

AN IMPRINTED POLYMER FOR REMOVAL OF Cd^{2+} FROM WATER SAMPLES: OPTIMIZATION OF ADSORPTION AND RECOVERY STEPS BY EXPERIMENTAL DESIGN

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Abstract A new ion-imprinted polymer (IIP) was synthesized by copolymerization of 4-vinylpyridine (monomer), ethyleneglycoldimethacrylate (cross-linker) and 2,2-azobis-isobutyronitrile (initiator) in the presence of Cd^{2+} and quinaldic acid (complexing agent). It was found that the adsorption capacity of IIP and blank polymer were 45.0 and 6.2 mg g^{-1} , respectively. The relative selectivity coefficients of the imprinted polymer for different binary mixture were also calculated. Compared to non-imprinted polymer (NIP), the IIP had higher selectivity for $\text{Cd}(\text{II})$. The IIP was used as a sorbent for cadmium extraction from water samples by using a simple batch extraction procedure. The effect of different parameters on Cd^{2+} extraction and its recovery from the IIP were evaluated and optimized by using experimental design methodology. The optimized adsorption/desorption procedure was applied for cadmium removal from the real water samples. The obtained recoveries proved that this IIP could be used for removal of trace cadmium ions from water samples.

Keywords: Cd^{2+} removal; Ion imprinted polymer; Solid phase extraction; Experimental design.

INTRODUCTION

In recent years, ion imprinting technique has been reported as a powerful tool for preparing a highly selective polymeric materials, used in the extraction and preconcentration of variety of ions such as UO_2^{2+} [1–4], Pd^{2+} [5–8], Cu^{2+} [9–12], Fe^{2+} [13, 14], Hg^{2+} [15, 16], Ni^{2+} [17, 18], Cr^{2+} [19] and Zn^{2+} [20]. The designing and synthesis of cadmium (II) imprinted polymer is particularly important because cadmium(II) is among the 13 toxic metal species on the priority pollutant list of the Environmental Protection Agency (EPA) [21, 22]. Also, the international agency for research on cancer has classified cadmium as a human carcinogen [23]. Cadmium can enter the organism *via* the alimentary and respiratory tract [23]. The amount of cadmium in geological and environmental samples is lower than the detection limits of most of analytical methods. Thus, the extraction, preconcentration and determination of trace cadmium from the natural water are very important and need much more attention [24].

Nishide and Tsuchida have reported one of the first ionic template phenomena in the synthesis of imprinted polymers [25]. A cadmium imprinted resin (poly $\text{Cd}(\text{II})$ -DAAB-VP) has been prepared by reaction of $\text{Cd}(\text{II})$ -diazaminobenzene-inylpyridine with cross-linker ethyleneglycoldimethacrylate (EGDMA) [24]. Zhai *et al.* have reported selective solid-phase extraction of trace cadmium(II) with an ion imprinted polymer (IIP), prepared by a dual ligand monomer [26]. An imprinted organic/inorganic hybrid sorbent for selective separation of cadmium from aqueous solution has been proposed by Lu and Yan [27]. In the other work, a $\text{Cd}(\text{II})$ -imprinted polymer containing epoxy resin, has been synthesized and characterized by Pan and co-workers [28]. Recently, phenol-formaldehyde- $\text{Cd}(\text{II})$ -2-(*p*-sulphophenylazo)-1,8-dihydroxynaphthalene-3,6-disulphonate (PF- $\text{Cd}(\text{II})$ -SPANDS)

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has been reported by Singh and co-worker^[29].

In this study, a new Cd(II)-imprinted polymer with better adsorption capacity and selectivity (compared to previously reported Cd(II)-imprinted polymers) was synthesized by using quinaldic acid as Cd²⁺ complexing reagent and vinyl pyridine as functional monomer. The prepared IIP was then used for extraction of Cd(II) in different water samples. The extraction and recovery steps of the proposed method were optimized by applying experimental design methodology.

EXPERIMENTAL

Apparatus

A Shimadzu model 6300 atomic absorption spectrometer (Japan) was used to measure the concentration of metal ions (Cd, Cu, Pb, Co, Ni and Zn) in aqueous solutions. Hollow cathode lamps were used as the radiation sources. Radiation wavelengths of 228.8, 253.6, 217.0, 213.9, 324.7, 232.0 and 240.7 nm were used for Cd, Hg, Pb, Zn, Ni and Co, respectively. Cold vapor atomic adsorption spectroscopy was applied for Hg determination. Other mentioned elements were analyzed by flame atomic absorption spectroscopy. A digital pH meter (Metrohm) model 691, equipped with a glass electrode (Sentek, Braintree, UK) was used for pH measurements.

Reagents

Vinyl pyridine (Merck, Germany) was purified by passing through a short column of neutral alumina, followed by distillation under reduced pressure. Ethylene glycol dimethacrylate (EDMA) (Sigma-Aldrich, USA) was distilled under reduced pressure in the presence of hydroquinone inhibitor and stored at 4°C until use. 2,2'-Azobis(2-methylpropionitrile) was obtained from Acros Organic (Geel, Belgium). Quinaldic acid, dimethyl sulfoxide (DMSO) and Cd(NO₃)₂·4H₂O were from Merck (Germany). Other chemicals were of analytical grade and purchased from Merck (Germany).

