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Article

Application of a Novel Ion-Imprinted Polymer to the Separation of Traces of Cd^{II} Ions in Natural Water: Optimization by Box-Behnken Design

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This study describes the preparation of a novel ion-imprinted polymer (IIP) to apply pre-concentration of cadmium ions in water samples of the Pontal Bay in Ilhéus, Brazil. First, cadmium ion was complexed with 2-(2-thiazolylazo)-*p*-cresol (TAC). Subsequently, there was the polymerization using ethylene glycol dimethacrylate and methacrylic acid monomers along with the radical azobisisobutyronitrile initiator. The mold ions were removed using 2:1 (v v^{-1}) nitric acid. The thermal stability of the polymer was evaluated by thermogravimetry and the characterization was performed by Fourier transform infrared spectroscopy. The maximum adsorption capacity for IIP (q_{max} = 84.75 mg g^{-1}) could be described by the Langmuir isotherm. The variables: sample flow rate, pH and eluent (nitric acid) were optimized using Box-Behnken design with determination by flame atomic absorption spectrometry (FAAS). The enrichment factor, as well as the limits of detection and quantification (LOQ), were found to be 44, 0.14 and 0.46 µg L^{-1}, respectively. Selectivity was evaluated by using solutions containing Cd^{II}, Cu^{II}, Ni^{II}, Pb^{II}, Co^{II}, SO_4^{2-}, and Cl^- ions. The concentration of cadmium ions in the samples varied between < LOQ to 1.25 µg L^{-1}.

Keywords: ion-imprinted polymer, pre-concentration, Box-Behnken design, cadmium, natural water

Introduction

Potentially toxic metal ions are becoming increasingly present in the environment, mainly as a result of industrialization. Among them, the element cadmium is very toxic and is classified as a carcinogen, since it is not necessary to the human organism.[1,2] The main pathway of cadmium contamination is its absorption by the digestive tract.[3] Related to this is the occurrence of various symptoms and diseases such as nausea, vomiting, excessive salivation, diarrhea, and abdominal pain. When there is an extended contact time with the metal, damage to the kidney and gastrointestinal and respiratory systems occur.[4]

Often extraction of cadmium has been performed using multivariate optimization through Box-Behnken design (BBD). These strategies allow evaluating the effects of the interactions between the variables studied.[5] The experiments required for the application of the BBD are defined as N = k2 + k + cp, where k is the number of variables involved, and cp are the replicates of the central point. An advantage of this design is that it does not have runs at the extreme combinations (–1, –1, –1 or +1, +1, +1) in the case of three variables.[6]

The first studies on ion-imprinted polymers (IIP) were conducted by Nishide *et al.*[7] IIP was a potential technique to produce selective adsorbents. In this technique, the selectivity for specific metal ions can be achieved once, during the synthesis of the polymer, the same ions are additioned and serve as a mold for the formation of a specific binding site. With the subsequent removal of the mold ion from the polymer matrix, the cavity of the ion-imprinted polymer will be formed.[8]

Ion-imprinted polymers have attracted attention as a selective material for the separation of metal ions such as

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Bi^{III},[9] Ce^{III},[10] Cr^{III},[11] Fe^{II}/Fe^{III} speciation,[12] Hg^{II},[13] lanthanide ions,[14] Ni^{II},[15] Rh^{III},[16] and U^{VI}.[17] Some recent studies have presented the synthesis of IIP for cadmium extraction. A hybrid ion-imprinted polymer was presented for pre-concentration of cadmium ions coupled to thermospray flame furnace atomic absorption spectrometry.[18] A magnetic IIP was prepared by the use of ethylene glycol dimethacrylate (EGDMA) as a cross linker, mesoporous silica SBA-15 as a functional monomer, and diphenylcarbazide as a ligand.[19] Imprinted polymer nanoparticles were synthesized by polymerization of 4-vinylpyridine, EGDMA, 2,2'-azobisisobutyronitrile, 2-aminobenzimidazole, and Cd^{II}, in acetonitrile medium.[20] IIP-Cd^{II} was hydrothermally synthesized by the use of silica gel, methanesulfonic acid, and 3-mercaptopropyltrimethoxysilane.[21] Cd^{II}-imprinted sorbent with interpenetrating polymer network (IPN) has been applied to the determination of Cd^{II} ions in water samples.[22] Ion-imprinted hydrogel/IPN has been also applied to other ions from aqueous solution.[23,24]

This study is the first report on the use of 2-(2-thiazolylazo)-*p*-cresol (TAC) as a ligand for the synthesis of IIP-Cd^{II}. EGDMA was used as a crosslinked reagent, besides the methacrylic acid monomer reagent. The polymer was characterized using Fourier transform infrared spectroscopy (FTIR), Langmuir isotherm, and thermogravimetric analysis (TGA). The variables that affect the sorption of Cd^{II} ions were optimized by Box Behnken design. The method was successfully applied to the analysis of water samples from Pontal Bay, Ilhéus City, Brazil.

