup> to study surface chemistry of MAC monomer, MAC-Cd<sup>2+</sup> complex and mag-MIP beads in the solid state (FTIR 8000 Series, Shimadzu, Japan). The magnetism degree of the mag-p(HEMA-MAC) beads was measured in a magnetic field by using a vibrating-sample magnetometer (Princeton Applied Research, USA). The presence of magnetite particles in the polymeric structure was investigated with electron spin resonance (ESR) spectrophotometer (EL 9, Variant).

### 2.1.3. Adsorption of Cd<sup>2+</sup> Ions from Aqueous Solutions

Adsorption of Cd<sup>2+</sup> ions both on the mag-MIP and mag-NIP beads from aqueous solutions was studied in batch-wise. Nitrate salt was used as the source of Cd<sup>2+</sup> ions. Effects of Cd<sup>2+</sup> concentration on the adsorption rate and adsorption capacity were studied. For this purpose, 10 mL volume of Cd<sup>2+</sup> solutions (in the range of 0.1-50 mg/L) were treated with 25 mg of the mag-MIP and mag-NIP beads at room temperature and magnetically stirred at a speed of 600 rpm. The effects of pH, contact time and initial concentration of Cd<sup>2+</sup> ions on the adsorption capacity were studied. The pH and time range in the experiments were changed between 4,0–8,0 and 0–120 min, respectively. The effect of the initial concentration was investigated in the concentration range of 5-100 mg/L. After the desired treatment periods, the concentration of the Cd<sup>2+</sup> ions in the aqueous phase was measured by using cold vapor atomic absorption spectrometry (CVAAS). A Vapor Generation Accessory (FIAS-100 Perkin Elmer) connected to an Atomic Absorption Spectrometer (Analyst 800-Perkin Elmer, USA) was used in this study. The instrument response was periodically checked with known Cd<sup>2+</sup> solution standards. The experiments were performed in replicates of three and the samples were analyzed in replicates of three as well. For each set of data present, standard statistical methods were used to determine the mean values and standard deviations. Confidence

intervals of 95 % were calculated for each set of samples in order to determine the margin of error. The amount of  $\text{Cd}^{2+}$  adsorption per unit mass of the beads was evaluated by using the mass balance (Eq. 2.1)

$$Q = [(C_o - C) \cdot V] / m \quad (2.1)$$

## 2.2. Selectivity Experiments

In order to measure  $\text{Cd}^{2+}$  (Mw: 112.41 g/mol, ionic radius: 97 pm) specificity of the mag-MIP beads, competitive adsorptions of lead ( $\text{Pb}^{2+}$ ; Mw: 207.2 g/mol, ionic radius: 133 pm), and zinc ( $\text{Zn}^{2+}$ ; Mw=65.39 g/mol, ionic radius: 88 pm) were studied. The mag-MIP and mag-NIP beads were treated with this competitive ions. Initial concentration of  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  solutions was 10 mg/L. After adsorption equilibrium, the concentration of  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$  ions in the remaining solution was measured by AAS.

Distribution and selectivity coefficients of  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$  with respect to  $\text{Cd}^{2+}$  can be obtained from equilibrium binding data according to Eqs (2.2) and (2.3);

$$K_d = [(C_i - C_f) / C_f] \times V / m \quad (2.2)$$

Here,  $K_d$  represents the distribution coefficient;  $C_i$  and  $C_f$  are initial and final concentrations of metal ions, respectively.  $V$  is the volume of the solution (mL),  $m$  is the mass of beads used (g)

$$k = K_d (\text{Cd}^{2+}) / (K_d (\text{X}^{m+})) \quad (2.3)$$

Where  $k$  is the selectivity coefficient and  $\text{X}^{m+}$  represents  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$  ions. A comparison of the  $k$  values of the mag-MIP beads with those metal ions allows an estimation of the effect of imprinting on selectivity. A relative selectivity coefficient  $k'$  (Eq. 2.4) can be defined as

$$k' = k_{\text{imprinted}} / k_{\text{control}} \quad (2.4)$$

## 2.3. Desorption and Repeated Use

Desorption of  $\text{Cd}^{2+}$  ions were studied with 0.1 M acidic thiourea ( $\text{NH}_2\text{SHNH}_2$ ) solution. The MAG-MIP beads were placed in this desorption medium and stirred continuously (at a stirring rate of 400 rpm) for 1 h at room temperature. The desorption ratio was calculated from the amount of  $\text{Cd}^{2+}$  ions adsorbed on the beads and the final  $\text{Cd}^{2+}$  ions concentration in the desorption medium.  $\text{Cd}^{2+}$  ions adsorption-desorption procedure was repeated ten times

using the same beads for the reusability of the mag-MIP beads. The beads were washed by using 0.1 M  $\text{HNO}_3$  solution to regenerate after desorption.