Cd(II) Imprinted Polymer Preparation

In order to prepare Cd(II) imprinted polymers, different amounts (mmol) of Cd(NO₃)₂ and quinaldic acid (shown in Table 1) were dissolved in 20 mL DMSO and then varying amounts (mmol) of 4-vinyl pyridine were added to the solution. The solution was allowed to be at this state for 1 h in order to complete the complexation reaction. Finally, 0.15 g initiator (2,2'-azobisisobutyronitrile) and cross-linker (EDMA), dissolved in 3 mL DMSO, were mixed with the previous solution and followed by purging with N₂ gas for 10 min. The polymerization was carried out in the water bath at 70°C for 24 h. The resulting polymer was ground in a mechanical mortar. The obtained particles (ranging from *ca.* 100 nm to about 1 µm) were first washed with ethanol and then washed with solution of HCl (4 mol/L). Finally, the particles were washed with distilled water and dried at 60°C. The non-imprinted polymer (NIP) was prepared using the same protocol except that Cd(II) did not exist in the polymerization mixture.

Table 1. Synthesis of Cd(II) imprinted polymers under varying conditions and their adsorption capacities

Sample	QA (mmol)	Cd (mmol)	VP (mmol)	EGDMA (mmol)	Adsorption capacity (µg/g)
IIP1	1	1	2	4	1058
IIP2	–	1	4	20	9151
IIP3	2	1	2	10	5041
IIP4	1	1	3	10	8380
IIP5	1	1	3	20	45043
IIP6	1	1	2	20	23920

Cd²⁺ Loading Capacity

In order to determine the loading capacity of Cd(II) imprinted polymer, 0.3 g of target polymer was added to 40 mL solution containing different amount of Cd²⁺ ions (0.05 mg to 1 mg) and then the solution was adjusted to pH = 7. The mixture was shaken at 25°C for 2 h and then it was centrifuged. Afterwards, the Cd²⁺ content of the solution was determined by the atomic absorption spectroscopy technique (AAS). Loading capacity of the aimed

polymer was calculated by the following equation:

$$Q = (c_o - c_e)V/W \quad (1)$$

where Q is the loading capacity of the polymer ($\mu\text{g}\cdot\text{g}^{-1}$); c_o and c_e are the concentrations of the ions in the initial solution and in the aqueous phase after adsorption, respectively ($\mu\text{g}\cdot\text{L}^{-1}$); V is the volume of the aqueous phase (mL) and W is the amount of polymer (g).

Cd²⁺ Containing Sample Preparation Method

200 mL of aqueous solution containing Cd^{2+} was contacted with 0.05 g of IIP for 30 min at the stirring rate of 400 (r/min). Then, the mixture was passed through sintered glass filter forced by a vacuum pump. The retained IIP on the filter was first washed with 10 mL distilled water and subsequently the retained target molecules on the IIP were eluted with 4 mL of HCl solution (containing HCl 2.5 mol/L). The eluted solution was used for Cd analysis using FAAS. The used IIP could be reused for the next experiments after washing with 10 mL distilled water.

RESULTS AND DISCUSSION

IIP Formulation Optimization

In order to synthesis the Cd^{2+} imprinted polymer, a new formulation was developed in this work. In this method, quinaldic acid was selected as complexing agent. Furthermore, vinyl pyridine was applied as both functional monomers and complementary complexing agents. Figure 1 shows schematically the Cd(II) imprinted polymer preparation methodology.

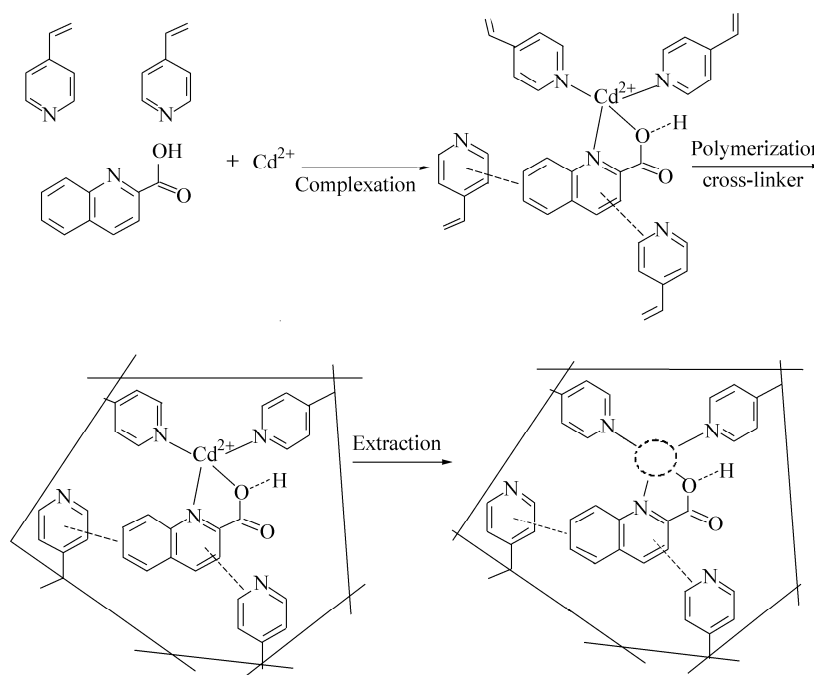


Fig. 1 Schematic illustration of the Cd^{2+} imprinted polymer preparation methodology