Experimental

Reagents

All chemicals used in the study were of analytical grade. The aqueous solutions were prepared using ultrapure water generated by a Milli-Q purification system. (Millipore, Bedford, MA, USA). A series of buffer solutions including acetate, phosphate and ammoniacal (Aldrich, St. Louis, MO, USA) was used to adjust the pH. Standard Cd solutions were prepared daily by dilution of a stock solution of 1000 mg L^{-1} (Fluka, Steinheim, Germany). Nitric acid solutions were prepared by diluting concentrated nitric acid (67%, Merck, Darmstadt, Germany). The ethylene glycol dimethacrylate (Aldrich, St. Louis, MO, USA), methacrylic acid (Fluka, Steinheim, Germany), 2-(2-thiazolylazo)-*p*-cresol (TAC, Aldrich, St. Louis, MO, USA), methanol (CRQ, São Paulo, Brazil) and 2,2-azobisisobutyronitrile (Aldrich, St. Louis, MO, USA) were used for the polymer synthesis. All glassware and containers were previously decontaminated by immersion in a 10% (v v^{-1}) nitric acid solution for 24 h, and then rinsed and cleaned with double-distilled water.

Instrumentation

A flame atomic absorption spectrometer (FAAS, PerkinElmer, AAnalyst 200, Norwalk, CT, USA) was used for absorbance measurements. The hollow cathode lamp of cadmium was operated following the conditions suggested by the supplier (wavelength 228.8 nm and current 7.5 mA). The burner height (13.5 mm) and bandwidth of the slit (1.0 mm) were used with conventional values. The fuel was acetylene (flow rate: 2.0 L min^{-1}) and the oxidant was air (flow rate: 13.5 L min^{-1}). Nebulizer gas flow rate was of 5.0 mL min^{-1}.

A peristaltic pump (Milan, model BP-200, Colombo, Brazil) equipped with Tygon tubes was used to propel all solutions. A Rheodyne 5041 6-way manual valve (Cotati, California, USA) was used for pre-concentration and elution steps. A Digimed pH-meter (Model DM 20, Santo Amaro, Brazil) was used for pH measurements. Sartorius analytical balance model BL D105 (Göttingen, Germany) and magnetic stirrer with heating (Fisatom, Brazil) were also used.

For the polymer characterization, PerkinElmer FTIR spectrum two (Waltham, MA, USA), and Shimadzu TGA50 Thermogravimetric (Kyoto, Japan) were used.

Synthesis of ion-imprinted polymers IIP-Cd^{II} and NIP

The synthesis of IIP-Cd^{II} was performed by the bulk polymerization technique. A mass of 0.056 g of TAC and 0.044 g of cadmium chloride was dissolved in methanol (50.0 mL) and then stirred for 20 min. After complete dissolution, 6.0 mL of EGDMA, 6.0 mL of methacrylic acid (MMA), and 0.06 g of azobisisobutyronitrile (AIBN) were added to a round-bottom flask. The mixture remained under constant stirring for 3 h in a nitrogen atmosphere. The polymer was washed with ethanol (50 mL) and 6.0 mol L^{-1} nitric acid. The non-imprinted polymer (NIP) was synthesized using a similar method, but without the presence of Cd^{II} ions. The materials were characterized by FTIR, TGA, and Langmuir isotherm.

Pre-concentration system

The online system used for extraction of Cd^{II} ion is depicted in Figure 1 and it consists of a peristaltic pump (P), a 6-way valve (V) with two positions (pre-concentration and elution) and a container for waste (W). Between the ways 1 and 4 of the valve, a minicolumn (C) constructed with polytetrafluorethylene (PTFE) tubes (4.0 mm internal diameter and 3.0 cm long) was connected. This minicolumn was packed with 0.1 g of IIP-Cd^{II} polymer. In the way 2, there is a capillary tube connected to the sample (S). In the way 3, a capillary was connected to waste. A capillary tube immersed in the eluent (E) was linked to the way 5 and the spectrometer (FAAS) is connected to the way 6.

