Selective Solid-Phase Extraction of Cd(II) Using Double Imprinting Strategy[†]

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ABSTRACT

Molecular imprinting technology is a strategy for producing chemically selective binding sites, which recognize a particular molecule, in a macroporous polymer matrix. Molecular recognition-based separation techniques have received much attention in various fields because of their high selectivity for target molecules. In this study, we have used a molecular imprinting approach to achieve specific metal binding utilizing 3-amino-propyltrimethoxysilane (APTS) as a metal-complexing ligand. In the first step, APTS has complexed with Cd(II) ions and then reacted with 3-mercaptopropyl-trimethoxysilane. Then, polymeric particles have crosslinked with tetraethoxysilane (TEOS). The imprinted Cd(II) ion has removed from the polymeric matrix by 0.1 M HNO3. Double-imprinted particles have characterized by Fourier Transform Infrared (FTIR). Maximum binding capacity, optimum pH, and equilibrium binding time have found as 548 mg g-1, pH 6.0, and 45 min, respectively. In selectivity study, it has found that imprinting results in increased affinity of the material toward Cd(II) ion over other competitor metal ions with the same charge. It was established that double-imprinted polymers can be used repeatedly without a considerable adsorption capacity loss.

Key Words: Ion-imprintined polymer (IIP), double-imprinting, Cd(II) removal, solid phase extraction.

1. INTRODUCTION

In recent years, molecularly imprinted polymers (MIPs) have attracted much attention due to their outstanding advantages, such as predetermined recognition ability, stability, relative ease and low cost of preparation, and potential application to a wide range of target molecules [1,2]. MIPs are synthetic polymers with highly specific recognition ability for target molecules. In the most common preparation process, monomers form a complex with a template through covalent or non-covalent interactions and are polymerized using a cross-linking agent. After the removal of the template by a chemical reaction or extraction, binding sites are exposed which are complementary to the template in size, shape, and position of the functional groups, and consequently allow its selective uptake. MIPs have been widely used as artificial receptors in separations [3]. Sample preparation is crucial for the analysis of compounds in real samples, since it is the most tedious and time-consuming step and a possible source of imprecision and inaccuracy of the sensors [4], catalysis [5], and drug development and screening [6]. Among these applications, the one most widely used is solid-phase extraction (SPE), for which MIPs are commercialized [7]. There have been several reviews five years ago [3, 8–11], by new applications of MIPs to SPE keep coming out constantly.

Ion-imprinted polymers (IIPs) are similar to MIPs, but they recognize metal ions after imprinting, while retaining all the virtues of MIPs [12-14]. Nishide and Deguchi [15] studied that poly(4-vinylpyridine) with 1,4-dibromobutane has cross-linked in presence of

metal ions, viz. Cu(II), Zn(II), Co(II), Ni(II), Hg(II) and Cd(II) as templates unlike small molecules, biological macromolecules, microorganisms or whole crystals as in the case of MIPs. Kabanov et al. [16] reported that a copolymer of diethylvinylphosphonate and acrylic acid with N,N-methylene diacrylamide have cross-linked in the presence of metal ions. Dai et al. [17] have prepared mesoporous sorbent materials by ion-imprinting technique for selective removal of uranyl ions using bifunctional ligands such as amines and sulphonic acids.

In this study, a novel double-imprinted particles were synthesized by ionic imprinted technique for selective solid-phase extraction (SPE) of trace Cd(II) from aqueous solution. In the first step, APTS was complexed with Cd(II) ions and then reacted with mercaptosilane. Then, polymeric particles was crosslinked with TEOS. Subsequently, the imprinted Cd(II) was completely removed by leaching the dried and powdered materials particles with 0.5 M HNO_3. The obtained double-imprinted particles exhibited excellent selectivity for target ion. After the removal of Cd(II) ions, double-imprinted particles were used for the preconcentration and separation of Cd(II) ions from aqueous solutions. Cd(II) adsorption and selectivity studies of Cd(II) versus other metal ions which are Zn (II), and Hg (II) were reported here. Finally, repeated use of the double-imprinted particles was also discussed.

