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Cloud point extraction and determination of Cd(II) in water by spectrophotometry and application of central composite design

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ABSTRACT

A method for the determination of trace Cd^{+2} in water by cloud point extraction: a preconcentration step in conjunction with detection by spectrophotometry is described. The effects of some important variables were studied using central composite design and the optimum experimental conditions were evaluated by the desirability function combined with response surface methodology (RSM). In this work 10 mL analyte solution containing 20 μg L^{-1} cadmium, pH was adjusted to 4.50×10^{-6}mol L^{-1} concentration of dithizone and 2.5% (v/v) triton X-114 was kept in thermostated bath at 60°C for 30 min. The conical tubes were then immersed in ice–water mixture for 5 min, allowing ease of removing the supernatant bulk aqueous phase. A small volume of surfactant-rich phase remained at the bottom of the tube. To facilitate sampling of the surfactant-rich phase 3 mL of ethanol was added. The proposed method allowed the determination of cadmium (II) in the range 5−60 μg L^{-1} with good precision and accuracy and the detection limit was found to be 2.85 μg L^{-1}.

Keywords: Cloud point extraction; Response surface methodology; Cadmium; Spectrophotometer

1. Introduction

Cadmium is a naturally occurring metal that is used in various chemical forms in metallurgical and other industrial processes; it is a serious environmental pollutant because of its toxic effects on all living organisms [1]. Exposure to cadmium can occur via the diet and drinking water [2–4].

Cadmium and its compounds cause serious diseases in different locations including the kidney, the skeletal and the respiratory systems, and is classified as a human carcinogen [5]. It is released into the environment through mining and smelting as well as through various industrial processes, entering in the food chain of flora and fauna from contaminated soil or water [4–6]. Cadmium has been widely dispersed into the environment through the air by its mining and smelting as well as by other man-made routes such as usage of phosphate fertilizers, presence in sewage sludge, and various industrial uses such as Ni–Cd batteries, plating, pigments and plastics [5,6]. The waters in vicinity of the industrial areas are important indicators for cadmium pollution. To control the quality of these waters, it is necessary to develop a selective, efficient and economical method for speciation of cadmium [7].

Separation and preconcentration are attracting increasing interest, particularly for enhancing the inherent capabilities of analytical signals and lowering the detection limits. Recently, with the use of surface-active agents and the development of the cloud point technique, another option to the extraction-preconcentration procedure has arisen. The coupling technique of cloud point extraction (CPE) and different kinds of instrumental methods is an effective method for this purpose [8,9].

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In this paper, CPE as a preconcentration step in conjunction with detection by atomic absorption spectrometer with hydride generation (AAS-GH) [10], flame atomic absorption spectrometer (F-AAS) [9,11,12], electrothermal atomic absorption spectrometer (ET-AAS) [13], inductively coupled plasma atomic emission spectrometry (ICP-AES) [14] for the speciation analysis of cadmium has been reported. All of the above-mentioned CPE methods involve binary chelate systems. As reported in the literature, FAAS is by far the most frequently used technique for analyte (Cd) detection after preconcentration by CP-extraction [9,11,12]. CPE as a preconcentration step in conjunction with detection by spectrophotometry for the determination of trace Cd(II) has not been reported. UV–Vis spectrophotometry offers the advantages of simple, low-cost instruments that are available at all laboratories. Running costs are minimal and no highly-skilled personnel is required for their operation.

2. Materials and method

2.1. Reagents and solutions

Stock standard solution of Cd^{2+} at a concentration of 1,000 mg L^{-1} was prepared by dissolving appropriate amounts of $Cd(NO_3)_2$ $4H_2O$. Working standard solutions were prepared daily from the stock standard solutions by appropriate dilution with deionized water. A stock solution of 10^{-2} mol L^{-1} of dithizone (DT) was prepared by dissolving suitable amount of this reagent in 100 mL of acetone/ethanol (30%/70%, respectively). This solution is stable in the refrigerator for 1 d. A solution of 4% triton X-114 was prepared by dissolving suitable amount of triton X-114 in hot distilled water. The solutions of other metals as well as those used for the interference study were obtained from the respective inorganic salts. Various buffer solutions were prepared using diluted solution of HNO_3 (0.1 mol L^{-1}) and NaOH (0.1 mol L^{-1}). 1 mL of acetate buffer solution was used to fix the pH constant.