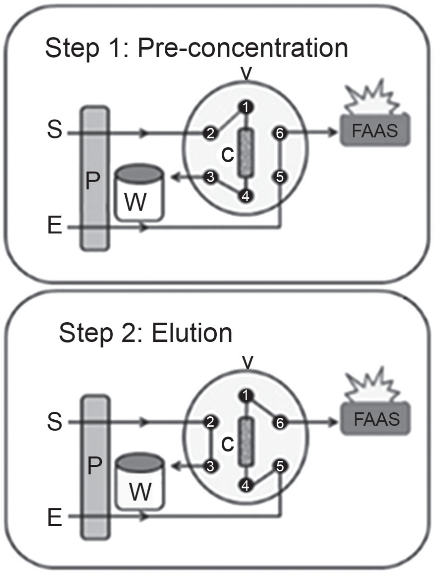

Figure 1. Pre-concentration system proposed using IIP-Cd^{II}. P: peristaltic pump; E: eluent; S: sample; C: mini-column; V: 6-way valve; W: waste; FAAS: flame atomic absorption spectrometer.

The online pre-concentration system (Figure 1) operates in a time-based mode. When the valve was turned on, a 10.0 µg L^{-1} Cd solution at pH previously adjusted to 7.5 using borate buffer solution was passed through minicolumn C (step 1), for an established period of time (120 s). In this step, the cadmium ions were chemically bound in the polymer matrix and the remaining solution was directed to disposal. Simultaneously, an eluent stream was directed to FAAS spectrometer. After 120 s, the valve was turned off (step 2) and the eluent stream (0.4 mol L^{-1} HNO_3) was passed through minicolumn C to desorb cadmium ions concentrated in step 1. Signal detection was performed using the FAAS.[25]

Optimization procedure

A Box-Behnken design[5] involving 15 experiments was carried out in order to optimize the following variables at 3 levels: eluent concentration (EC), sample flow rate (SF) and pH. The experiments were conducted randomly and the results were processed by using the Statistica Software[26] at 95% confidence. The experimental domain expressed as coded and real values and the obtained responses (absorbance) are shown in Table 1.

Table 1. Box-Behnken design and results for three variables

Experimental domain				
Variable	Low (–)	Intermediate (0)	High (+)	
pH	5.0	7.0	9.0	
SF / (mL min^{-1})	2.0	7.0	12.0	
EC / (mol L^{-1})	0.1	0.3	0.5	
Experimental matrix				
Run	pH	SF / (mL min^{-1})	EC / (mol L^{-1})	Absorbance
1	5.0 (–)	2.0 (–)	0.3 (0)	0.039
2	9.0 (+)	2.0 (–)	0.3 (0)	0.042
3	5.0 (–)	12.0 (+)	0.3 (0)	0.014
4	9.0 (+)	12.0 (+)	0.3 (0)	0.105
5	5.0 (–)	7.0 (0)	0.1 (–)	0.029
6	9.0 (+)	7.0 (0)	0.1 (–)	0.049
7	5.0 (–)	7.0 (0)	0.5 (+)	0.022
8	9.0 (+)	7.0 (0)	0.5 (+)	0.085
9	7.0 (0)	2.0 (–)	0.1 (–)	0.084
10	7.0 (0)	12.0 (+)	0.1 (–)	0.141
11	7.0 (0)	2.0 (–)	0.5 (+)	0.076
12	7.0 (0)	12.0 (+)	0.5 (+)	0.152
13 (CP)	7.0 (0)	7.0 (0)	0.3 (0)	0.142
14 (CP)	7.0 (0)	7.0 (0)	0.3 (0)	0.124
15 (CP)	7.0 (0)	7.0 (0)	0.3 (0)	0.142

SF: sample flow rate; EC: eluent concentration; CP: central point.

Sample collection

Seven water samples were collected using polyethylene bottles, in two different seasons, in Pontal Bay, Ilhéus, Bahia, Brazil (Figure S1, Supplementary Information section). The samples were then filtered under vacuum through cellulose acetate membrane with 47.0 mm diameter and 0.45 µm pore size, acidified and stored at low temperature (4 °C) in a refrigerator until analysis.