## 3. RESULTS AND DISCUSSION

The molecular formula of synthesized MAC comonomer and MAC-  $\text{Cd}^{2+}$  complex is shown in Figure 1. MAC- $\text{Cd}^{2+}$  is incorporated into the HEMA monomer by radical suspension polymerization. The incorporation of the MAC- $\text{Cd}^{2+}$  complex monomer into mag-MIP beads were found to be 41,8  $\mu\text{mol/g}$  polymer by using nitrogen stoichiometry, respectively.

FTIR spectrum of MAC has the characteristic stretching vibration amide I and amide II absorption bands at 1651  $\text{cm}^{-1}$  and 1558  $\text{cm}^{-1}$ , carbonyl band at 1724  $\text{cm}^{-1}$  (Fig. 2). For the characteristic determination of complex, due to linear coordinate covalent complex formation, the characteristic strong S-H stretching vibration bands at 970  $\text{cm}^{-1}$  slips to the higher frequency field at 750  $\text{cm}^{-1}$ , (show on FTIR spectrum as indicated in red arrow) as a result of decreasing the electron density of sulfhydryl group of MAC monomer.

Then, MAC- $\text{Cd}^{2+}$  complex was polymerized with HEMA comonomer by suspension polymerization technique. The FTIR spectrum of mag-MIP beads has the characteristic stretching vibration band of hydrogen bonded alcohol, O-H, around 3444  $\text{cm}^{-1}$ , carbonyl at 1731  $\text{cm}^{-1}$  amide II absorption bands at 1455  $\text{cm}^{-1}$ , respectively (Figure 3).

The mag-MIP beads were spherical in shape with a size range of 63-140  $\mu\text{m}$  in diameter mostly. The specific surface area of the NIP beads was found to be 20.3  $\text{m}^2/\text{g}$ . The specific surface area of the mag-MIP beads was also measured and obtained as 24.7  $\text{m}^2/\text{g}$ . The mag-MIP beads are crosslinked hydrophilic matrices. The equilibrium swelling ratios of the mag-NIP and the mag-MIP beads were found as 63 % and 70 %, respectively. The surface morphology and bulk structure of the mag-MIP beads are exemplified by the electron micrographs in Figure 4. All the beads have a spherical form and rough surface. In the SEM photograph of the bulk structure, a large quantity of well-distributed pores could be observed and they were netlike. It is well known that, in order to facilitate the transfer of metal ions, the gel beads should have large pores (i.e., mesopores). The

mag-MIP beads prepared in this study had this characteristics and these mesopores would increase the specific surface area, the adsorption capacity of mag-MIP beads, as well as the mass

transfer rate of releasing and rebinding template metal ions. It is clearly seen also that the mag-MIP beads were more porous than the corresponding mag-NIP beads.

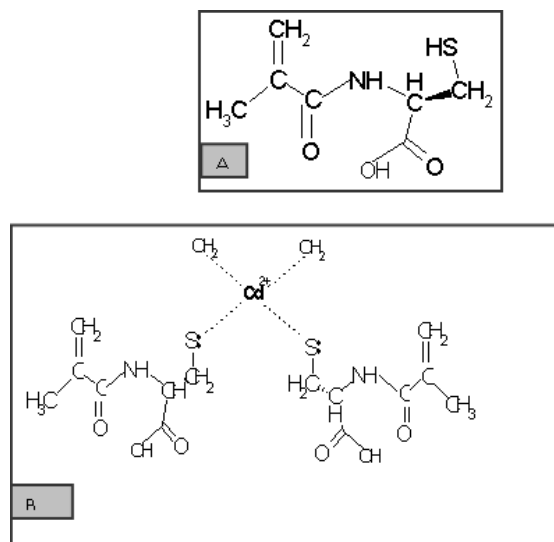


Figure 1. The molecular formula of (A) MAC monomer and the possible structure of (B) MAC-  $\text{Cd}^{2+}$  complex monomer.