2. EXPERIMENTAL

2.1. Materials

APTS, 3-mercaptopropyl-trimethoxysilane were supplied from Aldrich Chemical (USA). Mercury nitrate dihydrate, nitric acid, sodium hydroxide and zinc 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. Instrumentation

A Hitachi 180-70 polarized Zeeman atomic absorption spectrophotometer (Hitachi, Japan) with deuterium background correction was used for the determination of Cd(II), Hg(II) and Zn(II) and absorbance measurements were made at 228.8, 253.7 and 213.8 nm, respectively.

FTIR spectroscopy was used in the 4000-400 cm^{-1} range to investigate the double-imprinted particles in the solid state (FTIR 100 series, Perkin Elmer, USA). Jenway 3100 pH-meter (USA) was used to mesaure pH values.

2.3. Preparation of Double-Imprinted Particles

2.3.1. Single imprinted particles

$Cd(NO_3)_2.H_2O$ (3 mmol) was dissolved in 10 mL of methanol solution and mercaptosilane (24 mmol) was added slowly to this solution with continuous stirring at room temperature. The obtained mixture solution was

crosslinked by 4 mL of TEOS under refluxing conditions in an oil bath (ca. 110 °C) for 8 h. After vacuum filtration, the product of crosslinked particles was washed with 0.1 M HNO_3 and deionized water several times to remove Cd(II) ions.

2.3.2. Double-imprinted particles

$Cd(NO_3)_2.H_2O$ (3 mmol) was dissolved in 10 mL methanol solution and APTS (24 mmol) was added slowly to this solution with continuous stirring at room temperature. Then, the mixture was reacted with mercaptosilane (24 mmol) for 48 h. The obtained mixture solution was crosslinked by 4 mL of TEOS under refluxing conditions in an oil bath (ca. 110 °C) for 8 h. After vacuum filtration, the product of crosslinked particles was washed with 0.1 M HNO_3 and deionized water several times to remove Cd(II) ions.

The IR spectra of the double-imprinted particles showed R-S-H band at 2558 cm^{-1}, aliphatic $C-NH_2$ band at 2932 cm^{-1}, aliphatic C-H band at 2932 cm^{-1}, Si-O-Si band at 1047 cm^{-1}.

2.4. Adsorption of Cd(II) Ion

The adsorption of Cd(II) ions was investigated in batch experiments. The effect of the initial Cd(II) concentration on the adsorption rate and adsorption capacity was studied. In all experiments, polymer concentration was kept constant at 25 mg/25 mL.

The effect of pH on the adsorption rate of the double-imprinted particles was investigated in the pH range of 2.0-7.0 at 25°C. The suspensions were brought to the desired pH by adding NaOH and HNO_3. The pH was maintained in a range of $\pm$ 0,1 U until equilibrium was attained. Ions were treated with the double-imprinted particles at room temperature, in the flask stirring magnetically at 600 rpm.

The concentration of the ions in the aqueous phases after desired treatment periods were measured by using FAAS. The effect of the initial ion concentration on the adsorption was investigated at a suitable pH between the concentration of Cd(II) ions in the adsorption medium was varied between 25 and 1000 mg L^{-1}.

The amount of adsorbed ions was obtained using the following expression.

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

Where 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 (mg L^{-1}); V is the volume of the aqueous phase (mL); and M is the amount of polymer (g).

For the preconcentration of Cd(II) ions, 100 mL of the aqueous solution containing 1.0 ng mL^{-1} of Cd(II) was treated with 25 mg imprinted microparticles at pH 7.0. Finally, double-imprinted particles were separated from the adsorption media by filtration and 10 mL of HNO_3 solution was added and stirred at 400 rpm. Imprinted polymers were separated from the desorption media and

the concentration of Cd(II) ions in the desorption media was injected to FAAS system.

