Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1072742

57 (2016) 14280–14289
June

Taylor & Francis
Taylor & Francis Group

Preparation of a new nanoparticle Cd(II)-imprinted polymer and its application for selective separation of cadmium(II) ions from aqueous solutions and determination via inductively coupled plasma optical emission spectrometry

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Received 15 December 2014; Accepted 6 June 2015

ABSTRACT

A new nanoparticle Cd(II) ion-imprinted polymer (IIP) has been prepared via precipitation polymerization using 2-vinylpyridine (the functional monomer), ethylene glycol dimethacrylate (the cross-linker), 2,2´-Azobisisobutyronitrile (the initiator), diphenylcarbazide (the ligand), and cadmium nitrate (the template ion). The prepared IIP was characterized by FT-IR spectroscopy, scanning electron microscopy, and transmission electron microscopy. The optimal pH value for the quantitative sorption was 6.0 and maximum sorbent capacity was 16.52 mg/g. Under the optimized conditions, the method had a linear analytical range from 1 to 50 µg/L. The detection limit, relative standard deviation, and recovery of the method were evaluated as 0.14 µg/L, 2.6% and 96–98%, respectively. The prepared IIP revealed good selectivity over a wide variety of other cations. The developed method was successfully applied for the selective extraction and determination of trace amount of cadmium ions in synthetic and real water samples and some medicinal plants by inductively coupled plasma optical emission spectrometry.

Keywords: Extraction; Inductively coupled plasma optical emission spectrometry; Imprinted polymer; Cadmium ion

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1. Introduction

Cadmium is a toxic heavy metal with a wide variety of adverse effects on heart, lungs, bones and especially kidneys. It has an extremely long biological half-life and accumulates in the body [1]. The International Agency for Research on Cancer classified cadmium as a human carcinogen [2]. It is among thirteen toxic metal species on the priority pollutant list of the

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Environmental Protection Agency [3,4]. Therefore, determination of trace levels of cadmium in different samples is important and needs much more attention due to human exposure and environment parameters.

As previous stages for trace element determinations, a separation and preconcentration method is commonly required, because of low concentration of metal ions and presence of interferences [5]. Preconcentration is an effective means for extending the limits of detection (LOD) of instrumental analysis [6].

The traditional preconcentration and separation methods for cadmium are coprecipitation [7], liquid–liquid extraction [8], ion exchange [5], etc. Although satisfied results have been achieved by the above methods, majority of them require large amounts of high purity organic solvents, some of which are harmful to health and create environmental problems. Moreover, all of these methods are applied for nonspecific absorption in industry, exhibiting low selectivity [9]. Among different techniques, solid-phase extraction attracted a considerable amount of interest for the preconcentration of toxic metal ions due to the higher enrichment factors, better recoveries, and low consumption of organic solvent. This method is simple, efficient, and cost-effective, and it is also safe, regarding to the reagents employed [10]. By advent of SPE, several types of sorbents have been used for cadmium ions preconcentration, such as activated carbon [11], nanoporous silica [12], chelex-100 chelating resin [13], and carbon nanotubes [14].

The main problem associated with SPE is the low selectivity for cadmium [9]. The need of more selective system for separation of cadmium has increased the development of the synthesis of new extractants and adsorbents. One of the most promising groups of new sorbents is ion-imprinted polymers. Ionic imprinted polymers have been investigated as highly selective sorbents for SPE in order to concentrate and clean up samples prior to analysis [15,16].

The great advantage of these synthetic polymers is that, high degree of recognition can be achieved by arranging a functional monomer around a template (metal ion) in the presence of a crosslinker. The reaction proceeds via a free radical initiator in an appropriate solvent to produce a three-dimensional polymer network. Removal of the template ion results in a functional polymeric matrix with selective recognition sites, in which complexing ligands are arranged so as to match the charge, coordination number, and size of the template ion [2,17,18].

Different methods of polymerization can be utilized to prepare IIPs nanoparticles, namely suspension, multistep swelling, and precipitation polymerization. Among them, the precipitation technique is the most convenient one, because there is no need to add stabilizers or surfactants to the reaction system, and the polymer obtained according to this procedure requires no crushing and sieving steps. Particles with the most uniform size, morphology, porosity, and a better accessibility of binding sites can be produced by this method [19–21]. For these reasons, we used a precipitation polymerization technique to prepare Cd(II)-imprinted nanoparticles.

