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SINGLE AND DOUBLE IMPRINTED POLYMER FOR SELECTIVE RECOGNITION OF Cd(II) IONS IN AQUEOUS MEDIA

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ABSTRACT

In this paper, we have reported the synthesis of a new single and double-imprinted polymeric material for the separation of Cd(II) ions in aqueous solutions. Chitosan has choosen as the Cd(II) metal complexing big polymer for single and double imprinted polymers. In the synthesis of single imprinted polymer, Cd(II)-complexed chitosan has crosslinked by epichlorohydrin. In the synthesis of double imprinted polymer, Cd(II)-complexed chitosan was reacted with 3-mercaptopropyltrimethoxysilane. Then, the polymeric beads have crosslinked with tetraethoxysilane (TEOS). The imprinted cadmium ions have removed from the polymeric matrix by 0.1M HNO_3 (to prepare Cd(II) templates). Optimum pH for rebinding of Cd(II) on the single and double-imprinted polymers was 7.0. Equilibrium binding time and sorbent capacity have been found as 120 and 60 min, 342 and 172 mg g^{-1} for single and double imprinted polymers, respectively. In selectivity studies, it has been found that double imprinted results in increased affinity of the material toward Cd(II) ion over other competitor metal ions with the same charge. The prepared single and double-imprinted polymers have repeatedly used and regenerated for thirty times without a significant decrease in polymer binding affinities.

Keywords: Ion imprinted polymer, Double imprinted polymer, Cadmium determination, Chitosan, Sol-gel, Solid Phase Extraction (SPE).

SULU ORTAMDA Cd(II) İYONLARININ SEÇİCİ TANIMLANMASI İÇİN TEK VE ÇİFT BASKILI POLİMERLER

ÖZ

Bu çalışmada, sulu ortamda Cd(II) iyonlarının ayrımı için yeni tek ve çift baskılı polimerik materyal sentezi gerçekleştirilmiştir. Kitosan, tek ve çift baskılı polimer için metal kompleksleyici, büyük polimer olarak seçilmiştir. Tek baskılı polimerin sentezinde, Cd(II)-kitosan kompleksi epiklorohidrin ile çapraz bağlandı. Çift baskılı polimerin sentezinde ise, Cd(II)- kitosan kompleksi 3-merkaptopropiltrimetoksisilan ile reaksiyona sokuldu. Daha sonra polimerik tanecikler, tetrametoksisilan (TEOS) ile çapraz bağlandı. Polimerik matrikste Cd(II) iyonlarına uygun yuva oluşturmak için, baskılı Cd(II) iyonları polimerden 0,1M HNO_3 ile uzaklaştırıldı. Tek ve çift baskılı polimerlerde, Cd(II) iyonlarının tekrar bağlanmsı için, optimum pH 7'dir. Tek ve çift baskılı polimerler için bağlanma denge zamanları, sırasıyla 120 ve 60 dak. Olarak; Cd(II) sorbent kapasitesi ise sırasıyla 342 ve 172 mgg^{-1} olarak bulundu. Seçicilik çalışmalarında; çift baskılama sonuçları, Cd(II) iyonlarının diğer benzer yüklü yarışmacı iyonlara göre afinitesinin yüksek olduğunu göstermiştir. Hazırlanmış tek ve çift baskılı polimerlerin bağlanma kapasitelerinde kayda değer bir değişklik olmaksızın 30 kez tekrar kullanıldı.

Anahtar Kelimeler: İyon baskılanmış polimer, Çift baskılanmış polimer, Kadmiyum tayini, Kitosan, sol-jel, Katı faz ekstraksiyonu.

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1. INTRODUCTION

Cadmium is very toxic and causes serious damage to the kidneys and bones. It is best known for its association with itai–itai disease (Kasuya, 2000). Cadmium ions have little tendency to hydrolyze at pH values <8 but above 11, all cadmium exists as its hydroxo-complex (Bodek et al.,1998). Cd(II) predominates in fresh water at pH 7–8. $CdOH^+$, $Cd(OH)_2$, $Cd(OH)_2$, $Cd(OH)^-$, $Cd(OH)^{2-}$ 4 also exist depending upon the solution pH (Bodek et al.,1998; Mohan et al, 2006). The chlorocomplexes $CdCl^+$, $CdCl_2$, CdCl- predominate in sea water and Cd(II) is present in very small amounts (Bodek et al., 1998). Cadmium accumulates in humans, causing erythrocyte destruction, nausea, salivation, diarrhea, and muscular cramps, renal degradation, chronic pulmonary problems, and skeletal deformity (Mohan, 2002). The major sources of cadmium release are the manufacturing of alloys, batteries, pigments and plastics. Mining and refining processes are also significant sources (Tsezos, 2001; Ho et al., 2006). The drinking water guideline recommended by theWHO and AWWA is 0.005 mg Cd L^{-1}.

Separation of toxic Cd(II) is of intense current interest in research and environmental cleanup. Selective removal of toxic metal ions from aqueous solutions is usually achieved by solvent extraction and solid-phase extraction (SPE) with sorbents. SPE possesses many advantages over conventional solvent extraction, including a higher enrichment factor, absence emulsion; safety with respect to hazardous samples, minimal costs due to low consumption of reagents, and flexibility and incorporation into automated analytical techniques (Thurman et al., 1998). Development of new solid sorbents for selective separation of toxic Cd(II) from aqueous solutions, therefore, is of great significance.

