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ARAŞTIRMA MAKALESİ / **RESEARCH ARTICLE**

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SELECTIVE REMOVAL OF Cd(II) USING DOUBLE IMPRINTED POLYMER FROM SYNTHETIC WATER

ABSTRACT

The aim of this study is to prepare ion-imprinted polymers which can be used for the selective removal of Cd(II) from synthetic water. Ion-imprinted polymer particles have been prepared by molecular imprinting technique using 3-mercaptopropyl-trimethoxysilane as monomer, tetraethoxysilane as crosslinking agent in the presence of Cd(II) and dodecylamine. After that, the template ions have been removed using 0.1 M HNO_3/ethanol. A batch procedure has been used for the determination of the characteristics of the Cd(II) solid phase. The obtained results have shown that IIP has a large adsorption capacity (98.2 mgg^{-1}). Optimum pH and adsorption time have found to be 5.0 and 2 h, respectively. In selectivity study, it has found that imprinting have been increased affinity of the material toward Cd(II) ion over other competitor metal ions with the same charge. The selectivity of Cd(II)/Zn(II), Cd(II)/Cu(II) and Cd(II)/Hg(II) have found to be 2.73, 8.83 and 112 respectively.

Keywords: Ion-imprinted, Cadmium Separation, Preconcentration, Sol-gel

SENTETİK SUDAN ÇİFT BASKILI POLİMER KULLANILARAK Cd(II)'NİN SEÇİCİ UZAKLAŞTIRILMASI

ÖZ

Bu çalışmanın amacı, sentetik sudan Cd(II)'nin seçici uzaklaştırılması için kullanılabilecek iyon baskılı polimer hazırlamaktır. İyon baskılı polimer partikülleri, dodesilamin ve Cd(II) varlığında, çapraz bağlayıcı olarak teraetoksisilan, monomer olarak 3-merkaptopropil-trimetoksilanın kullanıldığı moleküler baskılama tekniği ile hazırlanmıştır. Daha sonra baskı iyonları 0,1 M HNO3/etanol kullanılarak uzaklaştırılmıştır. Beç işlemi, Cd(II) katı faz özelliklerinin belirlenmesi için kullanılmıştır. Elde edilen sonuçlar, iyon baskılı polimerin büyük adsorpsiyon kapasitesine (98.2 mgg-1) sahip olduğunu göstermiştir. Optimum pH ve adsorpsiyon süresi sırasıyla 5.0 ve 2 saat olarak bulunmuştur. Seçicilik çalışmalarında, baskılama aynı yüklü diğer yarışmacı metal iyonları üzerinden Cd(II) iyonlarına doğru materyalin afinitesinin arttığı bulunmuştur. Cd(II)/Zn(II), Cd(II)/Cu(II) and Cd(II)/Hg(II)'ın seçicilikleri sırasıyla 2,73; 8,83 ve 112 olarak bulunmuştur.

Anahtar Kelimeler: İyon baskılama, Kadmiyum ayırma, Önderiştirme, Sol jel

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1. INTRODUCTION

Cadmium is widely used in several industries including metallurgy, surface treatment, dye synthesis or battery production. Due to its severe toxicity to animals and humans, even at low concentrations, cadmium is known to be one of the most toxic heavy metal elements. Consequently, cadmium removal has been given great priority in the last decade (Lu and Yan 2004; Lemos and. Baliza, 2005; Fang et al., 2005; Amorim et al., 2005; Davis et al., 2006). Owing to the co-existence of various heavy metal ions in industrial effluents or other water resources, selective removal of toxic metal ions attracts much attention in both industries and researches. Sorption based on suitable sorbent possessing selectivity toward the offending heavy metals, is inherently attractive and more popular for selective removal of metal ion from aquatic environment, especially from dilute aqueous solutions(Lu and Yan 2004; Fang et al., 2005) Therefore, development of novel solid sorbents for selective cadmium clean-up in environmental and biological samples is of great significance.