The experiments were performed in replicates of three and the samples were analyzed in replicates of three as well. Adsorption values (mg g^{-1}) were calculated as the difference in Cd(II) concentration of the pre- and post-adsorption solutions divided by the weight of imprinted particles.

Distribution and selectivity coefficients of Cd(II) with respect to Hg(II), and Zn(II) were calculated as explained below:

K_d = (C_i - C_f) Volume of the solution (mL) Mass of microparticles (g)   (2)

where K_d, C_i and C_f represent the distribution coefficient, initial and final solution concentrations, respectively. The selectivity coefficient (k) for the binding of an anion in the presence of competitor species can be obtained from equilibrium data according to the Eqn.3;

k= K_d (template ion) / K_d (interferent ion)   (3)

A comparison of k values of the imprinted polymers with those Cd(II) compound allows an estimation of the effect of imprinting on selectivity. A relative selectivity coefficient (k´) (Eq. (4) can be defined as [18,19]:

k´ = $k_{imprinted/ kcontrol}$ (4)

2.5.2. Desorption and reusability

Adsorbed Cd(II) ions were desorbed by the treatment with 0.1 N HNO$_3$ solution. The imprinted polymer adsorbed with cadmium ions in the following

conditions: initial concentration of the metal ions: 25 ppm; amount of the imprinted polymers: 25 mg; volume of the adsorption medium: 25 mL; pH: 6.0**;** temperature: 25 °C; and adsorption time: 45 minutes. Then, these imprinted polymers were placed in this desorption medium and stirred at a stirring rate of 400 rpm up to 2h. The imprinted polymers were washed few times with 0.1 N HNO$_3$ solution and water. The concentrations of ions in the aqueous phase were followed as mentioned before. Desorption ratio was calculated from the following expression.

Desorption ratio=(Amount of ions desorbed to the elution medium)/(Amount of ions adsorbed onto the sorbent)X100

In order to obtain the reusability of the double imprinted particles, adsorption–desorption cycles were repeated ten times by using the same double imprinted particles.

3. Results and Discussion

3.1. Adsorption Capacity of Double-Imprinted Particles

3.1.1. Adsorption rate

Figure 1 shows adsorption rates of Cd(II) ions onto the double-imprinted particles from aqueous solutions containing 25 mg L^{-1} of Cd(II) ions at a constant pH of 6.0. Note that the ordinate values were calculated by using the expression given in eq. (1). As seen here, high adsorption rates were observed at the beginning, and then plateau value (i.e., adsorption equilibrium) was gradually reached within 45 min.
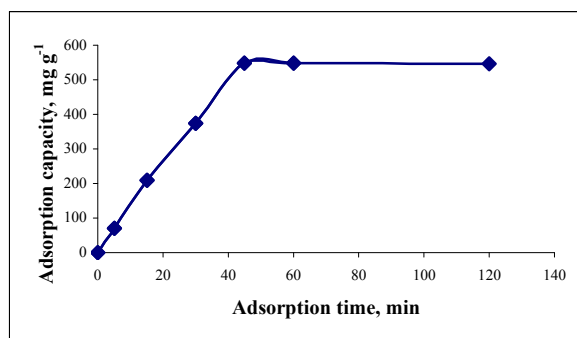

Figure 1. Adsorption rates of Cd(II) ions on the double-imprinted particles; pH, 6.0;T, 25 °C.

Shamsipur et al. used ion imprinted polymer for selective recognition of copper(II) ions in aqueous media and found 45 min. as an equilibrium time [20]. Birlik et al. have investigated selectivity removal of copper using double-imprinted polymer and reported 30 min. equilibrium time [21]. The adsorption rate obtained in this study (45 minute) would seem to be sufficient to propose the double-imprinted particules as MIP sorbent.