SPE has become the most often used sample preparation technique for trace analysis. But the selectivity of custom SPE sorbents is limited since they differentiate only by some physicochemical property like hydrophobicity. Recently, new types of SPE materials, such as highly cross-linked polymers (MIPs) are therefore currently being developed to allow more attractive extractions (Sellergren, 1999; Mullett et al., 2001; Berggren et al., 2000; Matsui et al., 2000; Mullett et al., 1999; Jodlbauer et al, 2002; Mena et al., 2002). MIPs are selective sorbents towards a particular substance, called “template”. The selectivity is generated during the synthesis of the MIP by the presence and interaction of the template (or a similar compound) with the functional monomers. The template is either covalently or noncovalently bound to the polymer network during polymerization. After the polymerization, it is removed by a suitable treatment but it leaves behind its binding sites. These can then rebind the template from different media with appreciable selectivity.

A double imprinting methodolgy is developed to synthesize novel materials. This new methodology makes use of the recent advances in the conrolled synthesis of mesoporous materials and combines them with molecular level imprinting techniques. This procedure produces imprinted mesoporous hybrid sorbent materials that exhibit not only fast binding kinetics and high capacities but also molecular recognition capabilities (Lu et al., 2004; Birlik et al., 2006; Özkütük et al., 2010).

In this study, the recognized templates chemical structure of adsorption material for Cd (II) ions were designed by molecular imprinting technique. We have selected chitosan as the metal complexing polymer by template polymerization, with the goal preparing a solid phase which has the high selectivity for the Cd(II) ions. Single and double-imprinted polymers have prepared with the use of 3-mercaptopropyltrimethoxysilane, chitosan-Cd(II) complex monomer, ephyclorohydrin and TEOS. After removal of Cd(II) ions, single and double-imprinted beads have used for the separation of Cd(II) ion from aqueous solution. Cd(II) adsorption and selectivity studies of Cd(II) versus other metal ions, which are Ni(II) and Hg(II) have reported here. Finally, repeated use of the ion-imprinted polymers has also discussed.

2. EXPERIMENTAL

2.1 Chemicals

Chitosan and 3-mercaptopropyltrimethoxysilane were supplied from Aldrich Chemical (USA). Mercury nitrate dihydrate, nitric acid, sodium hydroxide and nicel nitrate tetrahydrate were purchased from Merck (Darmstadt, Germany). Tetraethoxysilicate (TEOS) from Acros Organics (Belgium) and cadmium nitrate monohydrate from Fluka (Poland) were used in this study.

2.2 Apparatus

A Hitachi 180-70 polarized Zeeman atomic absorption spectrophotometer (AAS) with deuterium background correction was used for the determination of Cd(II), Hg(II) and Ni(II). Jenway 3100 pH-meter was used to mesaure pH values.

2.3 Preparation of Double-Imprinted Polymers

2.3.1 Single Imprinted Polymer (Cd(II)-Imprinted Chitosan)

Chitosan (1g) was dissolved in the acetic acid (5 %) and $Cd(NO_3)_2.H_2O$ (2g) was added slowly to this solution with continuous stirring at room temperature. The mixture solution was slowly dropped into 150 mL of 1 M aqueous NaOH. The suspended solution was stirred at 200 rev/min for 12 h. After filtering this white suspended solution and drying in vacou, the obtained Cd(II)-complexed chitosan was crosslinked by 5 mL of epichlorohydrin in 250 mL of the acetic acid (5 %) under refluxing conditions in an oil bath (ca. 110°C) for 1 h. Then, 250 mL of 0.1 M aqueous NaOH solution was added to complete the crosslinking reaction. After vacuum filtration, the polymer of crosslinked Cd(II)-complexed chitosan was washed with 0.1 M HNO_3 and deionized water several times to remove Cd(II) ions and clearly yellow product was obtained, after the removing of Cd(II) ions from the Cd(II)-complexed chitosan.

2.3.2 Double (Cd(II)/solgel)-imprinted polymer

Chitosan (4 g) was dissolved in the acetic acid (5 %) and $Cd(NO_3)_2H_2O$ (3.708g) was added slowly to this solution with continuous stirring at room temperature. Then, 4.48 mL of 3-mercaptopropyl-trimethoxysilane was added to above mixture. The mixture solution was slowly dropped into 150 mL of 1M aqueous NaOH. The suspended solution was stirred at 200 rev/min for 12 h. After filtering this suspended solution and drying in vacou, the obtained mixture was crosslinked by 3 mL of TEOS in 250 mL of the acetic acid (1 %) under refluxing conditions in an oil bath (ca. 110°C) for 2 h. Then, 250 mL of 0.1 M aqueous NaOH solution was added to complete the crosslinking reaction. After vacuum filtration, the product of double-imprinted polymer was washed with 0.1 M HNO_3 and deionized water several times to remove Cd(II) ions and the white product was obtained, after the removing of Cd(II) ions from the double-imprinted polymer.