Molecular imprinting has been defined as a synthetic approach by which a molecular receptor is assembled via template-guided synthesis (Wulff G, 1995). Binding sites are created by polymerization of the functional and crosslinking monomers in the presence of the target molecule (template) (Ramstrom et al.,1996). Leaching out to the template leaves behind binding sites that are complementary in size and shape to the imprinted molecule. An ion-imprinted polymer is obtained when a metal ion is used as template in the above-described synthesis. In most cases, specific ligands capable to form a stable complex with the metal ion (or metal ion complexes with such specific ligands) are used in the polymerization process. The high selectivity of IIP can be explained by the polymer memory effect toward the metal ion interaction with a specific ligand, coordination geometry, metal ion coordination number, charge and size (Wulff G, 1995). Numerous studies on IIPs and their use for selective preconcentration and separation of metal ions have been reported (Bae et al.,, 1999; Saunders et al.2000; Gladis et al. 2003; Rosatzin et al.1991; Daniel et al., 2005; Daniel et al., 2005; Biju et al., 2003; Prasad et al.;2006; Makote and Dai 2001; Say et al. 2003; Birlik 2006; Ersöz et al., 2004; Liu et al.,2004; Kala et al., 2004; Büyüktiryaki et al.,2005; Andac et al.,2006; Karabork et al.,2008; et al., 2005).

In this study, an ion-imprinting polymer was prepared preorganizing 3-mercaptopropyl-trimethoxysilane monomer, dodecylamine (DDA) and cadmium (template) ion with the goal of preparing a solid-phase which has the high selectivity for Cd(II) ions. Ion-imprinted beads were polymerized with the use of 3-mercaptopropyl-trimethoxysilane-Cd(II)-DDA complex monomer and tetraethoxysilane (TEOS). After removal of Cd(II) ions, ion-imprinted beads were used for solid-phase extraction and preconcentration of Cd(II) ions.

Cd(II) adsorption and selectivity studies of Cd(II) versus other metal ions such as Hg(II), Cu(II) and Zn(II), were reported here. Finally, use of Cd(II) receptor beads for the separation and preconcentration of Cd(II) was also discussed.

2. EXPERIMENTAL

2.1 Chemicals

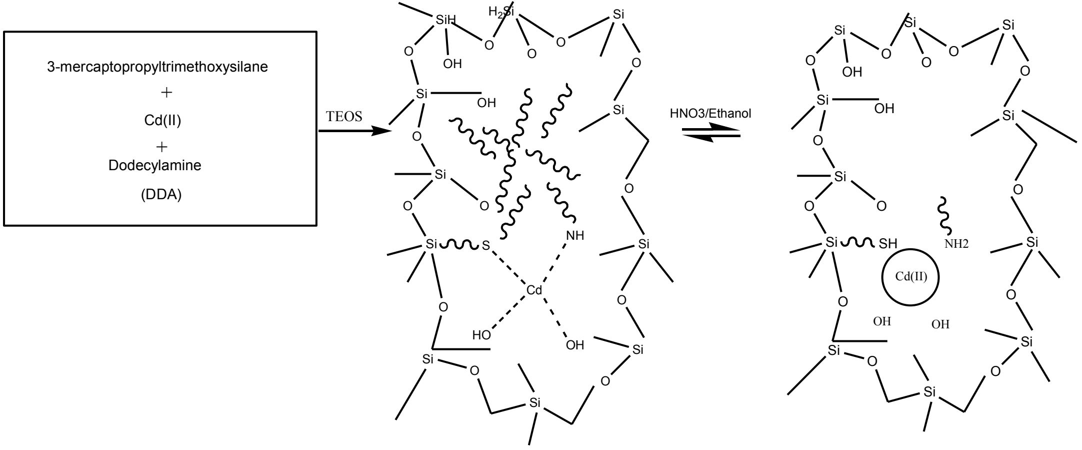
DDA (dodecylamine) and 3-mercaptopropyl-trimethoxysilane were supplied from Aldrich Chemical (USA). All other chemicals were analytical reagent grade and purchased from Merck (Darmstadt,Germany).

2.2. Apparatus

A Hitachi 180-70 polarized Zeeman flame atomic absorption spectrophotometer (FAAS) with deuterium background correction was used for the determination of Cd(II), Hg(II) and Zn(II) ions. FTIR was used in the range of 4000-400 cm^{-1} to investigate the double-imprinted polymer (FTIR 100 series, Perkin Elmer, USA). Jenway 3100 pH-meter was used to mesaure pH values.