3.1. Effect of pH

According to the recommended procedure, the effect of pH on the adsorption of Cd(II) was tested by equilibrating 25 mg of double-imprinted sorbent with 25 mL of 10 mg L^{-1} Cd(II) solutions under different pH conditions. Below pH 3, Cd(II) was extracted onto the doubly imprinted sorbent. This is mainly due to the protonation of the amine moiety of APTS, which diminished the ability of the amino group to be involved in chelate formation with the Cd(II) in aqueous. As seen in Figure 2, binding of Cd(II) ions increased with increasing pH and reached to maximum at pH of 6.0.
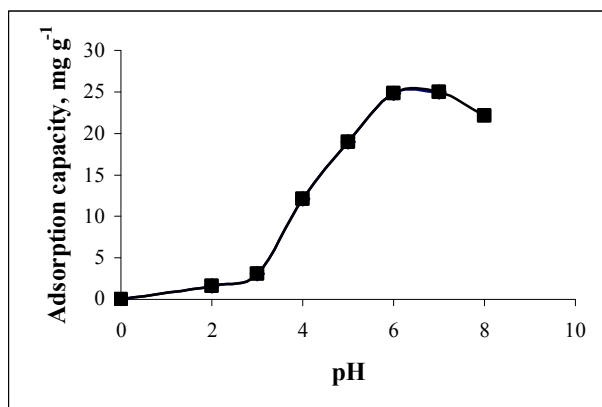
Figure 2. Effect of pH on sorption of Cd(II) on double-imprinted sorbent.

Zhai et al. [22] have been researched selective solid-phase extraction of Cd(II) with an ionic imprinted polymer and found pH 6.0 as an optimum pH. Lu and Yan [23] were prepared an imprinted organic-inorganic hybrid sorbent for selective separation of cadmium from aqueous solution and found pH 5.4 as an optimum pH.

3.2. Adsorption Capacity of Double-Imprinted Sorbent for Cd(II)

The adsorption capacity is an important factor because it determines how much adsorbent is required to quantitatively concentrate the analytes from a given solution. To measure the adsorption capacity, 25 mg of double-imprinted sorbent was equilibrated with 25 mL of various concentrations of Cd(II) solutions at pH 6. As can be seen in Figure 3, the amount of Cd(II) adsorbed per unit mass of double imprinted particles increased with the initial concentrations of Cd(II). The adsorption capacity of the double-imprinted sorbent for Cd(II) was calculated as 548 mg g^{-1}. The results showed that the double-imprinted particles had a high adsorption capacity for Cd(II) ions.
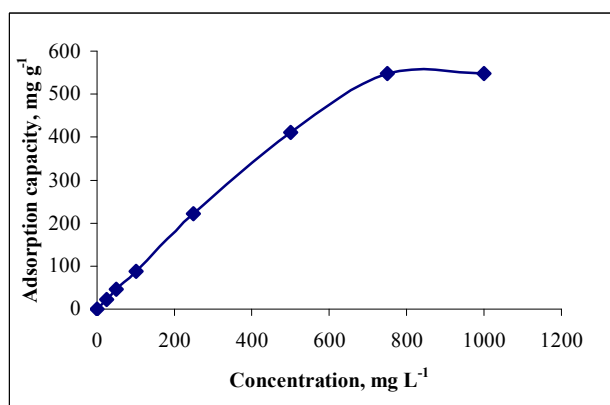

Figure 3. Adsorption capacity of Cd(II) ions on the double-imprinted particles; pH:6.0, T:25 °C.