Results and Discussion

Preparation of IIP-Cd^{II} and characterization

The polymer was synthesized in two steps: (*i*) binary complex formation with TAC and (*ii*) copolymerization of the complex with MMA (functional monomer) and EGDMA (crosslinking monomer) mediated by AIBN as a radical initiator.[27] Finally, Cd^{II} ions were removed from the polymer network by washing with 6.0 mol L^{-1} nitric acid. Thus, specific binding sites containing cavities and predetermined orientation were provided. The polymerization reaction was carried out at 60 °C in nitrogen atmosphere to avoid contamination by oxygen from the atmosphere. The polymerization temperature is an important parameter for the formation of the polymer network. When the external temperature is lower, polymerization is difficult to initiate.[28] On the other hand, at very high temperatures polymerization occurs very quickly, even developing into an implosion.[29]

The polymers were characterized by FTIR and TGA, as shown in Figures 2 and 3, respectively. The FTIR spectra presented in Figure 2 show that the main characteristic bands of the polymer (NIP) remained in both IIP-Cd^{II} and IIP-leached, indicating that neither complexation nor leaching significantly affected the structure of the polymer. TAC was used as a spectrophotometric reagent as it instantaneously forms stable complexes with numerous metal cations, with a composition 1:2 (metal: reagent).[30,31] Accordingly, bonds of the template ions with the N=N, C=N and COH groups of the ligand may be expected, forming a hexacoordinated complex.[32,33] Therefore, small shifts toward higher wavenumbers may also be expected after leaching the template ions from the polymer, namely, sample IIP-Cd^{II}. Actually, comparing the spectra obtained for IIP-Cd^{II} and IIP-leached, the vibration bands assigned to N=N and C=N, in the range of 1600-1630 cm^{-1}, shifted to 1630-1650 cm^{-1} and that of COH at 1385 cm^{-1} shifted to 1392 cm^{-1}, as a weak band, further indicating the removal of Cd^{II} ions.

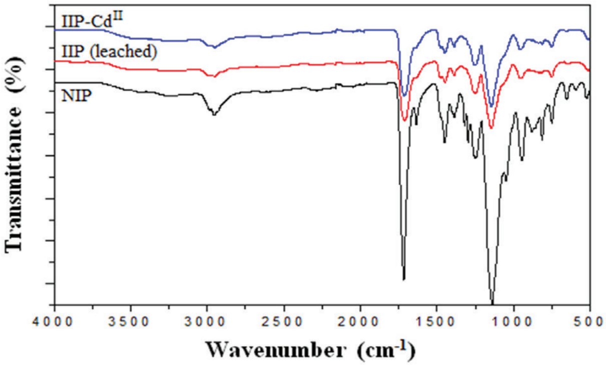

Figure 2. FTIR spectra of IIP-Cd^{II} (metal), IIP-leached and NIP.

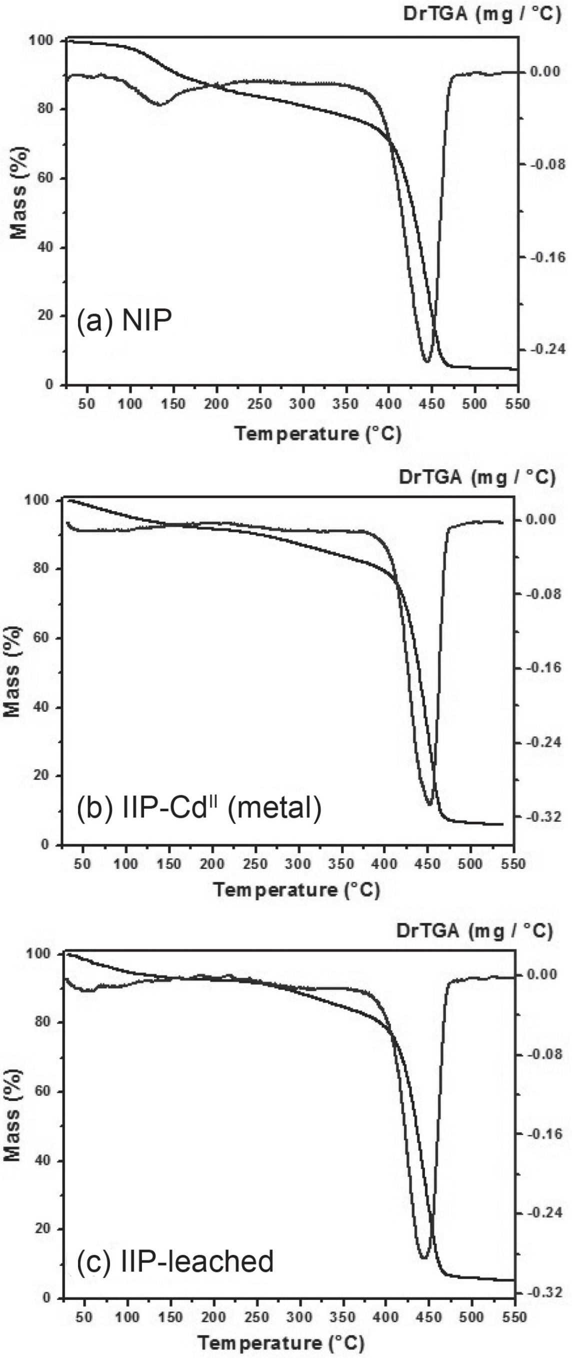

Figure 3. Thermogravimetric analysis of (a) NIP; (b) IIP-Cd^{II} (metal); (c) IIP-leached.