2.3.Preparation of Ion-Imprinted Polymers

5.561 g DDA was dissolved in 44.7/57.5 mL of methanol/ water mixture and 4.626 g $Cd(NO_3).H_2O$ was added into this solution with continuous stirring at room temperature. Then, this mixture was reacted with 3.5 mL of 3-mercaptopropyl-trimethoxysilane for 4 h. The obtained mixture was crosslinked by 3.5 mL of tetraethoxysilane (TEOS) under refluxing conditions in an oil bath (ca. 110 ^oC) for 8 h. The solid product was recovered by filtration. Then, it was refluxed in ethanol/HNO_3 to extract the surfactant templates with ethanol and to strip the Cd(II) ion templates by protonation of 0.1 M HNO_3. The product was washed with deionize water, and dried under vacuum. For comparison of single and double imprinted polymer, the ion-imprinted polymer was also prepared using an identical procedure, but without the addition of DDA. The non-imprinted polymer (NIP) was prepared in paralel without addition of Cd(II). The scheme 1 shows the synthesis of ion-imprinted polymer using Cd(II) and DDA.



Scheme 1. The schematic representation of ion-imprinted polymer using Cd(II) and DDA.

2.4. Sorption Experiments

The effect of pH on the sorption of Cd(II) was tested by equilibrating 25 mg prepared sorbent with 25 ppm, 25 mL of Cd(II) solutions under different pH conditions. The pH of the solutions was adjusted using $NaOH/HNO_3$ solution. Samples were regularly collected at appropriate time intervals, separated and analyzed for Cd(II) content. To measure the sorption capacity, 25 mg ion-imprinted sorbent was equilibrated with 25 mL of various concentrations of Cd(II) solutions at pH 5.0.

Competitive loading of Cd(II), Hg(II) and Zn(II) by IIP and NIP sorbents was investigated in Cd(II)/Zn(II) and Cd(II)/Hg(II) binary aqueous solutions at pH 5.0. 25 mg portion of IIP and NIP sorbent was treated with 10 ppm, 25 mL of Cd(II)/Zn(II), Cd(II)/Hg(II) mixtures. In all the above batch experiments, the mixtures were centrifugally separated. The cadmium concentration in the sorbent was determined by FAAS. The amount of adsorbed Cd(II) was calculated by the following Eq. (1):

$$Q = (C_0 - C_e)V/ m \quad (1)$$

Where C_0 and C_e represent initial and equilibration concentration of Cd(II), respectively, V is the volume of solution, m is the weight of the sorbent.

For the preconcentration of Cd(II) ions, 100 mL of the aqueous solution containing 5.0 ng mL^{-1} Cd(II) was treated with 25 mg imprinted microbeads at pH 5.0 for 2 h. Finally, IIPs were separated from the adsorption media by filtration and 10 mL of HNO_3 solution was added and stirred at 400 rpm for 3 h. Imprinted polymers were separated from the desorption media and the concentration of Cd(II) ions in the desorption media was determined by FAAS system.

2.5. Reusability of the Ion-imprinted Sorbent

The Cd(II) ion recognized on the sorbent was stripped washing with 0.1 M HNO_3. The acid-treated sorbent was rinsed several times with deionized water. The same sorbent was extracted and regenerated five times and then used to remove Cd(II) ion.

3. RESULTS and DISCUSSION

3.1. Characterization of IIP

The resulting imprinted particles were characterized by FTIR. The FTIR spectra of the ion-imprinted polymer showed aliphatic C-H band at 2926 cm^{-1}, Si-O-Si band at 1047 cm^{-1}, S-H band at 956 and 799 cm^{-1}. This result indicated that DDA-Cd(II) was connected to 3-mercaptopropyl-trimethoxysilane.

3.2. Cd(II) Sorption to The Sorbent

3.2.1. Equilibrium Adsorption Time

For the determination of adsorption time, 25 mg sorbent was added to 25 mL 25 mgL^{-1} of Cd(II) solution at pH 5.0. The resulting suspension was stirred for different periods of time in the range of 15 to 180 min., using magnetic stirrer. After the adsorption of Cd(II) ion by the imprinted polymer, the amount of Cd(II) ion in the solution was determined by FAAS.

Figure 1 shows adsorption rates of Cd(II) ions onto the ion-imprinted polymers from aqueous solutions. Note that the ordinate values on this were calculated by using the expression given eq. (1). As seen here, adsorption equilibrium was gradually reached within 2 h for ion-imprinted polymers.