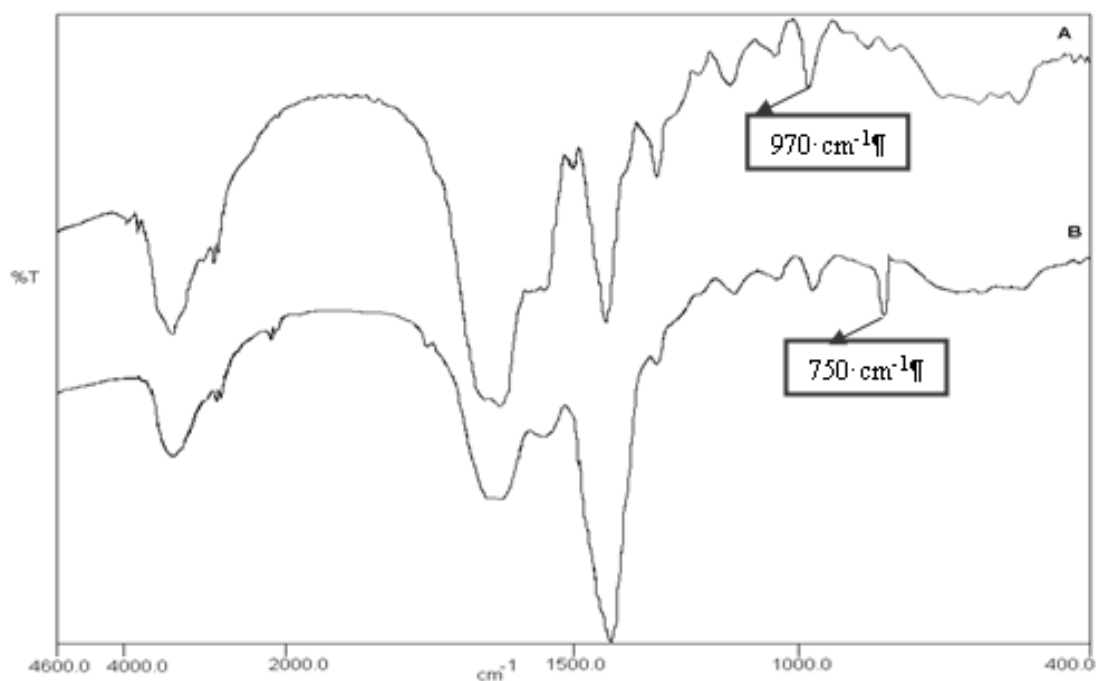


Figure 2. FTIR spectrum of MAC- $\text{Cd}^{2+}$  monomer (A) and MAC (B).

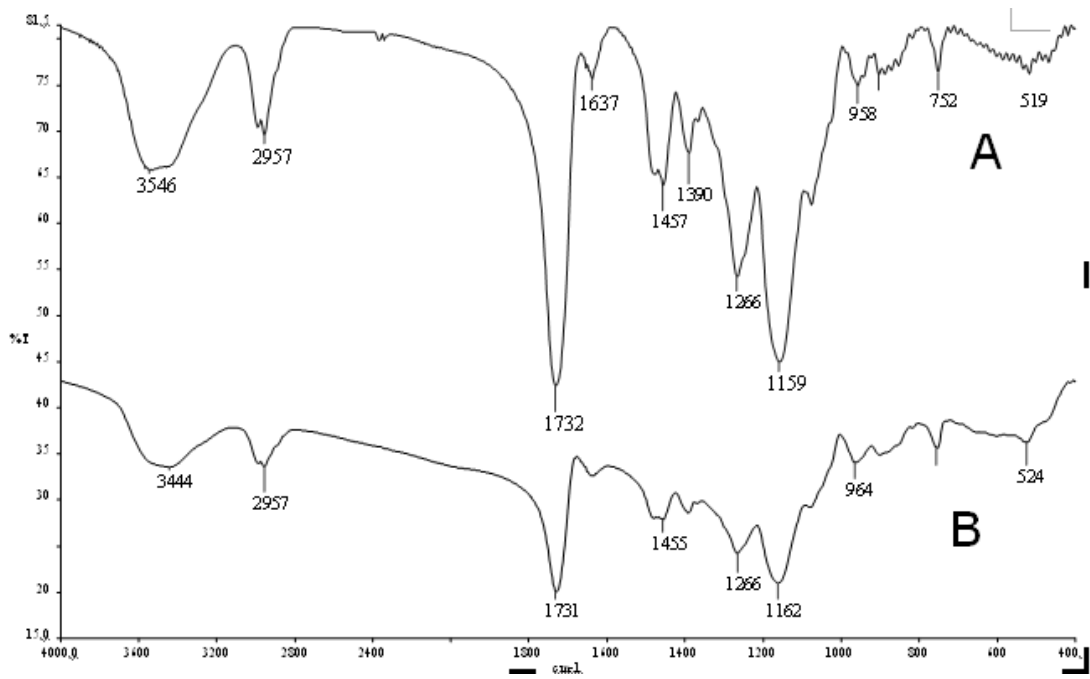


Figure 3. FTIR spectra of the mag-NIP (A) and the mag-MIP (B) beads.