2.4 Characterization of beads

The average size and size distribution of double imprinted polymer and non-imprinted polymer were determined by using a ZEN 3600 Model Zetasizer Nano-ZS (Malvern Inst. Ltd., UK). The optical device contains a 5mW He–Ne (638 nm) laser. The sample of 0.05 g of suspensions of double imprinted polymer and non-imprinted polymer (in 50 mL of lead(II) ions solution) were sonicated for 10 min. The suspension was then kept still for 5 min to let larger particles settle. About 10 mL of clear supernatant was placed into the vial.

The beads were examined using scanning electron microscopy (SEM). The samples were initially dried in air at 25°C for 7 days before being analyzed. Afragment of the dried bead was mounted on a SEM sample mount and was sputter coated for 2 min. The sample was then mounted in a SEM (Model: Zeiss Ultra Plus Electron Microscopy). The surface of the sample was then scanned at the desired magnification to investigate the morphology of the beads. FTIR spectroscopy was used in the range of 4000-400 cm-1 to chemistry of double-imprinted polymer in the solid state (FTIR 100 series, Perkin Elmer, USA). The beads (about 0.1 g) were thoroughly mixed with KBr (0.1 g, IR Grade, Merck, Germany), and pressed into a pellet and FTIR spectrum was then recorded.

2.5 Sorption study procedure

The sorption studies of the Cd(II) ions by the prepared imprinted polymer were carried out batch experiments, as follows. Aliquots of cadmium solutions (25.0 mL) in the concentration range of 25-500 mg L^{-1} were treated with the 25 mg polymer particles at different pHs. The pH of the suspensions was maintained to desired values by adding NaOH or HNO_3. The suspension was stirred for preselected periods of time using a magnetic stirrer. After centrifugation, cadmium contents of the solutions were determined by flame atomic absorption spectrophotometer (FAAS). The amount of adsorbed ions was obtained using the following expression.

$$Q=[(C_o-C).V]/M \qquad (1)$$

Q is the amount of ions adsorbed onto the unit amount of the polymer (mg g^{-1}); C_o and C are the concentrations of the ions in the initial solution and in the aqueous phase after adsorption, respectively (mgL^{-1}); V is the volume of the aqueous phase (mL); and M is the amount of polymer (g).

The distribution ratio (mL g^{-1}) of Cd(II) ions between the double-imprinted particles and aqueous solution was also determined by the following equation:

$$K_d = (C_i - C_f) x V / (C_f x\ m) \quad (2)$$

where V is the volume of initial solution and m is the mass of double-imprinted materials. Selectivity coefficients for Cd(II) ion relative to foreign ions are defined as:

$$k_{Cd(II)/M(II)} = K_{dCd(II)}/K_{dM(II)} \quad (3)$$

where $K_{dCd(II)}$ and $K_{dM(II)}$ are the distribution ratios of cadmium and foreign ion, respectively. In order to obtain the reusability of the prepared ion-imprinted polymer particles, the sorption experiments (adsorption–elution cycle) were repeatedly performed by using of the same particles.

3. Results and Discussion

3.1 Characterization

Double imprinted polymer was spherical in shape with particle size of 349 nm and non-imprinted polymer was size of 434 nm in diameter. The surface morphology and internal structure of double imprinted, non-imprinted and single imprinted polymers are exemplified by the electron micrographs in Fig. 1. As clearly seen here, the double and single imprinted polymeric beads have a spherical form and rough surface due to the pores which formed during the polymerization procedure. These images show that the single imprinted polymer has a macroporous and double imprinted polymer has a microporous interior surrounded by a reasonably rough surface, in the dry state. The size of the globules was roughly determined to be in 1.690 µm for single imprinted polymer and 486 nm for double imprinted polymer. It is clearly seen that the double imrinted particles were more porous than the corresponding non-imprinted and single imprinted particles. The large pores reduce diffusional mass transfer resistance.

The IR spectra of the double-imprinted polymer showed OH band at 3438 cm^{-1}, aliphatic C-H band at 2927 cm^{-1}, C-NH_2 band at 1385 cm^{-1}, Si-O band at 799 cm^{-1}.

3.2 Sorption Studies

3.2.1 Effect of pH

It is well known that metal ion adsorption both on non-specific and specific sorbents is pH dependent (Say et al, 2003; Ersöz et al, 2004; Birlik et al, 2006; Manohar et al, 2002; Suzuki et al, 2001; Denizli et al, 2003; Kesenci et al, 2002; Denizli et al, 1997). In order to inhibit the precipitation of cadmium hydroxide at alkaline conditions during the variation of pH, in this work, a total cadmium concentration of 25 mg L^{-1} was employed. The effect of pH on the sorption of Cd(II) ions was then investigated by varying the solution pH from 2.0 to 7.0. Several batch experiments were performed by equilibrating 25 mg of the imprinted particles with 25 mL of solutions containing 25 mg L^{-1} of Cd(II) under the desired range of pH. The pH dependence of Cd(II) adsorption is shown in Figure. 2. Cd(II) was extracted onto the double imprinted sorbent, below pH 4

This is mainly due to the protonation of the amine moiety of chitosan, which diminished the ability of the amino group to be involved in chelate formation with the Cd(II) in aqueous solution As seen, binding of Cd(II) ions increased with increasing pH and reached to maximum at pH of 7.0 for single and double imprinted polymer.