In order to optimize the IIP formulation, cadmium imprinted polymer was synthesized under varying conditions as outlined in Table 1. As can be seen, the highest adsorption capacity belongs to the formulation named as IIP-5. It can be seen that the selection of suitable amount for functional monomer is particularly important. In the absence of quinaldic acid the IIPs do not provide a proper affinity to Cd^{2+} . It seems that simultaneously sharing of both functional monomer and selected ligand in interaction with metal ion helps to get

a better recognition sites in the final polymer network, as it is common strategy in producing of the IIPs. Higher amounts of ligand decrease the ration of functional monomers in metal coordination space, decreasing subsequently the polymer affinity to target ions. It must be noticed that four coordination bonds are predicted for Cd^{2+} . When the mole ratio of functional monomer/quinaldic acid is adjusted at 2, two of four coordination bonds are supported by selected ligand and thus two others must be offered by functional monomers. Since a quinaldic acid molecule is capable to suggest two coordination bonds, it seems that if two molecules of this ligand are arranged around the Cd^{2+} , the functional monomers will not participate in interaction with metal ion and thus the prepared recognition sites in IIP will not contain the properly arranged functional monomers in the selective cavities of the IIP. Moreover, the amount of cross-linker is also important in defining the efficiency of final IIPs. For instance, In IIP₃, other than the above mentioned points, it seems that the cross-linker/functional monomer ratio is not optimum to achieve a proper formulation.

Figure 2 shows the scanning electron microscopy images of IIP-5 and its corresponding NIP. It can be seen that there is no considerable difference between IIP and NIP, regarding the size and morphology (magnified images in the insets). Thus, the higher adsorption capacity of IIP, compared to NIP, can be attributed to the imprinting event, taken place in the polymerization step.

IR spectra of the IIP, obtained before and after completely washing of the polymer, are shown in Fig. 3. Presence of strong bands in the regions around *ca.* 1721 and *ca.* 1130 cm^{-1} are respectively related to the $\nu_{\text{C=O}}$ and $\nu_{\text{C-O}}$ of quinaldic acid. Although, the completely washing of the polymer results in decreasing the heights of these bands; but, after washing, they are still strong, indicating the presence of considerable amount of ligand in the polymer network.

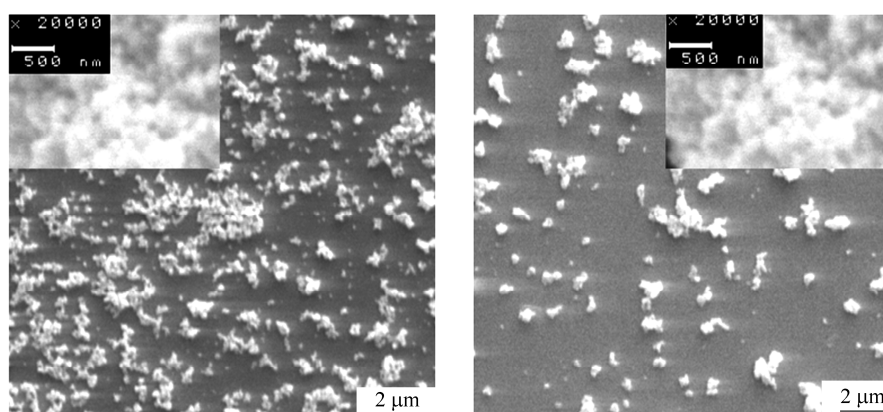


Fig. 2 Scanning electron microscopy images of Cd^{2+} imprinted polymer (left) and its corresponding NIP (right) Inset images are the locally magnified surface images of IIP and NIP.

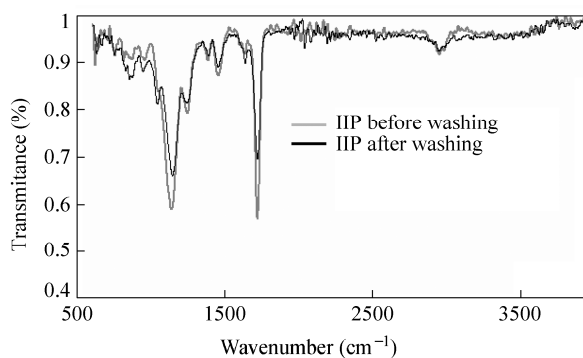


Fig. 3 IR spectra recorded for the washed and unwashed Cd^{2+} -IIP

Evaluation of Cd(II) Adsorption Capacities of IIP and NIP

In order to measure the adsorption capacities, 0.1 g of IIP and NIP were equilibrated with 25 mL of various concentrations of Cd(II) solutions at pH = 7 for 4 h. Concentration of Cd(II) in the solutions were measured by FAAS and the adsorption capacity of IIP or NIP for Cd(II) ions was calculated. As can be seen, in Fig. 4, the amount of Cd(II) adsorbed per unit mass of the imprinted and non-imprinted polymers increases with the increase in initial concentration of Cd(II). However, the IIP adsorption behavior is considerably different from NIP. In order to reach the saturation condition, the initial Cd(II) concentrations were increased till the plateau values where the adsorption capacity values were obtained. According to this experiment, the average maximum adsorption capacities equal to 45.0 and 6.2 mg·g⁻¹ were obtained for Cd(II)-imprinted and non-imprinted polymers, respectively. Obviously, the capacity of imprinted polymers is noticeably larger than that of non-imprinted polymers.