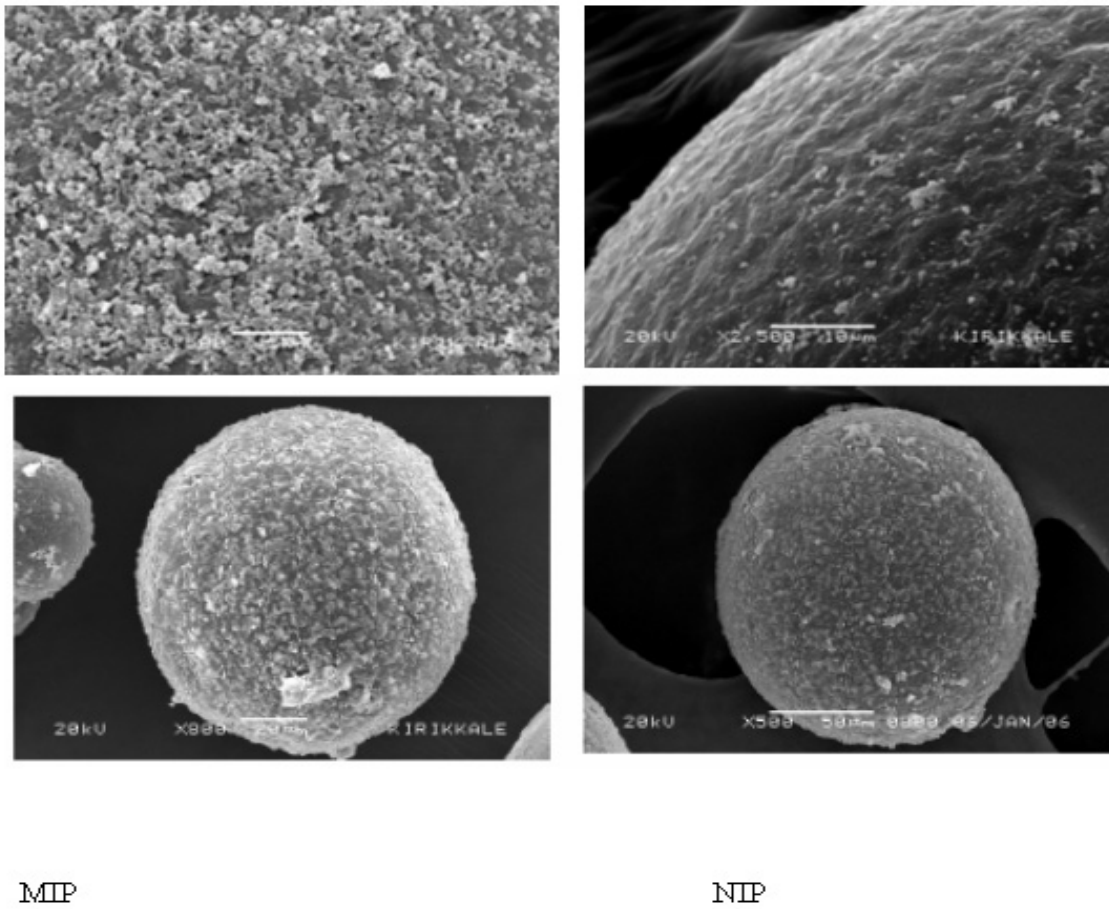


Figure 4. SEM micrographs of mag-MIP and mag-NIPbeads.

The presence of magnetite particles in the polymeric structure was confirmed by electron spin resonance (ESR). Intensity against magnetic field (Gauss) is shown in Figure 5. The application of an external magnetic field may generate an internal magnetic field in the sample which will add to or subtract from the external field. The local magnetic field generated by electronic magnetic moment will add vectorially to the external magnetic field ( $H_{ext}$ ) to give an effective field ( $H_{eff}$ ); that is,

$$H_{eff} = H_{ext} + H_{local} \quad (3.1)$$

The mag-MIP beads have a relative intensity of 120. This value shows that polymeric structure has a local magnetic field

because of magnetite in its structure.

$$g_{eff} = h_{\cdot} / e H r \quad (3.2)$$

The g factor given in Figure 5. can be considered as a quantity characteristic of the molecules in which the unpaired electrons are located, and it is calculated from Equation 3.2. The measurement of g factor for an unknown signal can be a valuable aid in the identification of signal origin. In the literature the g factor for  $Fe^{3+}$  (low spin and high spin complexes) is determined between 1.4-3.1 and 2.0-9.7, respectively. g factor was found as 2.65 for mag-MIP and 2.64 for mag-NIP structures, respectively.