Numerous studies on ion-imprinted polymers and their application for selective preconcentration and separation of cadmium ions have been reported [9,12,18,22–25].

In our knowledge, diphenylcarbazide has not been employed to prepare IIPs for cadmium ions. Diphenylcarbazide is a well-known ligand for coordinating to transition metals [12]. In this work, a new Cd(II)-IIP was prepared by precipitation polymerization method using diphenylcarbazide as ligand. Characterization of the synthesized polymer was evaluated by Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The effect of several variables on the separation and determination of Cd(II) ions was investigated. These variables included pH of solution, sorption, and desorption time, type and volume of eluent, and the effect of coexisting ions on the extraction recovery. Adsorption isotherms and reusability of polymer were also investigated. Finally, the prepared Cd(II)-IIP was applied for determination of Cd(II) ions in synthetic and real water samples and some medicinal plant with the use of inductively coupled plasmaoptical emission spectrometry (ICP-OES) technique.

2. Experimental

2.1. Chemicals

2-Vinyl pyridine, ethylene glycol dimethacrylate (EGDMA), and 1,5-diphenylcarbazide were obtained from Merck (Darmstadt, Germany), 2,2´-Azobisisobutyronitrile (AIBN) was purchased from Acros Organics (Morris Plains, NJ, USA). All solvents and other reagents used were of analytical grade and purchased from Merck. A certified reference material (NCS ZC73036 Green tea obtained from National Institute of Standards and Technology, Beijing, China) was used to verify the accuracy of the results of analyses. Stock standard solutions of individual metals (1,000 and 10,000 mg/L) were supplied by Merck. Stock standard solutions were diluted to 1 L with distilled water. More dilute standards were prepared daily by dilution of these solutions. The herbal samples were obtained from the institute of medicinal plants, ACECR.

2.2. Apparatus

FT-IR spectra of grounded polymeric samples were recorded on a Bomem FT-IR MB 155S spectrometer (Canada) using KBr pellets in the range of 400–4,000cm^{-1}. In all solutions, the pH was adjusted by digital Metrohm pH meter (model 744) equipped with a combined glass–calomel electrode. Morphology of polymers was characterized by scanning electron microscopy (SEM, Philips XL30 scanning microscope, Philips, Netherlands) and transmission electron microscopy (TEM, Philips EM208 transmission electron microscope, Philips, Netherlands). An ICP-OES instrument (Varian 760-ES) was used for the determination of all metal ions. The operational conditions for ICP-OES and wavelength of analytical lines were in accordance with manufacturer's instructions. Operating conditions for the ICP-OES instrument were forward power 1.2 kW, plasma flow rate 15 L/min, auxiliary gas flow rate 1.5 L/min, and nebulizer gas flow rate 0.85 L/min. The wavelengths used were as follows: Cd 214.439 nm, Cu 327.395 nm, Ni 231.604 nm, Zn 213.857 nm, Mn 257.610 nm, and Pb 220.353 nm. A microwave oven equipped with PTFE vessels, (Berghof Speed wave (Germany), was used for digestion of medicinal plants samples. Ultra-pure deionized water (18MΩcm) was prepared by Basic 360 Series-Younglin, coupled with Aqua MAX-ultra 354.

2.3. Preparation of Cd(II) ion-imprinted polymer

The Cd(II)-IIP particles were prepared by precipitation polymerization technique. In the first step, 0.5 mmol 1,5-diphenylcarbazide (ligand), 4 mmol 2-vinyl pyridine (functional monomer) were dissolved in 40 mL 1–1 of DMSO-AC (polymerization solvent) then 0.5 mmol $Cd(NO_3)_2{\cdot}4H_2O$ (template ion) was dissolved in 20 mL 1–1 of DMSO-AC and added slowly to this solution. The resulted mixture was stirred for 4 h at room temperature in order to ensure the equilibration of the complexation reaction. In the second step, 40 mmol EGDMA (cross-linker) and 0.8 mmol AIBN (Initiator) were added to the solution and then stirred at room temperature. The solution was purged with a stream of nitrogen for 10 min to remove molecular oxygen, since it traps the radicals and retards the polymerization. Then the flask was sealed immediately and heated in an oil bath at 65˚C for 24 h under magnetic stirring at 500 rpm to complete the polymerization. After polymerization, the excess amount of solvent was removed and the prepared polymer was washed with 1:4 (v/v) methanol/water to remove the unreacted materials and then by1 M HNO3 for leaching of the imprint ions until the washing solution was free from Cd(II) ions. Finally, it was washed with deionized water until neutral pH was achieved. The resulting powder was dried overnight at room temperature. The non-imprinted polymer (NIP) was also prepared simultaneously as the same procedure, except that Cd(II) did not exist in the polymerization mixture.