Lu and Yan were prepared an imprinted organic-inorganic hybrid sorbent for selective separation of cadmium from aqueous solution and found pH 5.4 as optimum pH (Lu et al, 2004). Zhai et al. (Zhai et al, 2007) was researched selective SPE of Cd(II) with an ionic imprinted polymer and found pH 6.0 as an optimum pH.

3.2.2 Equilibrium Adsorption Time

Determination of adsorption time, 25 mg of the sorbent was added to 25 mL of a 25 mg L^{-1} solution of Cd(II) at pH of 7.0. The resulting suspension was stirred for different periods of time (i.e., from 5 to 180 min) with magnetic stirring. After solution of the adsorbed Cd(II) ions from the single and double-imprinted polymers, the metal content of solutions was determined by FAAS.

Figure 3 shows adsorption rates of Cd(II) ions onto the single and double-imprinted polymers from aqueous solutions. Note that the ordinate values on this were calculated by using the expression given in eq. (1). As seen here, high adsorption rates are observed at the beginning, and then adsorption equilibrium are gradually reached within 60 min for double-imprinted polymers and 120 min for single-imprinted polymer. 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.

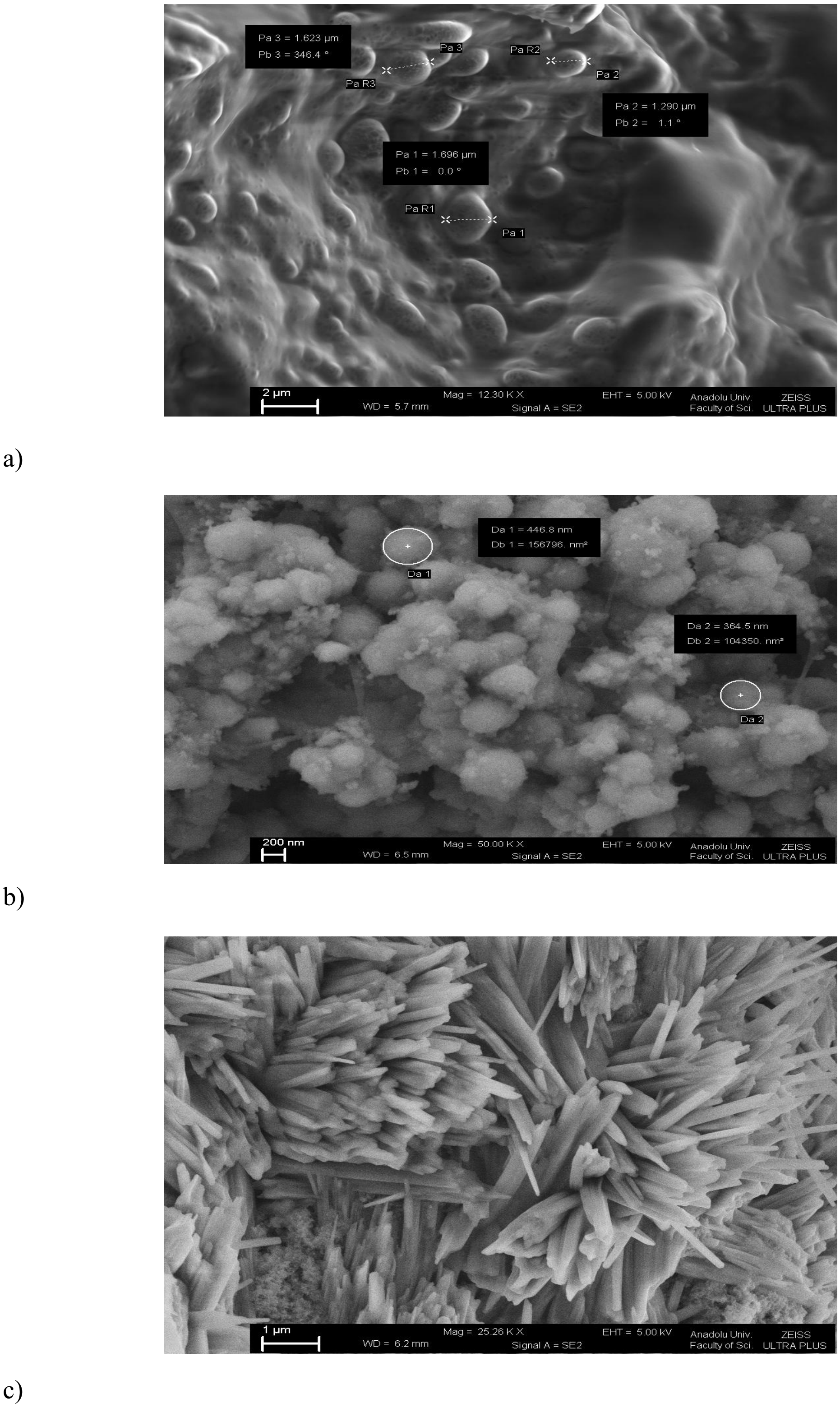


Figure 1. SEM micrographs of a) Single b) Double c) Non-imprinted polymer

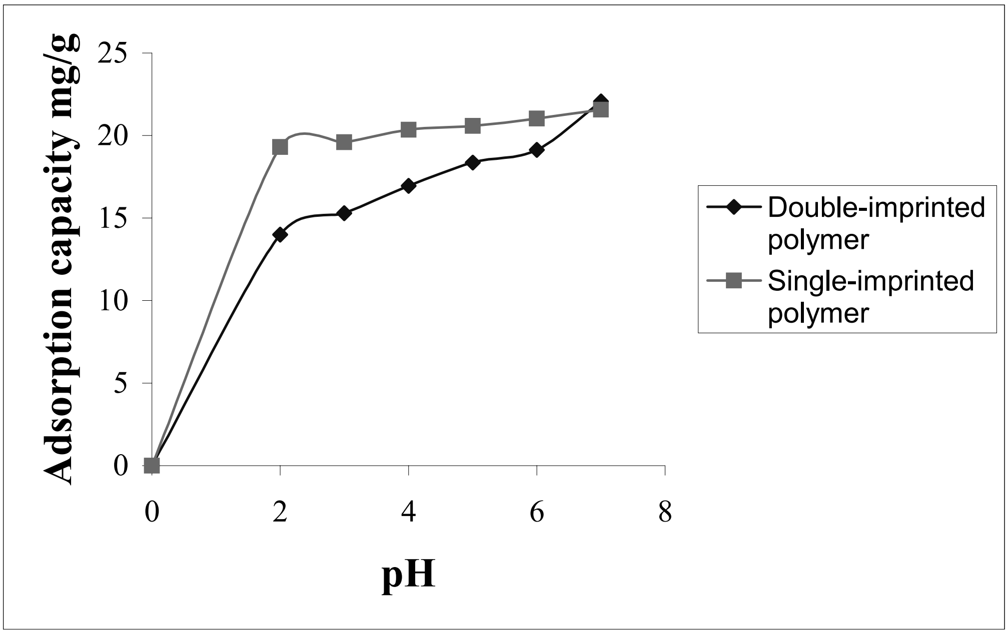


Figure 2. Effects of pH on Cd(II) adsorption; Cd(II) initial concentration, 25 ppm; T:25 ^{0}C