The influence of Cd ions on the thermal stability of the materials was evaluated by thermogravimetry. The thermal behavior was investigated in the thermogravimetric derivative (DTG) curves as presented in Figure 3. At temperatures below 100 °C, weight loss frequently occurs due to the loss of weakly bonded water, while at 150-250 °C, it is associated with the decomposition of residual organic compounds. The loss of residual organic compounds was then more significant for NIP, while the loss of weakly bonded water resulting from the complexation and leaching steps was more significant for IIP-Cd^{II} and IIP-leached, respectively. In addition, the main peak around 450 °C corresponding to polymer decomposition was shifted to higher temperatures, indicating that the thermal stability of the polymer slightly increased after complexation and leaching. At 600 °C, the full weight loss corresponded to 94.98; 94.09 and 95.16%, for NIP, IIP-Cd^{II} and IIP-leached, respectively. On the other hand, the analysis of the residues indicated that IIP-Cd^{II} contained nearly 9% of Cd species that were completely removed by leaching, along with a small amount of organic components in IIP-leached.

For the adsorption of Cd^{II}, a maximum adsorption capacity equal to 84.75 and 69.9 mg g^{-1} for IIP and NIP, respectively, was found, with favorable adsorption by the Langmuir isotherm model.

Optimization of variables

A BBD consisting of 15 experiments was applied to investigate critical factors on the pre-concentration system. The factors and experimental domain were: pH (5.0-9.0), SF (2.0-12.0 mL min^{-1}) and EC (0.1-0.5 mol L^{-1}). BBD is an efficient option since the experimental points are located on a hypersphere equidistant from the central points.[34] Table 1 shows the experimental matrix and the average of the absorbance measurements (n = 3). These assays yielded the surface responses presented in Figure 4. Through the visual inspection of the surfaces, it is possible to find the better conditions for the extraction of Cd^{II} ions (pH = 7.5, EC = 0.4 mol L^{-1} and SF = 12.0 mL min^{-1}). To avoid disruption of the connections and the PTFE tubes used to carry the solutions, a flow rate of 10 mL min^{-1} was established for the sample. The concentration of the buffer was fixed at 0.1 mol L^{-1} and eluent flow rate at 7.0 mL min^{-1}.

Through the surfaces, it is possible to observe that the increase in pH favors the adsorption of Cd^{II} ions. In acidic medium, adsorption is low due to excessive protonation of the lone pair of electrons on sulfur and nitrogen of the polymer. On the other hand, with increasing pH, the protonation of the polymer decreases and the formation of the complex becomes more favorable. However, above pH 8.5, recoveries are not quantitative, since Cd^{II} precipitates as Cd(OH)$_2$, decreasing the formation of IIP-Cd^{II}.[35]

The mathematical model was evaluated using the analysis of variance (ANOVA), shown in Table 2. Lack of fit test for the quadratic model was non-significant, with a *p*-value (0.2158) higher than 0.05. The model was also evaluated by predicted *versus* observed values and showed good correlation. Therefore, the mathematical model used was well suited to the experimental data. The significant terms are presented with letter a superscripted.