2.4. Preparation of samples and standard solutions

Plant samples and certified reference material (NCS ZC73036) were digested in a microwave digestion system. About 0.2 g of the material was accurately weighed into a PTFE digestion vessel. Five milliliter of concentrated HNO_3 and 2 mL of concentrated H_2O_2 were added and waited for about 20 min. When the foam caused by organic matter decomposition disappeared, the vessels were closed, placed on the rotating turntable of the microwave, and then digestion was started according to the following program: step 1 (T, 160˚C; ramp, 15 min; time, 10 min), step 2 (T, 175˚C; ramp, 15 min; time, 5 min). After cooling at room temperature, the extract was transferred into a volumetric flask and made up to 100 mL with deionized water.

The Cd(II)-IIP was also applied to the determination of cadmium in synthetic and tap water samples.

Stock standard solutions of individual metals (1,000 or 10,000 mg/L) were diluted to 1 L with distilled water. Standard solutions were prepared daily by appropriate dilution of diluted stock standard solutions.

2.5. Batch rebinding experiments

Batch rebinding experiments were used to estimate the binding capacity of the ion-imprinted polymer. In order to extract Cd(II) ion by the IIP, 30 mg of the synthesized IIP was added in volumetric flask (20 mL) containing Cd(II) ion in different concentrations (1–50 mg/L) in water. The pH of solutions was adjusted at 6.0 and the resulted solutions were stirred for 40 min at room temperature using a magnetic stirrer. After centrifugation (10 min, 10,000 rpm), the free concentration of Cd(II) ion in the supernatant solution was recorded by ICP-OES. In desorption step, elution of Cd(II) ions from IIP was performed by 5 mL of 0.1 M HNO_3 while stirring for 40 min at room temperature.

The amount of Cd(II) ion bound to the polymer was calculated by subtracting the concentration of free Cd(II) ion from the initial concentration. Extraction percent of cadmium was calculated by the following equation:

$$\%E = \frac{(C_i - C_e)}{C_i} \times 100 \tag{1}$$

C_i and C_e are the concentrations of Cd(II) ion before and after extraction in the solution.

3. Results and discussion

3.1. Characterization of polymers

The imprinted nanoparticles obtained from precipitation polymerization method were characterized by FT-IR and SEM.

The morphology of the Cd(II)-IIP and NIP was assessed by SEM (Fig. 1). It is observed that, both IIP and NIP polymers have colloidal nanoparticles of approximately 50–90 nm in diameter and slightly irregular in shape.

The IIP nanoparticles were also observed by TEM. It is indicated that the mean size of the IIP particles is about 20 nm.

The FT-IR spectra of unleached and leached cadmium-imprinted polymers were recorded using KBr pellet method (Fig. 2). The similarity in these IR spectra shows that these polymers have a similar backbone. The similarities between the IR spectrums of 1,5-diphenylcarbazide, unleached, and leached IIPs suggested that the ligand is incorporated inside the polymer and leaching process does not affect the polymeric network. As seen, the bands at 1,728, 2,360, 2,923, and 3,417 cm^{-1} in unleached IIP were shifted to 1,733, 2,368, 2,939, and 3,425 cm^{-1} in leached IIP. The shift and decrease in strength of vibration can be attributed to bonding between the cadmium with diphenylcarbazide.