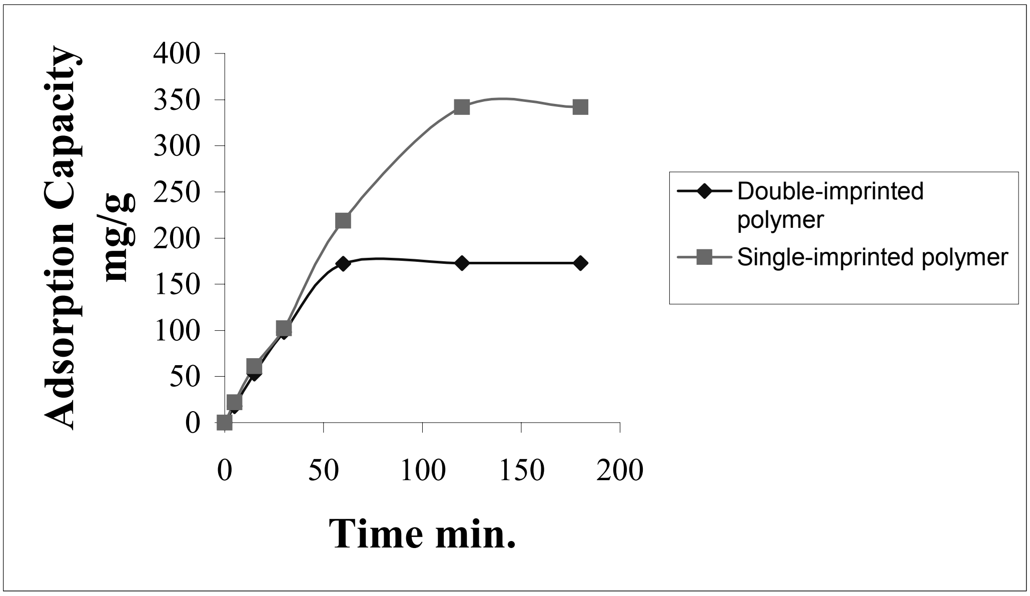


Figure 3. Adsorption rates of Cd(II) ions on the double-imprinted polymer; pH:6.0, T:25^{0}C

3.2.3 Desorption and Repeated Use

The regeneration of the adsorbent is likely to be a key factor in improving process economics. Desorption of the adsorbed Cd(II) ions from the imprinted particles was also studied in a batch experimental set up. The use of 0.1M HNO_3 could be quantitatively desorbed from the particles with 0.1M HNO_3 during 120 min. Figure 2 shows adsorption rates of Cd(II) ions onto the single and double-imprinted polymers from aqueous solutions.

When HNO_3 was used as desorption agent for single and double-imprinted polymers, the ions were released from the Cd(II) templates into desorption medium. In order to show the resuability of the single and double-imprinted polymers adsorption-desorption cycle was repeated 30 times by using the same imprinted particles. The results showed that the single and double-imprinted affinity microparticles can be used repeatedly without loosing significantly their adsorption capacities.

3.2.4 Maximum Binding Capacity

In several batch experiments, 25 mg portions of the imprinted sorbent were equilibrated with varying concentrations of Cd(II) at pH 7.0. After 45 min, the equilibrium concentrations of Cd(II) in solution and, consequently, the amounts of the metal ion bound to polymer were determined by FAAS.