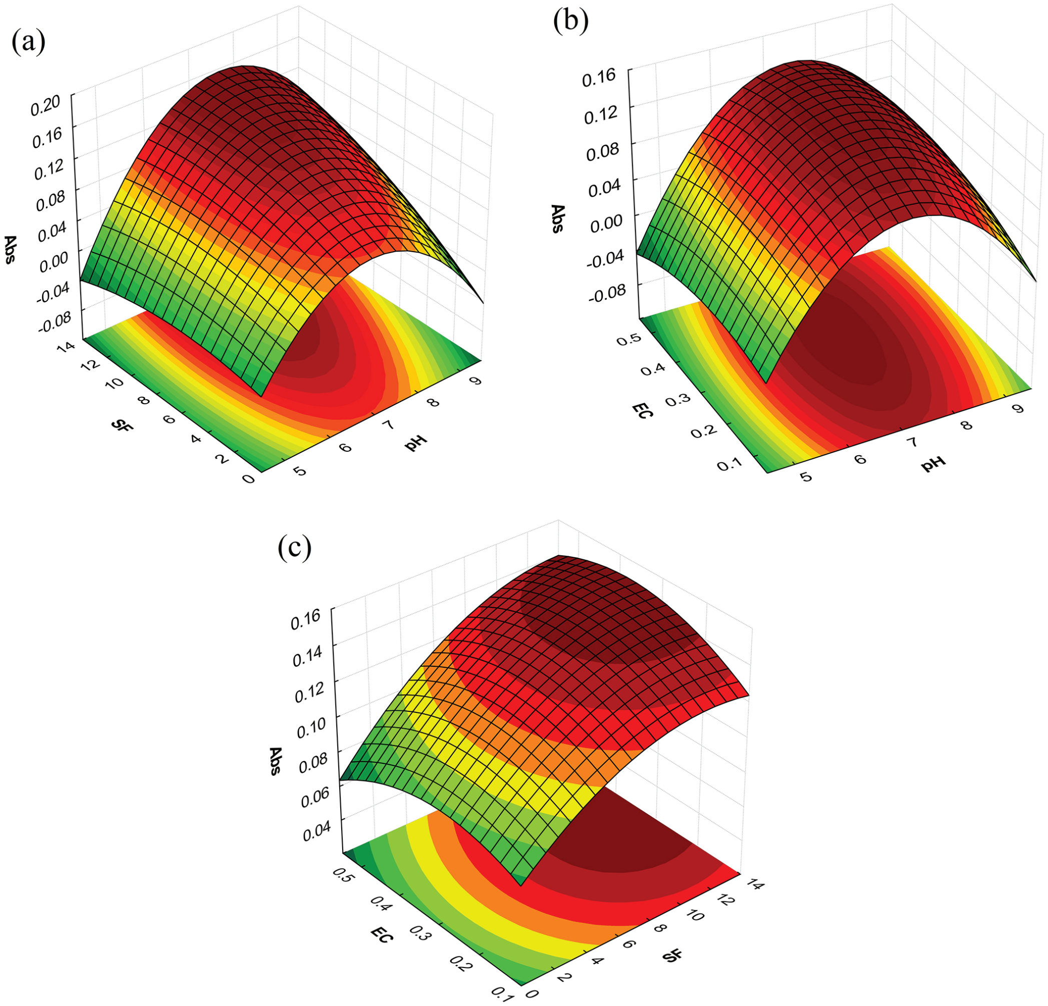

Figure 4. Response surfaces obtained through the Box-Behnken design: (a) pH × sample flow (SF); (b) pH × eluent concentration (EC); (c) eluent concentration (EC) × sample flow (SF).

Table 2. ANOVA for the quadratic model

	SS	df	MS	*F*	*p*-Value
pH (L)	0.003916^a	1^a	0.003916^a	36.2604^a	0.026487^a
pH (Q)	0.021608^a	1^a	0.021608^a	200.0769^a	0.004961^a
SF (L)	0.003655^a	1^a	0.003655^a	33.8437^a	0.028299^a
SF (Q)	0.000333	1	0.000333	3.0855	0.221076
EC (L)	0.000128	1	0.000128	1.1852	0.390006
EC (Q)	0.000648	1	0.000648	6.0021	0.133936
pH × SF	0.001936	1	0.001936	17.9259	0.051513
pH × EC	0.000462	1	0.000462	4.2801	0.174450
SF × EC	0.000090	1	0.000090	0.8356	0.457143
Lack of fit	0.001228	3	0.000409	3.7894	0.215800
Pure error	0.000216	2	0.000108		
SS total	0.033477	14			

^{a}Significant terms. SS: sum of squares; df: degree of freedom; MS: mean square; *F*: Fischer distribution; *p*-Value: probability level; L: linear; Q: quadratic; SF: sample flow rate; EC: eluent concentration.

IIP selectivity

The selectivity of the polymer was verified by the analysis of solutions containing 10.0 µg L^{-1} cadmium prepared concomitantly with other ions. Common interfering ions such as Cu^{II}, Co^{II}, Pb^{II}, Ni^{II}, Cl$^-$ and SO_4^{2-} were individually examined in a series of experiments and could be tolerated up to at least 2000 µg L^{-1}. The tolerance limit of ± 5% was considered for the interfering species, which is commonly applied in other studies.[36,37] Other species frequently present in the matrix such as alkali and alkaline earth metals do not form stable complexes under the optimized conditions for this system.