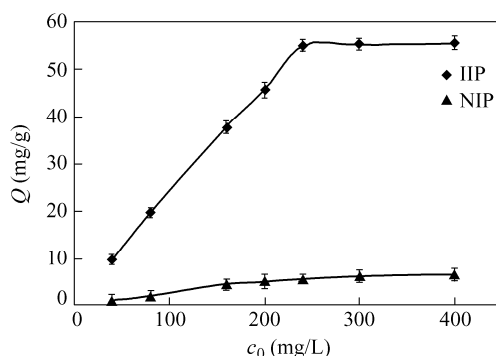


Fig. 4 The effect of initial concentration on the adsorption capacity of Cd(II)-IIP
IIP amount 0.1 g, pH = 6.0, V = 25 mL, shaking time = 4 h, temperature 25°C

Selectivity of the Cd²⁺ Imprinted Polymers Against Other Cations

Some important parameters including adsorption capacity, distribution ratio, selectivity factor of Cd(II) with respect to the other ions and relative selectivity factor were calculated from the following equations^[30]:

$$D = Q/c_e \quad (2)$$

$$\alpha = D_{Cd} / D_M \quad (3)$$

$$\alpha_r = \alpha_i / \alpha_n \quad (4)$$

where Q represents the adsorption capacity (μg·g⁻¹), and c_e is the equilibrium concentration of metal ions (μg·mL⁻¹). D_{Cd} and D_M (mL·g⁻¹) represent the distribution ratios of Cd(II) and other competitive ion, respectively. α_r , α_i and α_n represent the relative selectivity coefficient, the selectivity factor of imprinted sorbent and the selectivity factor of non-imprinted sorbent, respectively.

For the synthesized IIP, competitive adsorption of Cd(II)/Cu(II), Cd(II)/Zn(II), Cd(II)/Hg(II), Cd(II)/Co(II), Cd(II)/Ni(II) and Cd(II)/Pb(II) from their binary mixture was investigated by batch procedure. The obtained results are summarized in Table 2. As can be seen, the D value of the Cd(II) ion imprinted polymer for Cd(II) is large, while it is low significantly for Cu(II), Zn(II), Hg(II), Co(II), Ni(II) and Pb(II) ions. Also, the α_r values in the table indicate that Cd(II) can be selectively extracted even in the presence of high concentrations of Cu(II), Zn(II) and Hg(II). These data clearly indicate that the cadmium selective sites of IIP function properly. Moreover, the effect of different electrolytes such as NaCl, KBr, KI, Na₃PO₄, NaNO₃, CaCl₂, Na₂SO₄ and MgSO₄, on the adsorption of Cd(II) was studied using the batch procedure. The results showed that these electrolytes did not interfere with adsorption of Cd(II) even when their concentrations were 200 times as much as that of Cd(II) in the solution. This indicates that the proposed IIP can be suitably used as a sorbent for Cd(II) extraction in solutions containing high concentrations of electrolytes. The reported tolerance limit is defined as

the ion concentration causing a relative error $< \pm 5\%$.

Table 2. The selectivity parameters of copolymers for $\text{Cd}(\text{II})$

Metal ions	D_i (imprinted) (mL/g)	D_n (non-imprinted) (mL/g)	α_i	α_n	α_r
Cd(II)	6762	210.4			
Cu(II)	131.2	270.7	51.5	0.7	73.6
Zn(II)	110.3	241.9	61.4	0.8	76.7
Hg(II)	104.7	256.0	64.6	0.8	80.7
Co(II)	91.5	280.4	73.9	0.7	105.5
Ni(II)	89.1	166.7	75.9	1.2	63.2
Pb(II)	61.2	198.5	110.5	1.1	100.4

Identification and Optimization of the Parameters Effective on the Extraction and Desorption of Cd^{2+}

A simple batch solid phase extraction (SPE) procedure was applied for extraction of target ions by the prepared IIP. In order to identify the significant parameters, effective on the Cd(II) extraction, we used full factorial experimental design as a well-known screening design. In the extraction step, some parameters such as pH of solution (pH), IIP- Cd^{2+} solution contacting time (time), ethanol content of solution as added organic solvent ($\text{Et}_1\%$) and solution temperature (T) were chosen as the candidate parameters should be screened. In this design, the low and high levels of aimed parameters were selected according to the information obtained in the period of initial experiments and also from some previous works^[30]. The percent recovery of Cd(II) for the synthesized IIP was considered as the aimed response. The washing and elution in all runs of the design were constant.