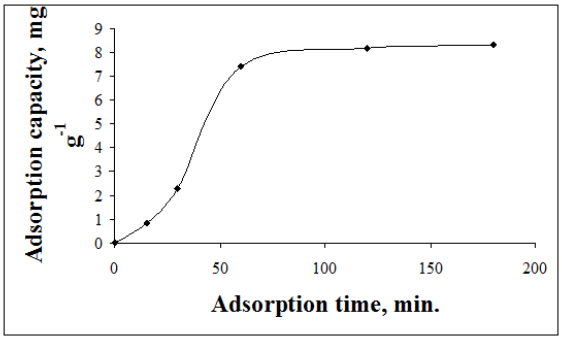


Figure 1. Adsorption rates of Cd(II) ions on the ion-imprinted polymers; pH: 5.0; T: 25 °C.

Several experimental data on the adsorption of various ions by chitosan have shown a wide range of adsorption rates. For example, Li et al. have prepared ion-imprinted sorbent for selective separation of Cd(II) from aqueous solution and beads and reported 20 min. equilibrium adsorption time (Li et al., 2007). Andaç et al. have used Cd(II)-imprinted polymer for cadmium removal from human plasma and found 60 min. as an equilibrium time (Andaç et al., 2004). These results can be explained that, the interaction between the binding sites which are produced by double-imprinted technique and Cd(II) ions needs more time to reach equilibrium than that of single imprinted technique.

3.2.2. Effect of pH

The effect of pH on Cd(II) sorption onto ion-imprinted composite sorbent was investigated varying the pH between 2.0 and 7.0, as shown in Figure 2. The sorption of Cd(II) increased as the pH increased. This mainly due to the protonation of the thiol moiety, which diminished the ability of thiol grup to be involved in chelate formation with the Cd(II) in aqueous solution at pH≤3. The pH 5.0 was chosen for further sorption performance, because in this pH, neither precipitation of the metal hydroxide nor the protonation of thiol with the active chelating group was observed.

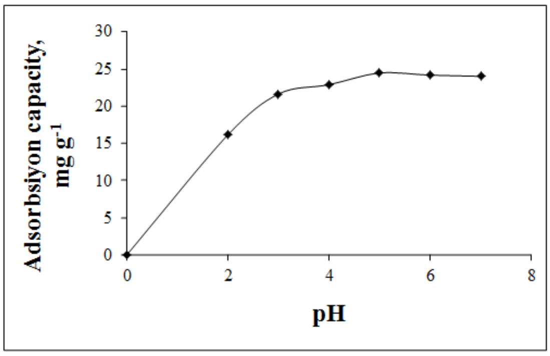


Figure 2. Effect of pH on sorption of Cd(II) ions on ion-imprinted polymers (T: 25 °C.

3.2.3. Adsorption Capacity

The adsorption capacity of Cd(II) sorption to the ion-imprinted composite sorbent was also investigated. Figure 3 shows effects of initial concentration of Cd(II) ions onto the adsorption capacity of the ion-imprinted polymer at pH 5.0. The amount of Cd(II) ions adsorbed per unit mass of the polymer (i.e., adsorption capacity) increased with the initial concentration of Cu(II) ions. The maximum adsorption (corresponding a 500 ppm Cu(II) ion initial concentration), which represents saturation of active points (which are available for Cd(II) ions) on the polymers was 98.2 mg Cd(II)/g polymer.

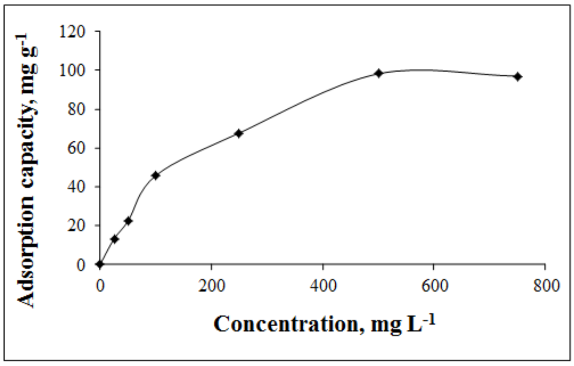


Figure 3. Adsorption capacity of Cd(II) ions on the ion-imprinted polymer; pH: 5.0; T: 25 °C.