3.2. Effect of pH

Among the tested variables, pH of the medium was found to be the most important parameter for adsorption of metals on the ion-imprinted polymer. In an acidic environment, the imprinted sites of the polymer are occupied by protons rather than cadmium ions, so that the polymer absorbs smaller amounts of cadmium ions. As the pH increased, the protonation of ligand is suppressed and condition becomes more favorable for sorption of Cd(II) ions to the imprinted polymer [26]. The effect of pH on the extraction of Cd(II) ions was studied by mixing 30 mg of the sorbents with 20 mL Cd(II) ion solution (1 mg/L) in the pH range between 1.0 and 8.0. According to the results (Fig. 3), the maximum extraction of cadmium ions was obtained at the pH of 6.0. The pH above 8.0 was not investigated because of the possibility of hydrolysis and precipitation of Cd(II) ions.

3.3. Effect of sorption and desorption time

In several batch experiments, 30 mg of the polymer was added to 20 mL Cd(II) aqueous solution (1 mg/L) at pH 6.0. The resulting suspension was stirred at different time intervals ranging from 5 to 60 min. After centrifugation, the concentration of Cd (II) ions in the supernatant solution was determined by ICP-OES. Higher adsorption rates were observed at the beginning of adsorption process, and then saturation values (98% extraction) were gradually reached within 40 min. In order to study the optimum desorption time, when the sorption process

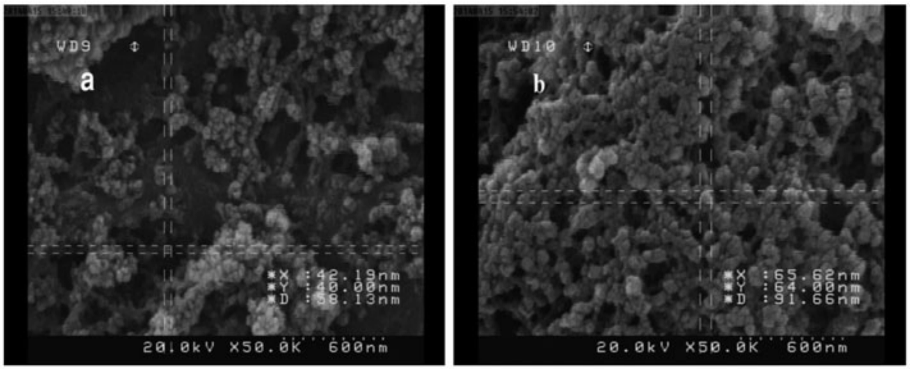

Fig. 1. Scanning electron micrograph of polymers: (a) IIP and (b) NIP.

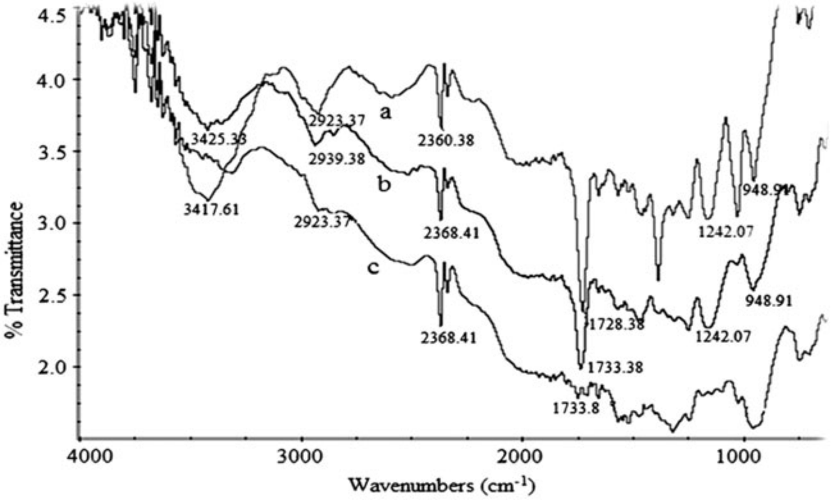

Fig. 2. The FT-IR spectra of (a) unleached IIP (b) leached IIP (c), and ligand.