Zhai et al. [22] was researched selective solid-phase extraction of Cd(II) with an ionic imprinted polymer and found 32.56 mg g^{-1} as maximum adsorption capacity. Li et.al. [23] 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. [24] 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. [14] were 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 (548 mg g^{-1}) would seem to be successful to propose the double-imprinted particles 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 4 shows the dependence of the equilibrium concentration on the adsorbed amount

of Cd(II) onto the double-imprinted particles. 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 [25]. 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:

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

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 found to be 0.99. The Langmuir adsorption model can be applied in this affinity adsorbent system. It should also be noted that Q_{max} was found to be 560 mg g^{-1}.
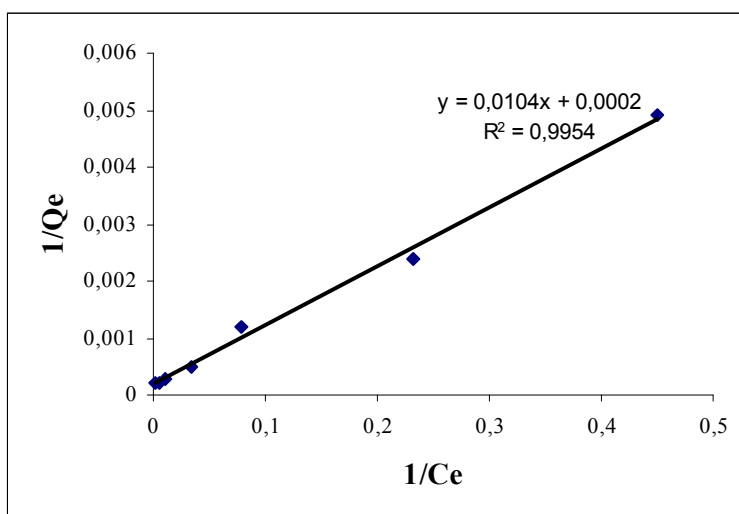

Figure 4. Adsorption isotherm of double-imprinted particles; pH, 6.0; T, 25 °C.

In order to examine the controlling mechanism of adsorption process, pseudo-first and second-order kinetic models were used [26]. A comparison of the experimental adsorption capacity and the theoretical values were 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 (R^2: 0,9868). So, the results suggested that the pseudo-first order adsorption mechanism is predominant for this double-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 against t for the pseudo-second-order equation 0.8111. The theoretical Qe value was slightly more different from the experimental value. This showed that this adsorbent system was not so well described by the pseudo-second-order kinetic model.

Table 1. Kinetic constants for the double-imprinted particles.

Langmuir Qe (mg/g)	Experimental Qe (mg/g)	First-order kinetic			Second-order kinetic		
		k_1	Qe (mg/g)	R^2	k_2	Qe (mg/g)	R^2
560	548	0.029	550	0.98	5.10^{-6}	1666	0.81

3.3. Selectivity of the Imprinted Sorbent

The Zn(II) and Hg(II) ions were chosen as the competitive species with Cd(II). As can be seen in Table 2, the K_D and k values of Cd(II) imprinted polymer are significantly larger in comparison to the single-imprinted sorbent. A comparison of the selectivity coefficient of double-imprinted polymers to the selectivity coefficient of non-imprinted polymers showed that the imprinted matrix for Cd(II)/Hg(II), and Cd(II)/Zn(II) was 7.39 and 6.07 times greater than non-imprinted matrix, respectively. The results indicated that the double-imprinted sorbent has higher selectivity for Cd(II), and these results demonstrated that Cd(II)

can be determined even in the presence of Zn(II), and Hg(II) ion interference solutions containing 10 mg L^{-1} of Cd(II).

Table 2. The effect of imprinting on selectivity.

Polymer	Cd(II) (mg/L)	Zn(II) (mg/L)	K_D (Cd(II))	K_D (Zn(II))	k	k´
Non-Mip	10	10	4949	5988	0.826	
Double-Imprinted Polymer	10	10	8328	1659	5.02	6.07
Non-Mip	10	10	5934	6013	0.987	
Single Imprinted Polymer	10	10	2626	2588	1.015	1.02
Polymer	Cd(II) (mg/L)	Hg(II) (mg/L)	K_D (Cd(II))	K_D (Hg(II)	k	k´
Non-Mip	10	10	10740	162900	0.066	
Double-Imprinted polymer	10	10	55490	113900	0.487	7.39
Non-Mip	10	10	6257	162900	0.038	
Single Imprinted Polymer	10	10	4970	162900	0.03	0.078

3.4. Desorption and Reusability

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.