During batch experiments, adsorption isotherms were used to evaluate adsorption properties. For the systems considered, the Langmuir model was found to be applicable in interpreting Cd(II) adsorption by imprinted polymer. Figure 4 shows the dependence of the equilibrium concentration on the adsorbed amonut of Cd(II) onto the double-imprinted polymer. Langmuir adsorption model assumes that the molecules are adsorbed at a fixed number of well-defined sites, each of which can only hold one molecule. These sites are also assumed to be energetically equivalent, and distant to each other so that there are no interactions between molecules adsorbed to adjacent sites (Labrou et al., 1995). The corresponding transformations of the equilibrium data for Cd(II) ions gave rise to a linear plot, indicating that the Langmuir model can be applied in these systems and describes by the equation:

$$Q=Q_{max}bC_e/(1+bC_e) \tag{3}$$

where Q is the concentration of bound Cd(II) ions in the adsorbent (µmolg^{-1}), C_e is the equilibrium Cd(II) ions concentration in solution (µmolL^{-1}), b is the Langmuir constant (gµmol^{-1}) and Q_{max} is the maximum adsortion capacity (µmolg^{-1}).

The maximum adsorption capacity (Q_{max}) data for the adsorption of Cd(II) ions was obtained from the experimental data. The correlation coefficient (R^2) was found to be 0.9713. The Langmuir adsorption model can be applied in this affinity adsorbent system. It should be also noted that maximum adsorption capacity (Q_{max}) was found to be 101.8 mgg^{-1}.

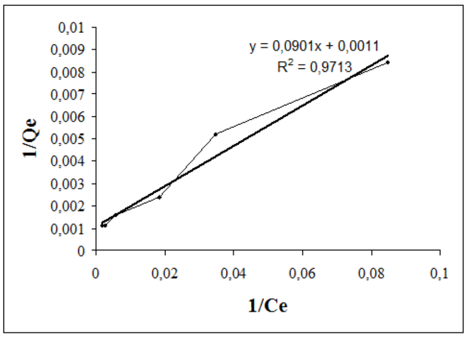


Figure 4. Adsorption isotherm of Cd(II) ion-imprinted polymer; pH: 5.0; T: 25 °C.

3.2.4. Selectivity Studies

The selectivity of the IIP and NIP sorbents was investigated by studying competitive loading of Hg(II), Cu(II) and Zn(II) in their binary mixture. Table 1 summarized parameters of distribution coefficient (K_d), selectivity coefficient (k) of the sorbent toward Cd(II), and the relative selectivity coefficient (k’). The k value for the imprinted sorbent showed significant increase compared with that of the non-imprinted sorbent.

A comparison of the selectivity coefficient of IIP to the selectivity coefficient of NIP showed that the imprinted matrix for Cd(II)/Zn(II), Cd(II)/Cu(II) and Cd(II)/Hg(II) were 2.73; 8.83 and 112.8 times greater than non-imprinted matrix, respectively (Table 1). This means that Cd(II) ions can be determined even the presence of Zn(II), Cu(II) and Hg(II) interferents.

3.2.5. Reusability of The Sorbent

The reusability of sorbent is very important for economic competition. Adsorbed Cd(II) ions were removed by the addition of 0.1 M HNO_3 (Afterwards, the sorption ability was resumed). In order to test the reusability, the adsorption/desorption cycle was repeated 7 times (Figure 5).

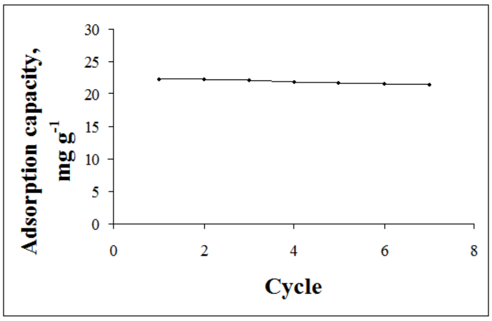


Figure 5. Adsorption-desorption cycle

The results showed that the adsorption capacity of the recycled double imprinted particles can still be maintained at 95 % of its original value at the 7th cycle.

3.2.6. Analytical Performance

For the preconcentration of cadmium ions, 100 mL of the aqueous solution containing 5.0 ng mL^{-1} Cd(II) ions was treated with 25 mg ion-imprinted microbeads at pH 5.0 for 2 h. Finally, polymeric microbeads were separated from the adsorption media and 10 mL of HNO_3 solution was added and stirred at 400 rpm for 2 h. Imprinted microbeads were removed from the desorption medium and concentration of Cd(II) ions in the desorption medium was determined by FAAS.

The characteristic performance data for the off-line preconcentration procedure were given in Table 2

.