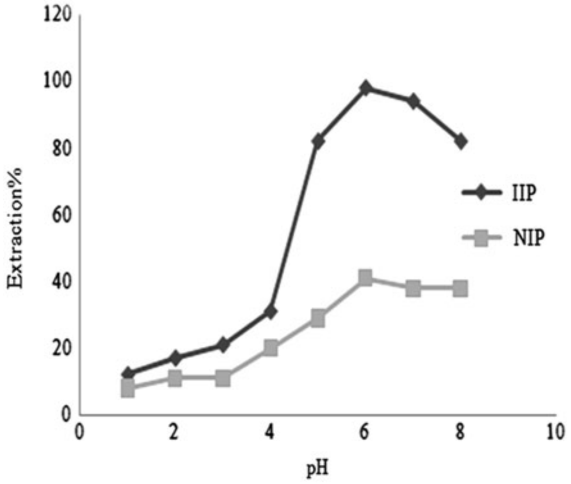

Fig. 3. Effect of pH on the extraction of Cd(II) ions by IIP and NIP particles in batch experiments. Conditions: 30 mg of polymer particles; sample volume, 20 mL; cadmium ion concentration, 1 mg/L.

was completed, the solution was centrifuged. The supernatant solution was removed, and then elution of Cd(II) ions from IIP was performed by 5 mL of 0.1 M HNO_3. The resulting suspension was stirred for different times (5–60 min). After centrifugation, the concentration of Cd(II) ion in this acidic solution was determined by ICP-OES. According to results, extraction percent was increased up to 40 min and it was constant in longer times. Therefore, the best quantitative time for the elution of Cd(II) ions from the imprinted polymer was 40 min.

3.4. Choice of eluent solution

In order to obtain the best solvent for the elution of Cd(II) from IIP, 5 mL portions of 0.1 M HCl, 0.1 M HNO_3, and 0.1 M H_2SO_4 were used. The results showed that 0.1 M HNO_3 provided the best recovery among other solvents. HNO_3 was selected as eluent not only because of its some better leaching characteristic over other two mineral acids, but also because of its compatibility with ICP-OES.

3.5. Capacity and adsorption isotherms

The maximum experimental sorption capacity of the imprinted polymer was determined after saturation of the polymer with cadmium ions under optimum conditions at room temperature. The sorption capacity (mg/g) of the IIP relative to the imprint metal ion was calculated as follows:

$$Q = \frac{(C_i - C_e)V}{m} \qquad (2)$$

where C_i and C_e are the concentrations before and after extraction (mg/L), respectively, V is the volume of initial solution (mL), and m is the mass of IIP materials (g). According to batch rebinding results, the maximum amount of Cd(II) ion that can be absorbed by IIP was found to be 16.52 mg/g at pH 6.0. Fig. 4 shows the effects of initial concentration of Cd(II) ions on the adsorption capacity of the IIP and NIP. The amount of Cd(II) ions adsorbed per unit mass of the polymers increased with increasing the initial concentration

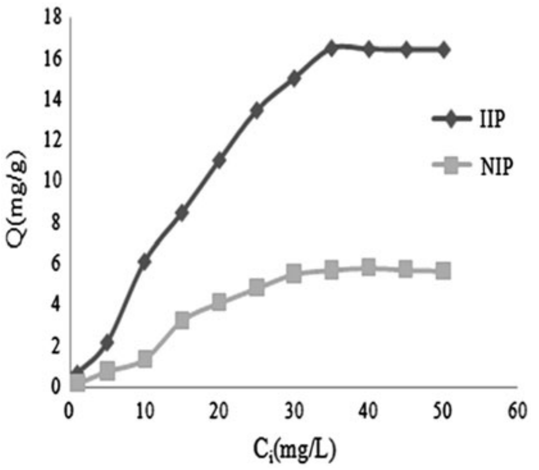

Fig. 4. Effects of initial concentration of Cd(II) ions onto the adsorption capacity of the IIP and NIP.

of Cd(II) ions, and reached a plateau determining the adsorption capacity values. The high adsorption capacity for IIP compared to NIP is due to the imprinted cavities and specific recognition sites created after removal of Cd(II) ion in the IIP, which are complementary to target ion in shape, geometry, and size, whereas no such specificity was found in NIP. The results demonstrate that imprinting plays an important role in the adsorption behavior [15].