When desorption agent is used as HNO$_3$ for double-imprinted polymers, the ions are released from the Cd(II) imprinted polymer into desorption medium. Desorption ratios were calculated using eqn.2 and was around 85%. In order to show the resuability of the double-imprinted polymers, adsorption-desorption cycle was repeated 10 times by using the same imprinted particles. The adsorption capacity of the recycled double imprinted particles can still be maintained at 92% of its original value at the tenth cycle. The results showed that the double-imprinted affinity particles can be used repeatedly without loosing significantly their adsorption capacities.

3.4. Analytical Performance

For the preconcentration of cadmium ions, 100 mL of the aqueous solution containing 0.1 ng mL^{-1} of Cd(II) ions was treated with 25 mg of double-imprinted microparticles at pH 6.0 for 45 min. Finally, polymeric microparticles were separated from the adsorption media and 10 mL of HNO$_3$ solution was added and stirred at 400 rpm for 120 min. Imprinted particles 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 3.

Table 3. Performance characteristics of the preconcentration procedure.

Parametreler	Cd
Precision (R.S.D)	3.7 %
Detection limit (3s)	0.23 ng/mL
Linear calibration range	0.6-1.0 ng/mL
Regression equation (after preconcentration)	AA=0.0113Cd + 9E-05
Conventional regression equation	AA=0.0131Cd + 0.0472
Enrichment factor	(0.0113ng/mLx1000μg/mL/0.0131=862

The precision of method for a standard, evaluated as the relative standard deviation (R.S.D:, n=7) was 3.7 ng mL^{-1} Cd(II) ions. The detection and determination limits, defined as the concentration of analyte giving signals equivalent to three and ten times, respectively, the standard deviation of the blank plus the net blank intensity for 100 mL of sample volume, were 0.23 and 0.79 ng mL^{-1}. The preconcentration procedure showed a linear curve within the concentration range from 0.1 to 1.0 ng mL^{-1}. The enrichment factor, defined as the ratio of the slopes of linear section of the calibration graphs before and after the preconcentration was 862.

Xie et al. [27] studied solid phase extraction of Cd(II) using gallic acid-modified silica gel and reported 0.65 µg L^{-1} as detection limit. Prasad et al. [28] 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}. When our results were compared with the above results the dedection limit (0.23 ng mL^{-1}) would seem to be suitable to propose the double-imprinted particules as MIP sorbent.

CONCLUSION

In this study, double-imprinted polymer which can be used for the selective removal of Cd(II) ion from synthetic waters was prepared. This double-imprinted polymer was used in the adsorption-desorption of Cd(II) ions from metal solutions. The equilibrium adsorption and desorption times were found to be 45 and 60 min, respectively. The double-imprinted particles can be repeatedly used and regenerated with no significant decrease in their binding affinities. The maximum adsorption capacity for Cd(II) ions was 548 mg g^{-1}. This fast adsorption equilibrium is most probably due to high complexation and geometric affinity between Cd(II) and Cd(II) cavities in the particles structure. The adsorption values increased with increasing concentration of Cd(II) ions, and a saturation value is achieved at ion concentration of 800 mg L^{-1}, which represents saturation of the active binding cavities on the double-imprinted particles. In comparison with the control non-imprinted polymer, the prepared double-imprinted particle possesses an increased selectivity toward Cd(II) ion over a range of competing metal ions (Hg(II), Zn(II)). The relative selectivity coefficient of double-imprinted particles for Cd(II)/Zn(II) and Cd(II)/Hg(II) systems found to be 6.07 and 7.39 times greater than that of the non-imprinted particles, respectively.

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