Table 1. The effect of imprinting on selectivity

Polymer	Cd(II) (mgL^{-1})	Zn(II) (mgL^{-1})	K_D (Cd(II))	K_D (Zn(II))	k	k'
Non-Mip	10	10	10160	23750	0.428	
Ion-Imprinted Polymer	10	10	48260	41190	1.171	2.73
Non-Mip(without DDA)	10	10	5934	6013	0.983	
Ion-Imprinted Polymer (without DDA)	10	10	2626	2588	1.01	1.028
Polymer	**Cd(II) (mg/l)**	**Hg(II) (mg/l)**	**K_D (Cd(II))**	**K_D (Hg(II)**	**k**	**k'**
Non-Mip	10	10	1799	162900	0.011	
Ion-Imprinted polymer	10	10	34840	28240	1.243	112
Non-Mip(without DDA)	10	10	6257	162900	0.038	
Ion-Imprinted Polymer (without DDA)	10	10	4970	162900	0.03	0.78
Polymer	**Cd(II) (mg/l)**	**Cu(II) (mg/l)**	**K_D (Cd(II))**	**K_D (Cu(II)**	**k**	**k'**
Non-Mip	10	10	5689	62290	0.091	
Ion-Imprinted polymer	10	10	35900	44670	0.8	8.83
Non-Mip(without DDA)	10	10	3468	6496	0.53	
Ion-Imprinted Polymer (without DDA)	10	10	2717	4394	0.618	1.15

Table 2. Performance characteristics of the preconcentration procedure

Parametreler	Cd
Precision (R.S.D)	7.9 %
Detection limit (3s)	0.04 ng/mL
Linear calibration range	0.01-15.0 ng/mL
Regression equation (after preconcentration)	AA=0.0034Cd + 0,0013
Conventional regression equation	AA=0.0131Cd + 0.0472
Enrichment factor	(0.0034ng/mLx1000µg/mL/0.0131=259

The precision of method for a standard, evaluated as the relative standard deviation (R.S.D:, n=7) was 7.9 ngmL^{-1} Cd(II) ions. The detection and determination limits, defined as the concentration of analyte giving signals equivalent to three the standart deviation of the blank plus the net blank intensity for 100 mL of sample volume, were 0.04 ngmL^{-1}. The preconcentration procedure showed a linear curve within the concentration range from 0.01 to 15 ngmL^{-1}. The enrichment factor, defined as the ratio of the slopes of linear section of the calibration graphs before and after the preconcentration, was 259.

Xie et al. (Xie et al., 2008) have studied solid phase extraction of Cd(II) using gallic acid-modified silica gel and reported detection limit as 0.65 µg L^{-1}. Prasad et al. (Prasad et al,2006) have investigated preconcentration of cadmium and lead from soils onto 5,7-dibromoquinoline-8-ol embedded benzophenone and found the detection limit as 0.1 µgL^{-1}.

4. CONCLUSIONS

IIP materials have attracted much attention in recent past as a highly selective polymeric sorbent material with microenvironment around the metal centre. Of late, IIPs have come to reckoning for selective removal of inorganics as this technique provides higher enrichment factors and selectivity coefficients compared to NIP. As shown in this study, IIPs can be successfully used as selective sorbents to clean up. In this study, IIP was prepared to preorganize 3-mercaptopropyl-trimethoxysilane monomer and cadmium ion and DDA with the goal preparing a solid-phase which has the high selectivity for Cd(II) ions. The amount of adsorbed Cd(II) ions per unit mass of the polymer increased with the initial concentration of the Cd(II) ions. The maximum adsorption capacity of IIP was 98.2 mgg-1 The adsorption was fast and the time required to reach equilibrium conditions was about 2 h for IIP and seems to be very satisfactory.

This adsorption equilibrium is most probably due to high complexation and geometric shape affinity (or between Cd(II) ions and Cd(II) ion cavities. The relative selectivity coefficient is an indicator to express an adsorption affinity of recognition sites to imprinted Cd(II) ions. The results showed that non-imprinted beads for Cd(II)/Zn(II), Cd(II)/Cu(II) and Cd(II)/Hg(II) were 2.73; 8.83 and 112.8 times greater than non-imprinted matrix, respectively, for ion-imprinted polymer. Ion-imprinted polymer was exhibited in most of the work to increase metal loading capacities and selectivity, as compared to ion-imprinted sorbent (without DDA). This succesful preparation of ion-imprinted polymer using metal ion and surfactant (DDA) templates demonstrated the feasibility of direct formation of the imprinted mesoporous sorbent with functional ligands for Cd(II) ion.

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