Table 3 shows the full factorial experimental design and resulted recovery responses in the corresponding runs of experiments. The recovery responses related to the runs of experiments were analyzed statistically and the results were evaluated in order to identify the main effects and the possible interactions among different variables. The obtained pareto chart (Fig. 5) indicates that only pH is significant and the other tested parameters as well as the interaction parameters are not significant ($p = 0.05$).

Table 3. Full factorial experimental design for evaluation of extraction parameters and the obtained recovery responses

No.	Factors				
	Time (h)	T ($^{\circ}\text{C}$)	pH	Et_1 (%)	Recovery (%)
1	5	50	9	1	90.8
2	5	50	9	5	89.6
3	5	25	3	5	4.7
4	0.5	25	3	1	5.0
5	0.5	50	3	1	2.3
6	5	25	9	1	96.5
7	0.5	50	9	1	88.4
8	5	25	3	5	5.9
9	5	50	3	5	4.1
10	5	25	9	5	97.2
11	0.5	25	9	5	95.7
12	0.5	25	9	1	96.0
13	0.5	50	3	5	2.9
14	5	50	3	1	3.4
15	5	25	3	1	5.2
16	0.5	50	9	5	90.1

According to the full factorial design results (as shown in the pareto chart), the changing of the time of extraction from 0.5 h to 5 h did not affect the response. But, further study showed that the extraction time lower than 0.5 h led to considerably decreased percent recovery. Thus, extraction time equal to 0.5 h was chosen as optimum for this parameter.

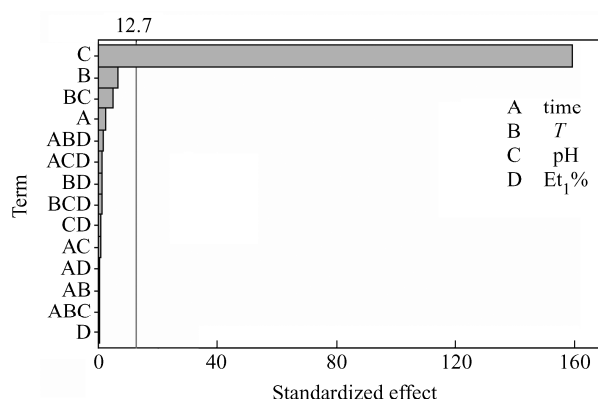


Fig. 5 Pareto chart obtained from statistical analysis of responses of full factorial design experiments ($p = 0.05$) for evaluation the effective parameters in the extraction step

As stated above, the pH was found to be a very effective parameter in the extraction step. Therefore, the effect of this variable was evaluated by determination of percent recovery of Cd^{2+} at different pH. Figure 6 shows the results of this experiment.

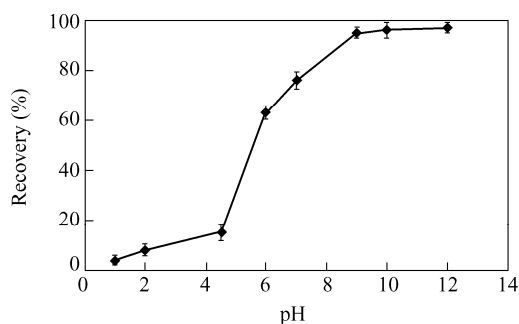


Fig. 6 Variation of Cd extraction recovery with changing the pH of extraction solutions
Extraction time = 0.5 h, stirring speed = 400 r/min, $T = 25^\circ\text{C}$

As can be seen, in acidic pH (below $\text{pH} = 6$) the percent recovery is very low. Conversely, in alkaline condition the percent recovery is high. The low recovery in acidic pH can be attributed to the protonation of carboxylic acid group of quinaldic acid and also nitrogen of vinyl pyridine which are responsible for complex formation with Cd^{2+} ions in the selective sites of IIP. Thus, $\text{pH} = 9$ was selected as optimal for Cd^{2+} ions extraction in the IIP.

Complete desorption of Cd(II) from the IIP is important, because it ensures the reusability of IIP in the next experiment. Furthermore, complete removal of adsorbed Cd^{2+} from the IIP enable us to measure the ability of IIP for adsorption of Cd^{2+} from the aimed solutions. In order to remove the adsorbed Cd(II) from the IIP, some solutions such as EDTA, nitric acid and hydrochloric acid were tested. HCl solution was the better option among the tested solutions. The concentration of HCl solution ($[\text{HCl}]$), used as the eluent, was evaluated by the experimental design approach. Because of swelling capability of the IIP in the presence of an organic solvent, the effect of ethanol as the organic solvent ($\text{Et}_2\%$) in the extraction was checked. The volume of the used eluent (V) was another important parameter for the desorption of Cd^{2+} from the IIP. In order to evaluate the significance of the described parameters, a full factorial experimental design with eight experimental runs were designed. Table 4 represents the runs of mentioned experiments and the obtained percent recoveries, related to designed experiments.