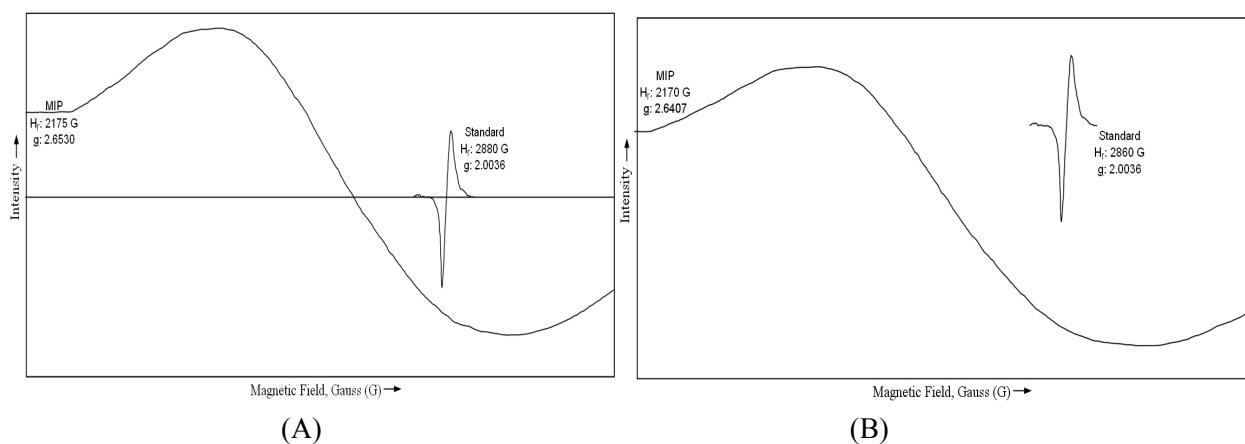


Figure 5. ESR spectra of mag-MIP (A) and mag-NIP (B) beads.

### 3.1. Adsorption of $Cd^{2+}$ from Aqueous Solutions

#### 3.1.1. Effect of pH

The pH influences the metal adsorption in two ways: (i) solubility and distribution of metal ions in the solution and (ii) overall charge of the adsorbent. The batch adsorption equilibrium was studied at different pHs in the range of 4.0–8.0. (ref- metal complexing ligand) Figure 6 shows the pH dependence of the adsorption values of  $Cd^{2+}$  ions on mag-MIP beads. As seen in Figure 6,  $Cd^{2+}$  adsorption by the mag-MIP beads was low at pH 4.0, but increased rapidly with increasing pH. Ionic interaction between  $Cd^{2+}$  and polymer increased with increasing pH. The maximum adsorption capacity for  $Cd^{2+}$  ions was observed at pH 7.4. At this pH, mag-MIP beads are effective for removal of  $Cd^{2+}$  ions from aqueous solution. The interaction between  $Cd^{2+}$  ions and thiolate groups reached

maximum. The adsorption capacity at pH 7.4 is 23.75  $\mu$ mol per gram dry weight of beads with an initial concentration of 25 mg/L.

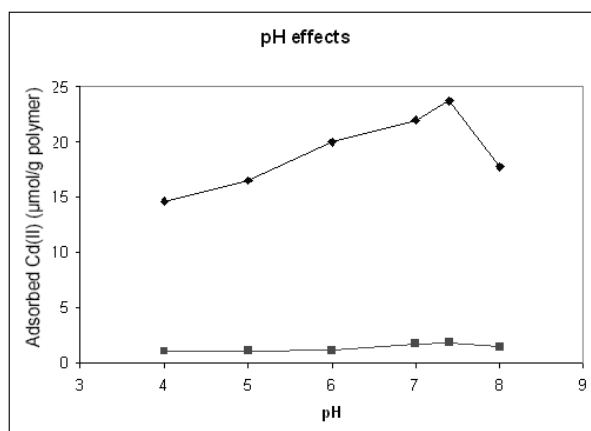


Figure 6. Effect of pH on adsorption of  $Cd^{2+}$  ions on mag-MIP beads, -♦- and on mag-NIP

beads, -■-  $V_{\text{total}}$ : 10 mL, 25 mg/L solution, 25 mg polymer, contact time: 60 min and T: 25°C.