Langmuir and Freundlich isotherm models are usually used to evaluate adsorption properties of IIPs. According to the Langmuir adsorption model, the sorption process occurs in a surface monolayer of homogenous binding sites whose number is fixed [27,28]. The linear Langmuir model is expressed by following equation:

$$C_e/Q = \left(1/Q_{\max}\right)C_e + 1/bQ_{\max} \tag{3}$$

where Q is the amount of Cd(II) ions adsorbed at equilibrium (mg/g), C_e is the final concentration of ion after rebinding experiment (mg/L), b is Langmuir constant (L/mg), and $Q_{\max}$ is the maximum adsorption capacity (mg/g).

The Freundlich model assumes heterogeneous adsorption and is applicable for multilayer coverage on adsorbent surface [29]. The Freundlich adsorption isotherm is expressed by following equation:

$$\log Q = (1/n)\log C_e + \log K_f \tag{4}$$

where K_f and n are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

The isotherm data were fitted with the above mentioned isotherm models and are shown in Figs. 5 and 6. The theoretical value of maximum adsorption capacity ($Q_{\max}$), Langmuir constant (b), and correlation coefficient (R^2) obtained from the Langmuir isotherm was found to be 17.66 mg/g, 0.676 L/mg, and 0.995. The experimental value of sorption capacity is very close to the calculated value of Langmuir model. The Freundlich constant (K_f), adsorption intensity (n), and correlation coefficient (R^2) were obtained to be 5.05, 2.11, and 0.955, respectively. Comparing the correlation coefficients of isotherms in fitting the adsorption data, it shows that Langmuir model provides better fitting for imprinted polymer.

3.6. Selectivity studies

Competitive adsorption of Cd(II) ion in the presence of Zn(II), Mn(II), Cu(II), Pb(II), and Ni(II) from their binary mixtures was investigated in batch experiments. The initial concentrations of pair of metal ions (1 mg/L) were extracted by 30 mg of polymers at pH 6.0. The distribution ratio (mL/g) of Cd(II) ions between the polymer and aqueous solution was evaluated by following equation:

$$K_d = (C_i - C_e)V/C_e m \tag{5}$$

where V is the volume of initial solution, m is the mass of IIP materials, C_i is the initial concentration in solution, and C_e is the final concentration of ion after rebinding experiment.

Selectivity coefficients for Cd(II) ions relative to foreign ions are defined as:

$$K_{Cu^{2+}} = K_d^{Cu^{2+}}/K_d^{M^{n+}} \tag{6}$$

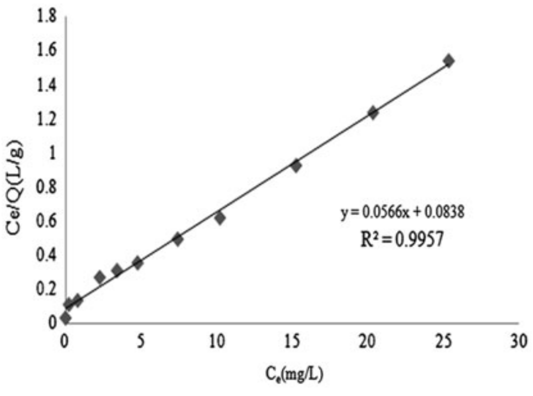

Fig. 5. Langmuir adsorption isotherm of Cd(II)-IIP.

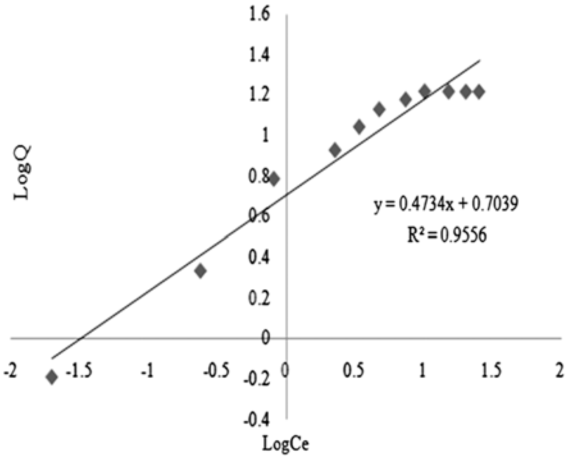

Fig. 6. Freundlich adsorption isotherm of Cd(II)-IIP.