Table 4. Full factorial experimental design for evaluation of elution parameters and the obtained recovery results

No.	Factors			
	Et_2 (%)	$[\text{HCl}]$ (mol/L)	V (mL)	Recovery (%)
1	20	2.0	4	90.1
2	20	1.0	20	95.2
3	2	1.0	4	87.7
4	20	1.0	4	87.7
5	2	1.0	20	95.4
6	2	2.0	4	92.5
7	20	2.0	20	97.3
8	2	2.0	20	97.0

In this Table, each represented recovery is the average of three separate determinations, obtained from replication of corresponding run of experiment.

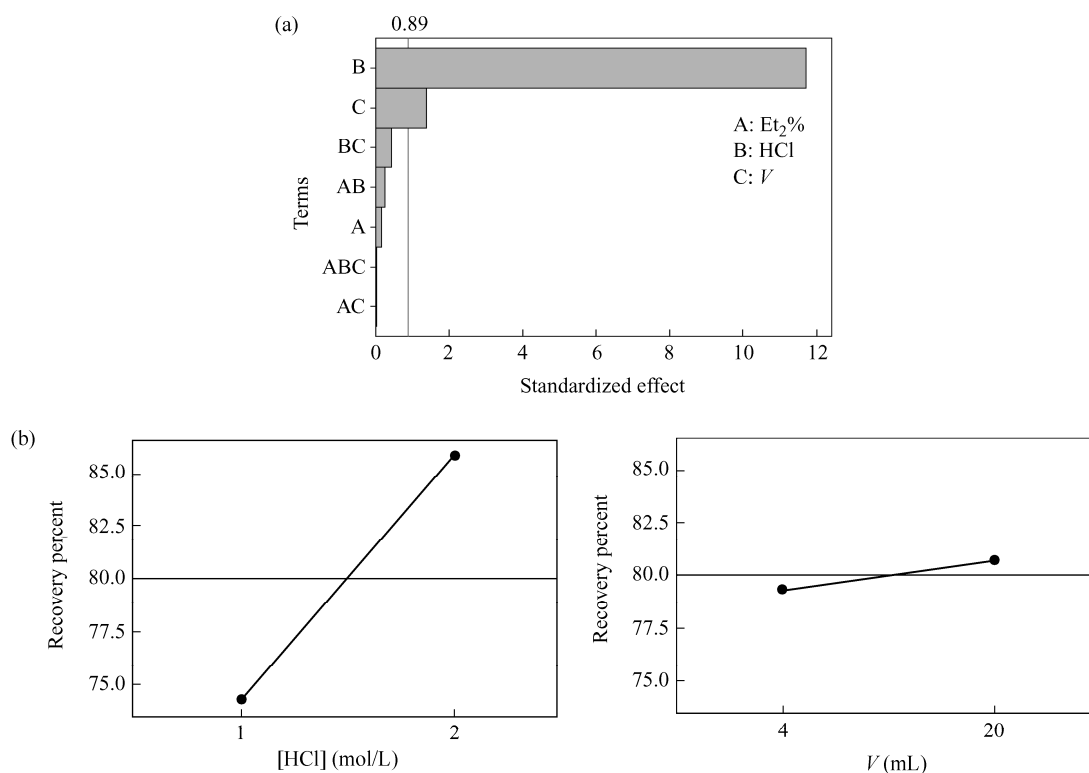


Fig. 7 Pareto chart obtained from the statistical analysis of results of full factorial design experiments ($p = 0.05$) for evaluation the effective parameters in the elution step (a), main effect plots indicating the intensity and modality of three factors' effects on the $\text{Cd}^{2+}(\text{II})$ recovery efficiency (b)

After performing the runs of experiments of full factorial design, the obtained recovery responses were statistically analyzed. Pareto chart presented in Fig. 7(a) indicates that the volume of eluent and its HCl content are significant and the parameter of $\text{Et}_2\%$ is not significant at the confidence level of 95%. The main effect plots, represented in Fig. 7(b), indicate that the effect of HCl content of eluent (as increases from 1 mol/L to 2 mol/L) on the percent recovery of cadmium is greater than that of the eluent volume (as increases from 4 mL to 20 mL). Thus, the volume of eluent can be decreased without considerable decrease in recovery value. Besides, the negative effect on the percent recovery, arisen from decreasing of eluent volume, can be compensated by increasing the concentration of HCl in the eluent solution. Thus, in the next response surface design, the

alteration region of HCl volume (V) values was confined in the lower values and that of the HCl content of the eluent was enhanced.

Response surface modeling methods are powerful experimental design tools applicable to different aims such as optimization. They represent a collection of experimental designs and multiple regression based techniques, which can be used to analyze problems when several factors may influence a response and where the goal is either to optimize or comprehend the system performance.

In order to approach the optimum response region of Cd^{2+} percent recovery, the significant independent variables ($[\text{HCl}]$ and V) were further explored according to three level full factorial designs. Table 5 represents the mentioned design and the obtained responses of the experiments.