The selective complexation for cadmium ions is certainly related to physico-chemical attributes such as ionic potential, hydrated ionic radius, charge distribution, atomic polarizability, and chemical hardness. Thus, the Cd^{II} ions present a relatively high value of electronegativity (1.69), and ionic radius (0.97 Å), favoring complexation with TAC reagent.

Other studies have evaluated the effect of potential ions in the complexation of cadmium ions using the 2-(2-thiazolylazo)-*p*-cresol reagent. Cerutti *et al.*[30] studied the interference by Zn^{II}, Cu^{II}, Ni^{II}, Pb^{II}, Co^{II}, Mn^{II}, and Fe^{III} and the system presented tolerance up to at least 2000 µg L^{-1}. Portugal *et al.*[38] showed that cobalt, nickel, iron, chromium, zinc, manganese, mercury, aluminum, vanadium and molybdenum ions do not interfere in the proposed procedure, at a concentration of 100 µg L^{-1}.

Several studies have used the TAC reagent for complexation of other ions such as Pb^{II},[39] Cu^{II},[40] Hg^{II},[41] and Ni^{II},[42] applying extraction conditions different from those optimized in this study. Therefore, IIP-Cd^{II} exhibits good selectivity and can be recommended for pre-concentration of cadmium ions in water samples.

Analytical parameters

Under optimum conditions, the analytical features of the proposed system were calculated (Table 3). The pre-concentration system presented a sampling frequency of 27 h^{-1} when 120 s of pre-concentration time and 15 s of elution time were used for solutions containing 10.0 µg L^{-1} cadmium. Following the definition of IUPAC,[43] the limits of detection (LOD = 3 s/m) and quantification (LOQ = 10 s/m) were calculated, where s is the relative standard deviation (RSD) of n measurements of a reagent blank and m is the slope of the calibration graph with pre-concentration. The enrichment factor (EF) was measured by the ratio between the linear section of the calibration graph obtained before and after pre-concentration. Concentration efficiency (in min^{-1}) is a function of the product of the sampling frequency and EF. The consumptive index (CI) is described as the necessary volume (Vs, mL) to reach a unit of enrichment factor (CI = Vs / EF).[44] The precision of the pre-concentration system was assessed in terms of the percentage of RSD for six replicates of cadmium solution (10.0 and 50.0 µg L^{-1}).

Table 3. Analytical features of the method using IIP-Cd^{II}

Parameter	Value
Enrichment factor	44
Sample frequency / h^{-1}	27
Consumptive index / mL	0.45
Concentration efficiency / min^{-1}	19.8
Limit of detection (n = 10) / (µg L^{-1})	0.14
Limit of quantification (n = 10) / (µg L^{-1})	0.46
Precision, RSD (10.0-50.0 µg L^{-1}) / %	4.31-4.40
Angular coefficient	0.0178
R^2	0.9942

RSD: relative standard deviation; R^2: determination coefficient.

The proposed system for pre-concentration of Cd^{II} ions was compared with other pre-concentration procedures reported in the previous literature (Table 4). It was found that the LOD of the developed method is comparable with that described in the literature. The analytical features obtained with the application of the novel polymer are very attractive, with low LOD, sensitivity and good enrichment factor for the extraction of cadmium ions from aqueous solution.

Table 4. Comparison with other procedures for pre-concentration of cadmium

Material	LOD / (μg L^{-1})	RSD / %	Sample	Detection	Reference
Fe_3O_4 nanoparticles-IIP	0.6	–	urine	FAAS	45
PAN-IIP	0.31	3.4 (20.0 μg L^{-1}) 2.1 (50.0 μg L^{-1})	water and food	voltammetry	46
Fe_3O_4 nanoparticles-IIP	0.09	1.7	diesel oil	FAAS	47
Multiwall carbon nanotubes-IIP	1.3	3.1	food	FAAS	48
Dibenzyldithiocarbamate	0.43	3 (20.0 μg L^{-1})	natural waters, urine and dialysis solutions	FAAS	49
2-Aminothiophenol	0.14	5.8	natural, drink and tap water	FAAS	50
Black stone (Pierre noire)	0.30	5.9 (10.0 μg L^{-1})	human blood and serum	ICP OES	51
1,10-Phenanthroline	5.8	2.9	potatoes	ICP OES	52
TAC-IIP	0.14	4.3 (10.0 μg L^{-1}) 4.4 (50.0 μg L^{-1})	water	FAAS	this work

LOD: limit of detection; RSD: relative standard deviation; IIP: ion-imprinted polymer; FAAS: flame atomic absorption spectrometer; PAN: 1-(2-pyridylazo)-2-naphthol; ICP OES: inductively coupled plasma optical emission spectrometry; TAC: 2-(2-thiazolylazo)-*p*-cresol.