where $K_{\mathrm{d}}^{\mathrm{Cu}^{2+}}$ and $K_{\mathrm{d}}^{\mathrm{M}^{n+}}$ are distribution ratios of Cd(II) and foreign ion, respectively. The relative selectivity coefficient is defined as:

$$k' = k_{\text{imprinted}}/k_{\text{non-imprinted}} \tag{7}$$

where $k_{\text{imprinted}}$ and $k_{\text{non-imprinted}}$ are selectivity coefficients of the imprinted and non-imprinted polymers, respectively [29]. The distribution ratios (K_{d}), selectivity coefficients (k), and relative selectivity coefficients (k') values of IIP and NIP material are listed in Table 1. According to the data, prepared imprinted polymer has a higher selectivity towards Cd(II) ions than the non-imprinted one. It can be seen that the foreign ions have no significant effects on adsorption of Cd(II) ions.

3.7. Reusability

In order to study the reusability of the prepared ion-imprinted polymer, the sorption–desorption cycles were performed for six times using the same nanoparticles. Batch rebinding experiment was performed for initial cadmium ion concentration of 1 mg/L under the optimal conditions.

Table 1
IIP and NIP selectivity studies for Cd(II) vs. closely related ions

Cation	K_{d} (IIP)[a]	K_{d} (NIP)	k (IIP)[b]	k (NIP)	k'[c]
Cd^{2+}	7666.66	272.30	–	–	–
Zn^{2+}	146.34	82.39	52.38	3.30	15.87
Ni^{2+}	166.66	117.65	46.00	2.31	19.91
Cu^{2+}	391.53	259.26	19.58	1.05	18.65
Pb^{2+}	246.57	156.38	31.09	1.74	17.87
Mn^{2+}	313.73	146.34	24.44	1.86	13.14

[a] Distribution ratio.
[b] Selectivity coefficient.
[c] Relative selectively coefficient.

The relative standard deviations for six replicates were found to be 1.8%. The results showed that the Cd(II)-IIP could be repeatedly used without any significant loss in the initial binding affinity.

3.8. Evaluation of the method performance

Under the optimized conditions, the preconcentration procedure showed a linear curve within a concentration range of 1–50 μg/L. A good linearity with squared correlation coefficient (R^2) 0.999 was obtained. The enrichment factor, defined as the ratio of the slopes of the calibration curves after (i.e. Int = 304.44 C_{Cd} + 17.726) and before (i.e. Int = 15.453 C_{Cd} + 39.524) preconcentration step, is calculated as 304.44/15.453 = 19.7. Meanwhile, the preconcentration factor evaluated from the ratio of the sample volume (100 mL) to the eluent volume (5 mL) is 20. The LOD and quantitation (LOQ) of this method, are defined as $C_{\mathrm{LOD}} = 3.3\ S_{\mathrm{b}}/\mathrm{m}$ and $C_{\mathrm{LOQ}} = 10\ S_{\mathrm{b}}/\mathrm{m}$, where S_{b} is the standard deviation of 10 replicate blank signals and m is the slope of the calibration curve after preconcentration, for a sample volume of 100 mL, were found to be 0.14 and 0.43 μg/L. The relative standard deviation for six separate batch experiments (RSD) with a cadmium concentration of 25.0 μg/L was 2.6%.

The accuracy of the proposed method was evaluated by analyzing a certified reference material, NCS ZC73036, with a cadmium concentration of 0.076 ± 0.004 μg/g. The cadmium content obtained (mean ± SD, $n = 3$) was 0.074 ± 0.005 μg/g, which is not significantly different from the certified value.

3.9. Applications

The proposed method has been applied for the determination of Cd(II) in synthetic and tap water samples and some medicinal plants. The reliability of the method was checked by the analysis of the samples spiked with the known concentration of Cd(II).

For the preconcentration of Cd(II) ions, 100 mL of the aqueous solution of real and spiked prepared samples were adjusted to pH 6.0 and equilibrated with 30 mg of Cd(II)-IIP. The resulting suspension was stirred for 40 min and then leaching process was carried out by 5 mL 0.1 M HNO_3 while stirring for further 40 min. The concentration of Cd(II) ions in leached solutions was determined by ICP-OES.