Table 5. Three level full factorial experimental design for optimization of elution step and the obtained recoveries

No.	Factors		
	$[\text{HCl}]$ (mol/L)	V (mL)	Recovery (%)
1	2.25	4.0	90.4
2	2.25	2.5	61.4
3	1.5	4.0	91.0
4	2.25	1.0	31.8
5	3.0	2.5	70.2
6	1.5	1.0	27.8
7	1.5	2.5	62.0
8	3.0	1.0	33.9
9	3.0	4.0	96.0

By using the obtained results, a model was calculated and its coefficients were estimated with multiple regression analysis. The mathematical model, describing the relation between percent recovery and the considered factors, is shown by Eq. (5):

$$R(\%) = 13.906 - 13.36 [\text{HCl}] + 27.02 V + 4.059 ([\text{HCl}])^2 + 0.244 ([\text{HCl}])V - 1.02741 V^2 \quad (5)$$

Statistical analysis of this mathematical model showed that the p -values for coefficients of parameters of $([\text{HCl}])^2$, $([\text{HCl}])V$ and V^2 were greater than the threshold value of 0.05, indicating the insignificance of these parameters. Thus, these parameters were removed from the primary model and a new mathematical model was rearranged as Eq. (6):

$$R(\%) = 1.988(\pm 0.027) + 4.288(\pm 0.131) [\text{HCl}] + 20.433(\pm 0.690) V \quad (6)$$

The quality of fitting of the equation was expressed by the coefficient of regression R^2 or in better way by R^2 -(adj). The R^2 values provide a measure of how much variability in the observed response values can be explained by the experimental factors and their interactions. When, R^2 or R^2 -(adj) approaches unity, the better the empirical model fits the actual data. The R^2 and R^2 -(adj), obtained for the model of elution, are 0.991 and 0.993, respectively. These results indicate that the calculated model is very appropriate for prediction of the recovery in relation to the elution parameters.

The experimental results are presented as a surface plot (Fig. 8), it describes the effects of examined variables on the Cd^{2+} recovery. It can be seen that the effect of eluent volume on the percent recovery of cadmium is greater than that of HCl concentration. This observation is against that observed in the previous experiment (factorial experimental design). It can be concluded that the effect of changing of eluent volume on the aimed response is higher when it is changed at lower amounts (from 1 mL to 4 mL). Furthermore, the effect of HCl concentration variation at higher values (1.5–3 mol/L, response surface design) on the response is greater compared to the effect of HCl concentration variation on the aimed response at lower values (1–2 mol/L, factorial design). This is probably related to the fact that, in this case, the aimed variation takes place at lower amounts of eluent volume.

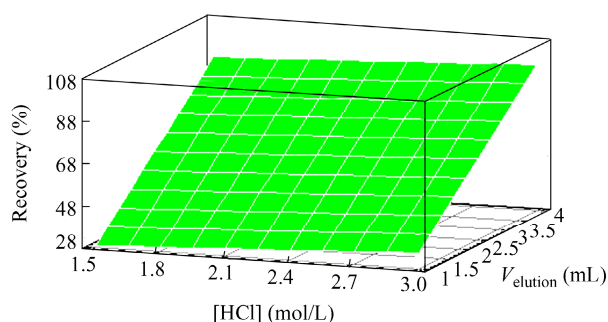


Fig. 8 Response surface plot; the recovery of the SPE method as a function of $[\text{HCl}]$ (mol/L)- V (elution)

As can be seen, there is no optimum point in the surface plot. It is evident that increasing in the HCl content of eluent and also the volume of eluent enhances the percent recovery. However, in order to compromise between these two parameters, we defined an acceptable range of percent recovery and then the values of the parameters, providing the desired recoveries, were identified according to the overlaid contour plot. The overlaid contour plots of percent recovery in three desirable recovery regions are presented in the Fig. 9.