### 3.1.2. Effect of Contact Time

Figure 7 shows the time dependence of the adsorption capacity of  $\text{Cd}^{2+}$  ions on the mag-MIP beads. The adsorption of  $\text{Cd}^{2+}$  ions is initially fast with the most cadmium being adsorbed within the first few minutes and a complete equilibrium between the two phases was established in 60 min. This fast adsorption equilibrium is most probably due to high complexation and geometric shape affinity (or memory) between  $\text{Cd}^{2+}$  ions and  $\text{Cd}^{2+}$  cavities in the mag-MIP beads structure. It is well known that removal of the template from the polymeric matrix leaves cavities of complementary size, shape and chemical functionality to the template. The maximum adsorption capacity for  $\text{Cd}^{2+}$  ions was 28.45  $\mu\text{mol}$  per gram dry weight of mag-MIP beads with an initial concentration of 40 mg/L. The adsorption time was comparable with our previous studies (Andac et al. 2004; Aşır et al. 2005).

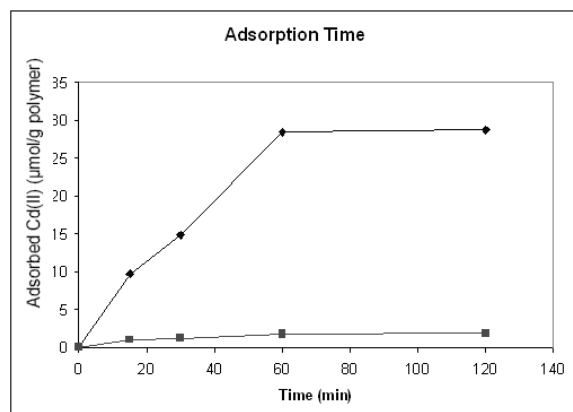


Figure 7. Time dependent adsorption of  $\text{Cd}^{2+}$  ions on the mag-MIP beads -◆- and on mag-NIP beads, -■- ;  $V_{\text{total}}$ : 10 mL, 40mg/L solution, 25mg polymer and T: 25°C.

### 3.1.3. Effect of Initial Concentration of $\text{Cd}^{2+}$ ions

Figure 8 shows the initial concentration of metal ions dependence of the adsorbed amount of the  $\text{Cd}^{2+}$  on the mag-MIP beads. The adsorption values increased with increasing concentration of  $\text{Cd}^{2+}$  ions, and a saturation value is achieved at ion concentration of 40 mg/L, which represents saturation of the active binding cavities on the mag-MIP beads. Mass

transfer limitations were also overcome by high driving force, which was the concentration difference of  $\text{Cd}^{2+}$  between the liquid and the solid phases, in the case of high  $\text{Cd}^{2+}$  concentration. Maximum adsorption capacity was 28.45  $\mu\text{mol/g}$  polymer.

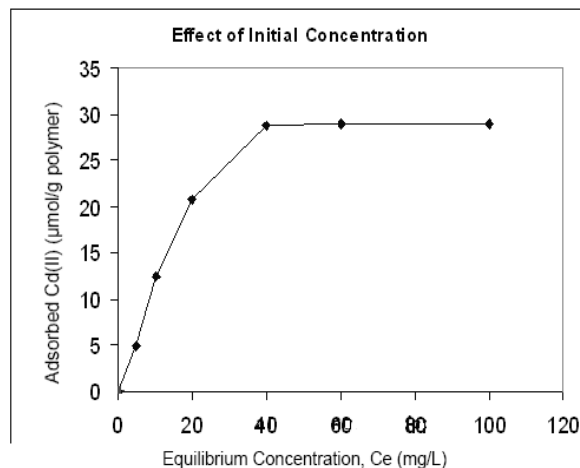


Figure 8. Effect of initial  $\text{Cd}^{2+}$  concentration on adsorption of  $\text{Cd}^{2+}$  ions on the mag-MIP beads; pH 7.4;  $V_{\text{total}}$ : 10 mL; 25 mg polymer, contact time: 60 min, T: 25 o C.

## 3.2. Adsorption Isotherms

Two important physico-chemical aspects for evaluation of the adsorption process as a unit operation are the kinetics and the equilibria of adsorption. Modelling of the equilibrium data has been done using the Langmuir and Freundlich isotherms (Freunlich, 1906; Langmuir, 1918). The Langmuir and Freundlich isotherms are represented as follows Equations 3.3 and 3.4, respectively.

$$1/q_e = (1/q_{\text{max}}) + [1/(q_{\text{max}} b)] (1/C_e) \quad (3.3)$$

$$\ln q_e = 1/n (\ln C_e) + \ln KF \quad (3.4)$$

where,  $b$  is the Langmuir isotherm constant,  $KF$  is the Freundlich constant, and  $n$  is the Freundlich exponent.  $1/n$  is a measure of the surface heterogeneity ranging between 0 and 1, becoming more heterogeneous as its value gets closer to zero. The ratio of  $q_e$  gives the theoretical monolayer saturation capacity of mag-MIP beads.