It was observed that the amount of Cd(II) ions adsorbed per unit mass of the imprinted microbeads increased linearly with the initial concentration of Cd(II) ions. The experimental maximum binding capacity was 342 mg g^{-1} and 172 mg g^{-1} for single and double imprinted polymer.

Zhai et al. (Zhai et al., 2007) was researched selective SPE of Cd(II) with an ionic imprinted polymer and found to be 32.56 mg g^{-1} as maximum adsorption capacity. Li et.al. (Li et.al, 2007) was studied an ion-imprinted silica-supported organic–inorganic hybrid sorbent prepared by a surface imprinting technique combined with a polysaccharide incorporated sol–gel process for selective separation of Cd(II) from aqueous solution and reported 1,14 mmol g^{-1} (128.4 mg g^{-1}) as maximum adsorption capacity. Candan et al. (Candan et al., 2009) was researched cadmium removal out of human plasma using ion-imprinted beads in a magnetic column and found 48.8 μmol g^{-1} (5.47 mg g^{-1}) as maximum adsorption capacity. Andac et al. (Andaç et al., 2004) prepared ion imprinted polymer for cadmium removal from human plasma and was reported 32.5 μmol Cd(II) g^{-1} (3.64 mg g^{-1}) maximum adsorption capacity. When our results were compared with the other studies, the maximum adsorption capacity (172 and 342 mg g^{-1}) would seem to be successful to propose the single and double-imprinted particules as MIP sorbent.

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 5 shows the dependence of the equilibrium concentration on the adsorbed amonut of Cd(II) onto the single and double-imprinted polymer. Langmuir adsorption model (Eqn 3). 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 could be applied in these systems and described by the equation:

$$Q=Q_{max}bC_e/(1+bC_e) \qquad (4)$$

Where Q is the concentration of bound Cd(II) ions in the adsorbent (μmol g^{-1}), C_e is the equilibrium Cd(II) ions concentration in solution (μmol L^{-1}), b is the Langmuir constant (g μmol^{-1}) and Q_{max} is the maximum adsortion capacity (μmol g^{-1}). This equation can be linearized.

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 0.98 and 0.99 for single and double imprinted polymer. The Langmuir adsorption model can be applied in this affinity adsorbent system. It should be also noted that maximum adsorption capacities (Q_{max}) were found to be 373 mg g^{-1} and 186 mg g^{-1} for single and double imprinted polymer, respectively.

In order to examine the controlling mechanism of adsorption process, pseudo-first and second-order kinetic models were used (Ho et al, 1999). A comparison of the experimental adsorption capacity and the theoretical values which obtained from Figure 6 and 7 are presented in Table 1. The theoretical Q value estimated from pseudo-first-order kinetic model is more close to the experimental value and the correlation coefficient. So, the results suggested that the pseudo-first order adsorption mechanism is predominant for single and double-ion-imprinted adsorbent system and that overall rate of the Cd(II) adsorption process appeared to be controlled by chemical reaction.

The correlation coefficient for the linear plot of t/Qt agaisnt t for the pseudo-second-order equation was 0.93 and 0.90 for single and double imprinted polymer. The theoretical Qe value was slightly more different from the experimental value. These data showed that these adsorbent systems were not so well described by the pseudo-second-order kinetic model.

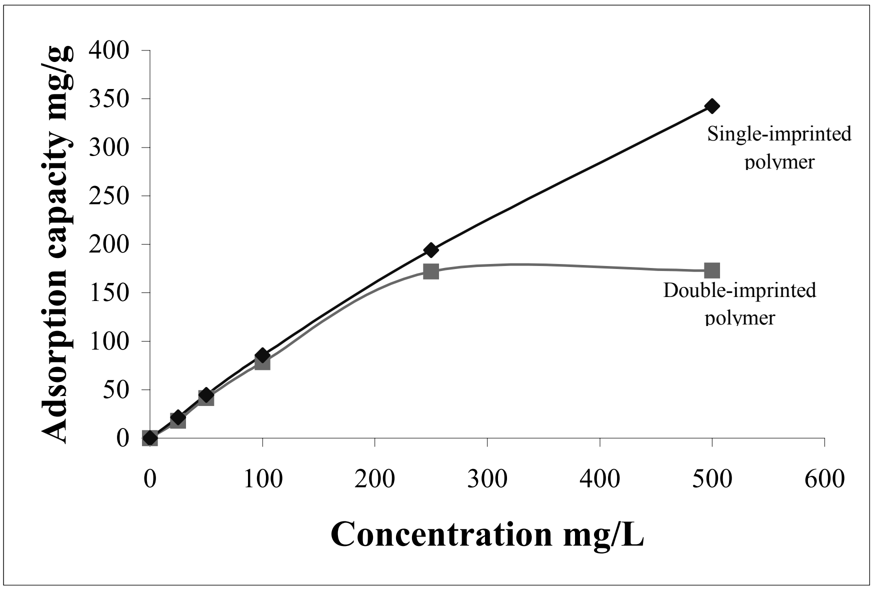
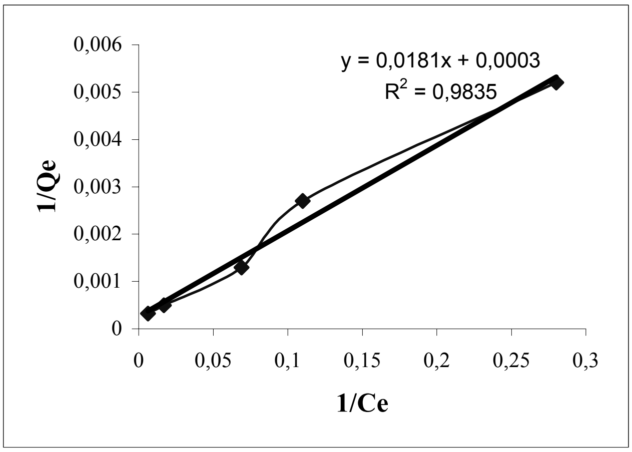