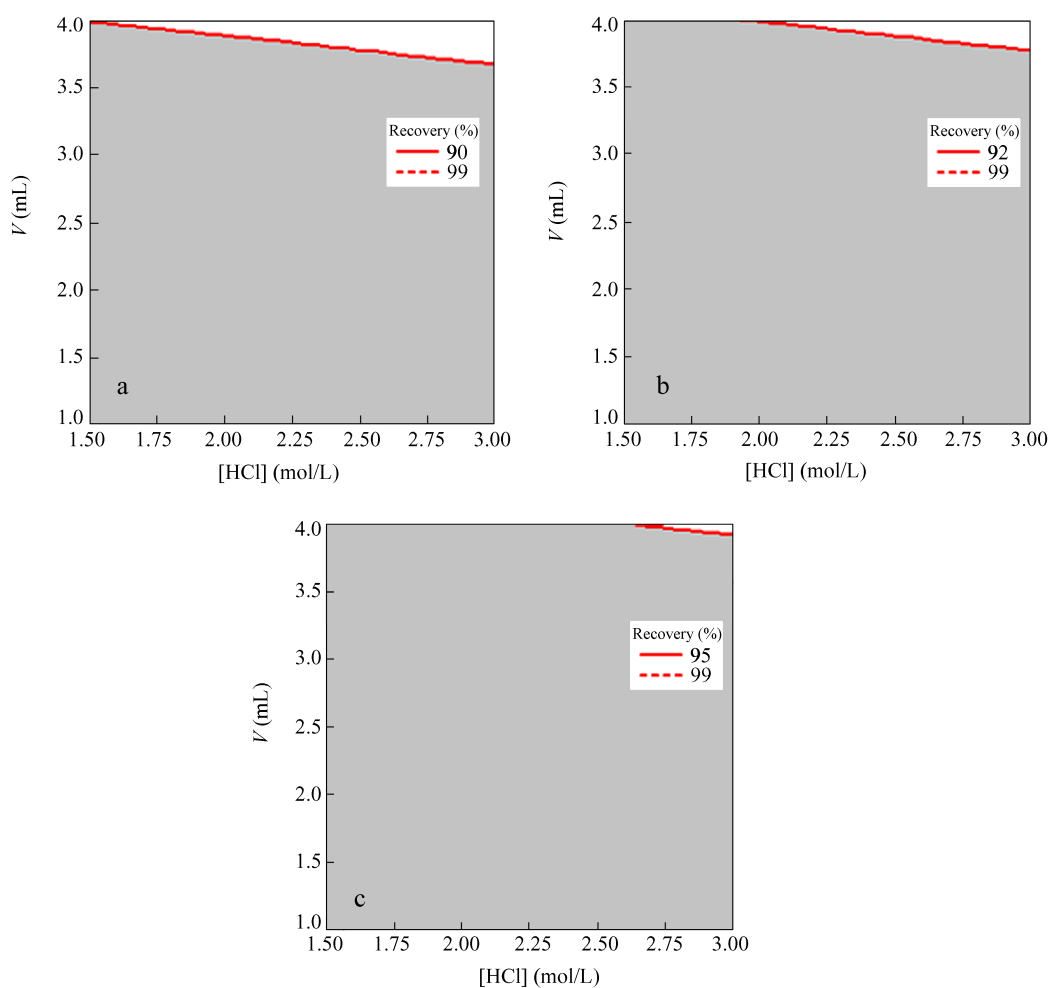


Fig. 9 Overlaid contour plots representing the desirability region in different values of $[\text{HCl}]$ and V (eluent)

As can be seen, improvement of the desirability region from 90%–99% to 95%–99% leads to considerably limitation in the ability for selection of values of V and $[HCl]$. Consequently, we selected V and $[HCl]$ values equal to 4 mL and 2.5 mol/L, respectively.

In order to verify the optimization results, an experiment was performed under the predicted optimal conditions. The obtained result (average of three percent recovery) was 95.1%. The great similarity between the predicted (94.5%) and observed results reflects the accuracy and applicability of the model as an extremely powerful method for modeling of this system.

Effect of Sample Volume / IIP Amount Ratio on the Efficiency of the Cd^{2+} Removal

Figure 10 shows the effect of the sample volume/IIP amount ratio on the efficiency of the Cd^{2+} removal by the applied method. It can be seen that there is no decrease in Cd^{2+} percent recovery till sample volume / IIP amount (mL/mg) ratio of 20. However, more than the referred ratio the capability of IIP for complete removal of cadmium ions from the water solution starts to slightly decrease. Therefore, this ratio of 20 should be considered for Cd^{2+} extraction from the water samples.

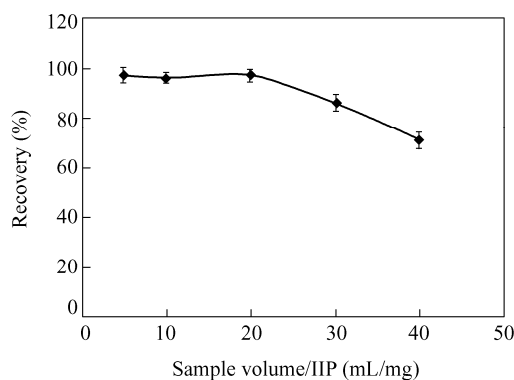


Fig. 10 Effect of sample volume/IIP amount ratio on the percent recovery of the Cd(II)

Reusability Test

In order to test the reusability of IIP, it was subjected to several loading (40 $\mu\text{g/mL}$ of Cd^{2+}) and elution operations. The elution operations were carried out with 4 mL of HCl (3 $\text{mol}\cdot\text{L}^{-1}$) found as the optimum elution condition. The calculated percent recovery of the imprinted polymer showed no considerable decrease after 10 cycles of repeated experiments. The percent recovery of the recycled Cd^{2+} imprinted beads could still be maintained at 94.5% at the 10th cycle. It can be concluded that the Cd^{2+} -imprinted polymer can be used for many times without significant decrease in its adsorption capacity.

CONCLUSIONS

In this work a new Cd(II) selective ion imprinted polymer was developed and its selectivity to Cd^{2+} in the presence of potential interferer ions such as Hg^{2+} , Pb^{2+} , Cu^{2+} and Zn^{2+} was investigated. Compared to previously reported Cd(II) imprinted polymers, this IIP showed higher Cd^{2+} adsorption capacity and more selectivity. Experimental design technique was used for optimization of different parameters effective on the adsorption and desorption steps. The synthesized polymer and developed adsorption/desorption method were applied for Cd^{2+} extraction from the water samples by using batch solid phase extraction method. The obtained suitable recoveries showed that this IIP could be applied for removal of trace Cd^{2+} from water samples.

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