Table 2
Analysis of cadmium ion in medicinal herbs and CRM

Sample	C_{added} (μg/g)	C_{found} (μg/g)[a]	Recovery (%)
Matricaria recutita (Asteraceae)	–	0.5 ± 0.01	–
	10	10.3 ± 0.2	98.1
Urtica dioica (Urticaceae)	–	0.4 ± 0.01	–
	10	10.2 ± 0.2	98.1
Hedera helix (Araliaceae)	–	–	–
	10	9.7 ± 0.2	97.0
Cichorium intybus (Asteraceae)	–	–	–
	10	9.6 ± 0.1	96.0
CRM (NCS ZC73036)	(Real) 0.076 ± 0.004	0.074 ± 0.005	97.4

[a] Mean ± SD, *n* = 3.

Table 3
Determination of cadmium ion in water samples

Sample	C_{added} (μg/L)	C_{found} (μg/L)[a]	Relative recovery (%)
Synthetic sample[b]	0	–	–
	10	9.6 ± 0.1	96.0 ± 1
Tap water	0	–	–
	10	9.6 ± 0.2	96.0 ± 2
Mineral water	0	–	–
	10	9.7 ± 0.2	97.0 ± 2

[a] Mean ± SD, *n* = 3.

[b] Solution contain Ni^{2+}, Cu^{2+}, Zn^{2+}, and Mn^{2+} ions of 10 μg/L concentrations.

Table 4
Analytical parameters of different Cd(II)-IIPs

Ligand	Polymerization method	Detection system	Relative selectivity coefficient					Maximum capacity	LOD (μg/L)	Refs.
			k´Ni	*k*´Zn	*k*´Cu	*k*´Mn	*k*´Pb			
MAC[a]	Suspension	GF-AAS	–	1,683	–	–	7.8			
SPANDS[b]	Bulk	Elemental analyzer	–	7.4	6.6	–	–	0.4(mg/g)	–	[1]
Salen[c]	Suspension	FI-FAAS	–	–	–	–	–	2(μg/g)	–	[22]
Dual-ligand[d]	Precipitation	ICP-AES	–	35.3	25.5	–	–	0.48 (mg/g)	0.11	[24]
1-vinylimidazol	Bulk	FAAS	–	1.38	4.44	–	157.5	32.56(mg/g)	0.14	[9]
DPC[e]	Precipitation	ICP-OES	19.91	15.87	18.65	13.14	17.87	4.56(mg/g)	0.11	[17]
								16.52(mg/g)	0.14	This work

[a] N-Methacryloly-(l)-cysteinemethylester.

[b] 2-(p-Sulphophenylazo)-1,8-dihydroxy-3,6 naphthalene disulphonic acid trisodium salt.

[c] 2,2-{Ethane-1,2-diylbis[nitrilo(E)methylylidene]} bis(6-allylphenol).

[d] (2Z)-N,N_-bis(2-aminoethylic)but-2-enediamide.

[e] 1,5-diphenylcarbazide.

The results listed in Tables 2 and 3 indicate the suitability of the present polymer for preconcentration of Cd(II) from aqueous solutions. The recoveries of Cd(II) ions from the real and spiked samples varied in the range of 96–98%.

4. Conclusions

In this paper, a new ion-imprinted polymer was synthesized via precipitation polymerization for selective extraction and separation of cadmium ions from aqueous solutions. The results obtained from this study revealed that diphenylcarbazide can be used as a chelating agent in conjunction with ion imprinting technology to create recognition sites with high affinities toward Cd(II) ions. The prepared Cd(II)-IIP can be repeatedly used and regenerated with no significant decrease in their binding affinities. Performance of the method was excellent in extraction and preconcentration of trace amounts of Cd(II) ions. As a result, the LOD, RSD, selectivity, and maximum adsorption capacity of this method are comparable or better than some of the previously reported methods (Table 4). The results showed that the prepared IIP could be employed as an effective sorbent in solid-phase extraction for the selective removal of Cd(II) from different matrixes.

Acknowledgments

The authors would like to acknowledge financial assistance from Tehran University of Medical Sciences, Tehran, Iran. The authors thank the MOH and ME Laboratory Research Center and Institute of Medicinal Plants, ACECR for the supply of some instruments.

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