Figure 4. Adsorption capacity of Cd(II) ions on the double-imprinted polymer; pH:7.0, T:25^{0}C

a)



b)

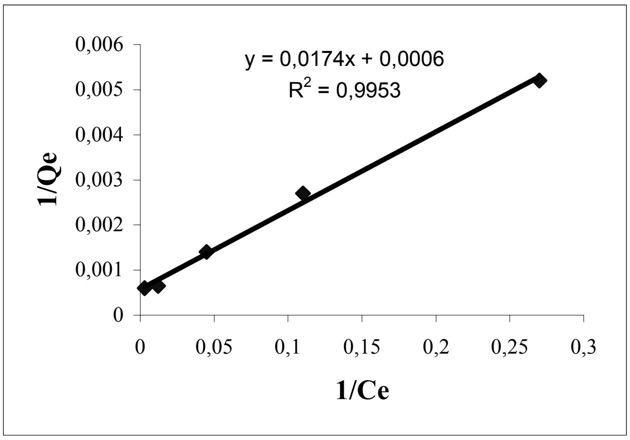
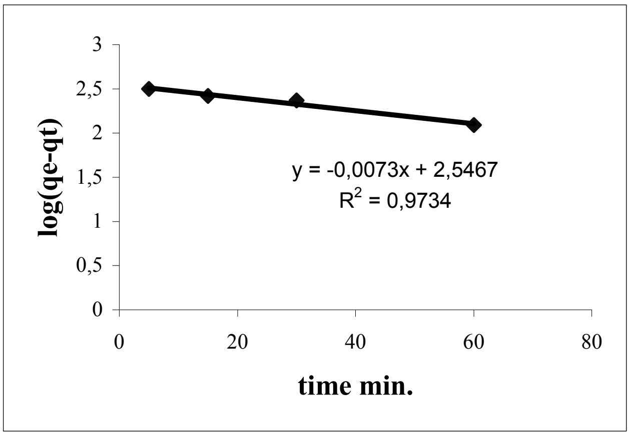


Figure 5. Adsorption isotherm of Cd(II) ions on the a) single and b) double-imprinted polymer; pH:7.0, T:25^{0}C

Table 1. Kinetic constants for the double-imprinted polymer

Polymer	Langmuir Qe (mg g^{-1})	Experimental Qe (mg g^{-1})	First-order kinetic			Second-order kinetic		
			k_1	Qe (mg g^{-1})	R^2	k_2	Qe (mg g^{-1})	R^2
Single-imprinted	373	342	0,01681	352	0,97	0.0038	588.23	0.93
Double-imprinted	186	172	0.0297	178	0.99	0.00006	277	0.90

a)



b)

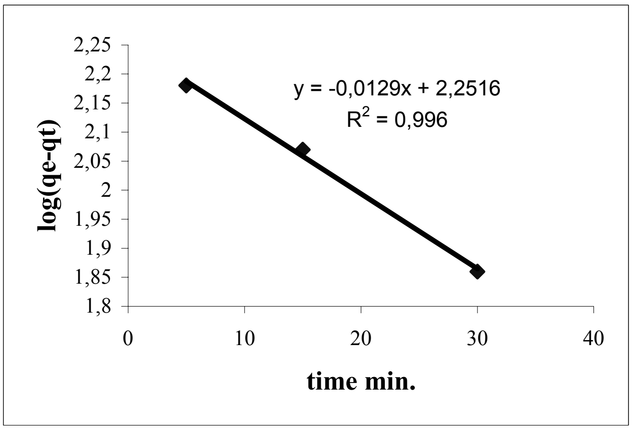
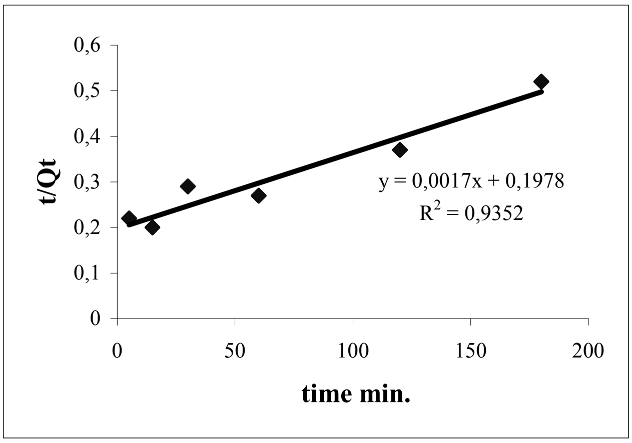