Table 5. Results for the determination of cadmium ions in samples from estuarine water

Sample	Cadmium concentration / (μg L^{-1})		Recovery / %
	Added	Found	
1.1	0.0	0.65 ± 0.08	
	10.0	10.6 ± 0.28	99
	20.0	20.6 ± 0.21	100
1.2	0.0	0.65 ± 0.08	
	10.0	10.6 ± 0.7	100
	20.0	21.5 ± 0.7	104
2.1	0.0	0.60 ± 0.16	
	10.0	10.6 ± 0.24	100
	20.0	21.4 ± 0.76	104
2.2	0.0	< LOQ	
	10.0	10.3 ± 0.7	102
	20.0	21.8 ± 0.6	109
3.1	0.0	< LOQ	
	10.0	10.7 ± 0.08	103
	20.0	21.4 ± 0.24	105
3.2	0.0	< LOQ	
	10.0	10.6 ± 0.1	103
	20.0	22.0 ± 0.4	108
4.1	0.0	< LOQ	
	10.0	9.7 ± 0.57	95
	20.0	19.1 ± 0.29	95
4.2	0.0	< LOQ	
	10.0	10.9 ± 0.6	105
	20.0	21.6 ± 0.4	106
5.1	0.0	< LOQ	
	10.0	9.5 ± 0.32	93
	20.0	19.7 ± 0.36	98
5.2	0.0	0.75 ± 0.08	
	10.0	10.9 ± 0.8	101
	20.0	21.4 ± 0.9	103
6.1	0.0	0.69 ± 0.08	
	10.0	11.1 ± 0.36	104
	20.0	20.9 ± 0.14	101
6.2	0.0	1.25 ± 0.08	
	10.0	10.5 ± 0.6	93
	20.0	21.5 ± 0.6	101
7.1	0.0	0.86 ± 0.08	
	10.0	10.8 ± 0.29	99
	20.0	20.9 ± 0.08	100
7.2	0.0	1.25 ± 0.08	
	10.0	11.4 ± 0.6	101
	20.0	21.6 ± 0.1	102

LOQ: limit of quantification (0.46 μg L^{-1}); n = 3.

Analysis of water samples

The proposed method was successfully applied for the extraction of Cd^{II} ions in estuarine water samples of the Pontal Bay (Ilhéus, Bahia, Brazil). The samples were analyzed using the same conditions optimized in the procedure. The results are presented in Table 5. The values of the recoveries (R) were calculated as follows: $R(\%) = [(C_{CdS} - C_{Cd}) / m] \times 100$, where C_{CdS} is the concentration of Cd ions in the spiked sample, C_{Cd} is the concentration of Cd ions in the original sample and m is the amount of Cd ions added. The recoveries (R) of the addition and recovery tests for spiked samples were calculated to be in the range of 93-109% (Table 5), demonstrating that there was no matrix interference, since it can be satisfactorily applied to the determination of traces of Cd^{II} in natural water samples.

According to the Brazilian legislation (National Environment Council (CONAMA), resolution No. 357/2005),[53] which establishes limits for various parameters of water quality, the maximum concentration of cadmium allowed in saline water class 2 is 40 μg L^{-1}. None of the samples analyzed exceeded this limit. The lowest concentration of Cd^{II} ions determined in the samples was 0.60 μg L^{-1} and the highest was 1.25 μg L^{-1}. In some samples the concentration found was below the LOQ of the method (0.46 μg L^{-1}).

Conclusions

A selective polymer was synthesized and characterized by FTIR, TGA, and adsorption isotherm in order to extract traces of Cd^{II} in water samples. The results indicate that the IIP-Cd^{II} synthesized in this study is an effective and reliable candidate for the elimination of cadmium ions from aqueous solutions.

Optimization through Box-Behnken design allowed to find quickly and efficiently a single optimum experimental combination for the pre-concentration of cadmium ions. The proposed pre-concentration procedure provides a rapid, economical, and simple method for the separation and enrichment of cadmium in aqueous samples. Low detection limit, selectivity and tolerance to interferences allowed the determination of cadmium ions in natural water samples. The detection capacity of the FAAS technique for determination of cadmium significantly increased with the proposed system. The analytical characteristics obtained are similar to other methods already reported for Cd^{II} ions pre-concentration. The proposed method demonstrated feasibility and potential to be applied to monitoring of cadmium ions in water samples.

Supplementary Information

Supplementary information (map of sample collection) is available free of charge at http://jbcs.sbq.org.br as PDF file.

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