Some model parameters were determined by nonlinear regression with commercially available software and are shown in Table 1.



Comparison of all theoretical approaches used in this study shows that the Langmuir equation fits the experimental data best. This means that the

interaction between polymer and Cd<sup>2+</sup> ions was monolayer.

Table 1. Adsorption constants of Langmuir and Freundlich isotherms.

	Experimental	Langmuir constants			Freundlich constants		
	q <sub>ex</sub> (μmol/g)	q <sub>e</sub> (μmol/g)	b (g/μmol)	R <sup>2</sup>	K <sub>F</sub>	n	R <sup>2</sup>
MIP beads	28.45 ± 3.85	34.01 ± 4.25	9.35 10 <sup>-3</sup>	0.97 ± 0.11	3.94 ± 1.02	0.32 ± 0.01	0.82 ± 0.11

### 3.3. Adsorption Dynamics

In order to quantify the extent of uptake in adsorption kinetics, the kinetic models (Pseudo-first- and second-order equations) can be used in this case assuming that the measured concentrations are equal to adsorbent surface concentrations (Ho and McKay, 1999). The pseudo first-order rate equation of Lagergren is one of the most widely used for the adsorption of solute from a liquid solution. It may be represented as follows:

$$\log (q_e - q_t) = \log (q_{1cal}) - (k_1 t) / 2.303 \quad (3.5)$$

where q<sub>e</sub> is the experimental amount of Cd<sup>2+</sup> adsorbed at equilibrium (μmol /g); q<sub>t</sub> is the amount of Cd<sup>2+</sup> adsorbed at time t (μmol /g); k<sub>1</sub> is the equilibrium rate constant of first order adsorption (1/min); and q<sub>1cal</sub> is the adsorption capacity calculated by the pseudo-first-order model (μmol /g).

The rate constant for the pseudo second-order adsorption could be obtained from the

following equation:

$$(t/q_t) = (1/k_2 q_{2cal}^2) + (1/q_{2cal}) t \quad (3.6)$$

where k<sub>2</sub> is the equilibrium rate constant of pseudo-second-order adsorption (g/ μmol.min); q<sub>2cal</sub> is the adsorption capacity calculated by the pseudo-second-order kinetic model (μmol /g).

Table 2 shows the results which are for both pseudo first order and the second order kinetic models. The results show that the pseudo-second order mechanism is applicable (R<sup>2</sup> values are the highest). These results suggest that the pseudo-second order mechanism is predominant. The rate-controlling mechanism may vary during the course of the adsorption process three possible mechanisms may be occurring (Oncel et al. 2005). There is an external surface mass transfer or film diffusion process that controls the early stages of the adsorption process. This may be followed by a reaction or constant rate stage and finally by a diffusion stage where the adsorption process slows down considerably (Allen et al. 2005).

Table 2. The pseudo first- and second-order kinetic constants for the mag-MIP beads.

Initial Conc. (mg/L)	Experimental	First-order kinetic			Second-order kinetic		
		q <sub>e</sub> (μmol/g)	k <sub>1</sub> (1/min)	q <sub>1cal</sub> (μmol/g)	R <sup>2</sup>	k <sub>2</sub> (g/μmol.min)	q <sub>2cal</sub> (μmol/g)
40	28.94 ± 2.89	2.8 x 10 <sup>-2</sup>	31.66±0.65	0.77 ± 0.18	5.3 x 10 <sup>-4</sup>	40.98± 3.25	0.94±0.28

### 3.4. Selectivity Experiments

Molecular recognition selectivity is the most important parameter in characterizing MIPs because molecular recognition is the essential character of MIPs. Competitive adsorptions of Pb<sup>2+</sup>/Cd<sup>2+</sup> and Zn<sup>2+</sup>/Cd<sup>2+</sup> from

their mixtures were also studied in a batch system. Pb<sup>2+</sup> (Mw: 207.2 g/mol, ionic radius: 133 pm) and Zn<sup>2+</sup> (Mw=65.39 g/mol, ionic radius: 88 pm) were chosen as competitive metal ions because of their similar ionic radii with respect to Cd<sup>2+</sup> (Mw: 112.41 g/mol, ionic radius: 97 pm). Table 3 summarizes K<sub>d</sub>, and k, values of