Figure 6. Pseudo-first-order kinetic of the experimental data for the a) single and b) double-imprinted polymer

a)



b)

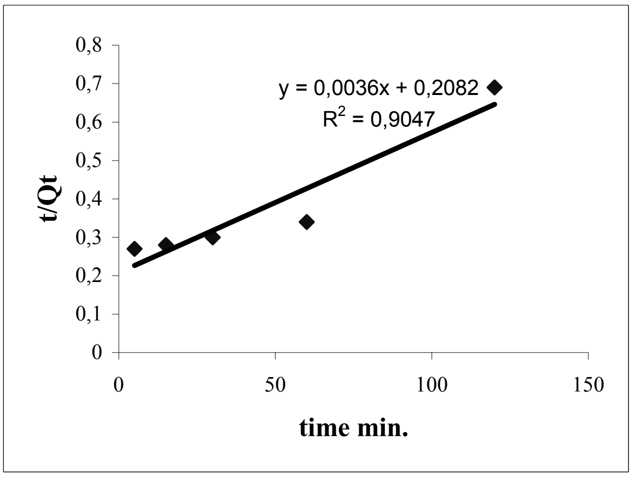


Figure 7. Pseudo-second-order kinetic of the experimental data for the a) single and b) double-imprinted polymer

3.2.5 Selectivity study

In the single and double-imprinted polymers, the cavities created after the removal of template is complementary to the imprinted ion in size and coordination geometries. Whereas, in non-imprinted sorbent, the random distribution of ligand functionalities in polymeric network results in no specificity in rebinding affinities.

In order to measure the selectivity of the imprinted material, competitive sorption of Cd(II)/Hg(II) and Cd(II)/Ni(II) from their binary mixtures was investigated in batch experiments. All of the selected competitor ions have the same charge and similar ionic radius. The initial concentrations of pair of metal ions (10 mg L^{-1}) were extracted by 25 mg of imprinted material at a pH of 7.0. Table 2 summarizes the percentage of adsorbed metal ion, distribution ratios (K_d) and selectivity coefficients (k) of Cd(II) over Ni (II) and Hg(II) ions calculated using Eqs ((1)–(3)), respectively. The relative selectively coefficient ($k' = k_{imprinted}/k_{non\text{-}imprinted}$) results from the comparison of the k value of the imprinted microparticles with non-imprinted microparticles allows an estimation of the effect of imprinting on selectivity. The double-imprinting effect is clearly observed by comparing selectivity results of imprinted and control material. The selectivity coefficients obtained on ion-imprinted polymer particles revealed the fact that the quantitative removal and determination of Cd(II) ions can be achieved even in the presence of excesses of Hg(II) and Ni(II) interferences.

Table 2. The effect of imprinting on selectivity

Polymer	**Cd(II) (mg L^{-1})**	**Ni(II) (mg L^{-1})**	**K_D (Cd(II))**	**K_D (Ni(II))**	**k**	**k'**
Double-Imprinted Polymer	10	10	4244	1116	3.80	2.58
Non-Mip	10	10	3988	2711	1.47	
Single Imprinted Polymer	10	10	1664	145	11.47	1.33
Non-Mip	10	10	1894	221	8.56	
Polymer	**Cd(II) (mg L^{-1})**	**Hg(II) (mg L^{-1})**	**K_D (Cd(II))**	**K_D (Hg(II)**	**k**	**k'**
Double-Imprinted polymer	10	10	453500	162900	2.783	5.55
Non-Mip	10	10	81650	162900	0.501	
Single Imprinted Polymer	10	10	1019	162900	0.006	0.072
Non-Mip	10	10	989	11950	0.083	

4. CONCLUSIONS

In this study, we have applied single and double imprinting concept to prepare two different sorbents with the selectivity of the cavities and the affinity of the functional ligands for selective separation of Cd(II) from aqueous solutions. Single and double imprinted polymers were synthesized by molecular imprinting thecnique in aqueos solution of epiclorohydrin and TEOS, in the presence of mercaptosilane and chitosan-Cd(II) complex. The effect of initial concentration of Cd(II) ion, adsorption time and imprinting efficiency on the adsorption selectivity for single and double imprinted polymer were investigated. Double imprinted polymer is prepared with molecular scale imprinting techniques. Microscale structure was developed from macroscale structure with double imprinted systems. 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 capacities were 342 and 172 mg g^{-1} for single and double-imprinted polymers The adsorption was fast and the time required to reach equilibrium conditions was about 120 and 60 min for single and double-imprinted polymers and seems to be very satisfactory. This adsorption equilibrium is most probably due to high complexation and geometric shape affinity (or memory) between Cd(II) ions and Cd(II) ion cavities. Double-imprinted polymer was good enough for Cd(II) separation in the complex matrixes containing interference ions, such as Ni(II) and Hg(II). Double-imprinted polymer was exhibited in most of the work to increase selectivity, as compared to single-imprinted polymer. Sol–gel in the double imprinted polymer was attributed to the flexibility of the cavity and whose specific binding sites contained functional groups in a predetermined orientation. This study also indicated that the design of polymer was very suitable for further development of ionic imprinted polymers techniques.

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