Pb<sup>2+</sup> and Zn<sup>2+</sup> with respect to Cd<sup>2+</sup>. A comparison of the  $K_d$  values for the mag-MIP samples with the control samples shows an increase in  $K_d$  for Cd<sup>2+</sup> while  $K_d$  decrease for Pb<sup>2+</sup> and Zn<sup>2+</sup>. The relative selectivity coefficient is an indicator to express metal adsorption affinity of recognition sites to the imprinted Cd<sup>2+</sup> ions. These results show that relative selectivity coefficients of the mag-MIP

beads for Pb<sup>2+</sup>/Cd<sup>2+</sup> and Zn<sup>2+</sup>/Cd<sup>2+</sup> were 28.65, 117.5 times greater than the mag-NIP matrix, respectively (Table 3). Thus ion-imprinted polymers with preorganized cavities can improve the selectivity of metal cations in separation. In our recent studies, we have separated Cd<sup>2+</sup> ions from their Pb<sup>2+</sup> and Zn<sup>2+</sup> mixtures with high selectivity by using non-magnetic ion-imprinted polymers (Andac et al. 2004).

Table 3.  $K_d$ ,  $k$ , and  $k'$  values of Pb<sup>2+</sup> and Zn<sup>2+</sup> with respect to Cd<sup>2+</sup>.

Mag-NIP beads		Mag-MIP beads			
Metal ions	$K_d$	$k$	$K_d$	$k$	$k'$
Cd <sup>2+</sup>	6.90 ± 1.85	-	297.2 ± 25.80		
Pb <sup>2+</sup>	10.26 ± 2.85	0.67 ± 0.11	15.40 ± 1.89	19.20 ± 1.65	28.65 ± 11.45
Zn <sup>2+</sup>	31.97 ± 4.28	0.21 ± 0.01	12.04 ± 0.98	24.68 ± 2.28	117.5 ± 22.48

### 3.5. Desorption and Repeated Use

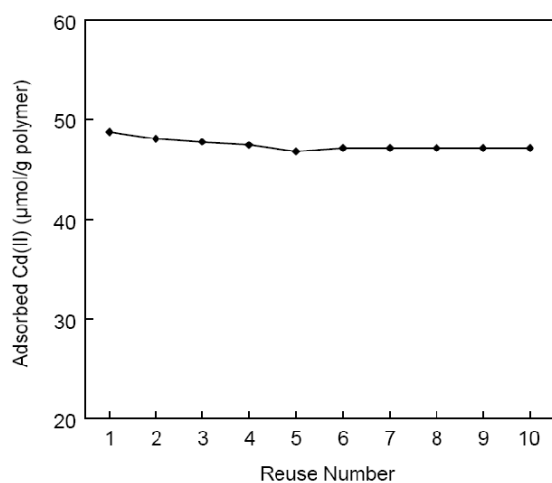


Figure 9. Adsorption-desorption cycle of mag-MIP beads. pH 7.4;  $C_i$ : 25 mg/L  $V_{total}$ : 10 mL; 25 mg polymer, desorption time: 60 min, T: 25 °C.

The regeneration of the adsorbent is likely to be a key factor in improving process economics. In order to show the stability and reusability of the MIP particles, the adsorption-desorption cycle was repeated ten times using the same polymeric particles in a batch experimental set-up. In this study, desorption time was found as 60 min. At the end of ten adsorption-desorption cycle, there was no

remarkable decrease in the adsorption capacity (Figure 9). As seen in Figure 9, the polymer beads are very stable, and maintain their adsorption capacity at almost constant value of 82%. It can be concluded that the mag-MIP beads can be used many times without decreasing their adsorption capacities significantly.

### 4. CONCLUSIONS

We have prepared mag-MIP beads for selective removal of Cd<sup>2+</sup> ions from aqueous solutions by the purpose of using these mag-MIP beads in batch systems. We have demonstrated that imprinted magnetic polymers removed Cd<sup>2+</sup> ions from aqueous solutions with high selectivity. The preorganized cavities in ion-imprinting process play important role on the observed selectivity. Since, the mag-NIP beads removed Cd<sup>2+</sup> ions from aqueous solutions non-selectively. The relative selectivity coefficients of the mag-MIP beads for Pb<sup>2+</sup>/Cd<sup>2+</sup> and Zn<sup>2+</sup>/Cd<sup>2+</sup> were 28.65, 117.5 times greater than the mag-NIP matrix, respectively. Furthermore, these mag-MIP beads can be used many times without decreasing their adsorption capacities significantly. Overall, the reported study can be used effectively to carry out in batch systems.

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