In this study, a Shimadzu Model UV-Visible spectrophotometer 1600 PC (VWR, China) equipped with a 1 cm quartz cell was used for absorbance measurements. The spectrophotometer has a wavelength accuracy of ±0.2 nm and a bandwidth of 5 nm in the wavelength range of 320–700 nm. An ultrasonic bath (Grant OLS 200, Gemini, and Pays-Bas) to maintain the temperature in CPE experiments. A centrifuge (Universal-320, Hettich Centrifuges, and England) was used. The pH measurements were carried out with a pH meter (pH meter 780 Metrohm, Switzerland).

2.2. Apparatus and procedures

2.2.1. Experimental design

Central composite design (CCD) using STATISTICA software for estimation, optimization of effective CPE parameters and interactive effects of these parameters on preconcentration of cadmium in aqueous solution was used. In general, CCD includes $N = 2k$, factorial points, $2k$, axial points (k is the number of factors) and Cp, central points and the test results for the response variables (Table 1). The effects of the main operating parameters including pH, dithizone volume, temperature and triton X-114 volume, were studied. The choice of these parameters and their levels was based on the previous experimental studies on the simultaneous CPE process. The mathematical relationship between the four independent variables by fitting a second-order polynomial equation in this design permitted the response to be modelled, which can be expressed as the following quadratic Eq. (15).

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{14}X_1X_4 + b_{23}X_2X_3 + b_{24}X_2X_4 + b_{34}X_3X_4 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 + b_{44}X_4^2 \quad (1)$$

2.2.2. Response surface methodology

Response surface methodology (RSM) is useful method for the modelling and analysis of all the industrial processes by using mathematical and statistical techniques. The main objective is to optimize the output by fixing the most significant variables which influence on the output or the response [16]. CCD method with the four most significant variables of the independent process was used to find the effect of these latters on the absorbance of the Cd–DT complex. All the coded values are shown in Table 1. Hence the four factors investigated are: pH (X_1), concentration of dithizone (X_2), temperature (X_3) and triton X-114 volume (X_4).

3. Results and discussions

3.1. Establishment of regression equation

A total of 30 experiments were carried out according to a 2^4. The total number and sequence of experimental data were determined using STATISTICA 7 software. Obtained results are presented in Table 1.

Eq. (2) expresses the empirical relationship between the response and input variables:

$$Y = 0.602 + 0.011X_1 - 0.039X_2 + 0.052X_3 + 0.016X_4 + 0.007X_1X_2 - 0.036X_1X_3 - 0.0012X_1X_4 + 0.0017X_2X_3 + 0.006X_2X_4 + 0.008X_3X_4 - 0.045X_1^2 + 0.041X_2^2 + 0.032X_3^2 + 0.012X_4^2 \quad (2)$$

where Y: the response, X_1; X_2; X_3; and X_4: the coded symbols of the independent factors.

3.2. Analysis of variance

To find the significant mean and interaction effect of factors affecting the removal efficiency analysis of variance (ANOVA) was followed (Table 2).

The p-value less than 0.05 indicates the statistical significance of an effect at 95% confidence level and F-test was used to determine the statistical significance of all terms in the polynomial equation within 95% confidence interval. The F-value for 95% confidence interval, 1 degree of freedom and 30 factorial runs ($F_{0.05,1,30}$) is 4.17 [17]. The smaller p-value of model (<0.000001) and the higher F-value (77.29) implied that the model was statistically significant. All effects with F higher than 4.17 are statistically significant. By observing the F and p-values from Table 2, it is shown that the

Table 1
Design of experiments with experimental and predicted values

Variables	Symbol	$-\alpha$	-1	0	+1	$+\alpha$
pH of Cd–Dithizone complex	X_1	2	3	4	5	6
Concentration of dithizone 50 (10^{-6} mol L^{-1})	X_2	20	30	40	50	60
Temperature (°C)	X_3	30	40	50	60	70
Triton X-114 volume (mL)	X_4	0.15	0.2	0.25	0.3	0.35
Response: Absorbance	Y					

Run order	X_1	X_2	X_3	X_4	Experimental values	Predicted values	Residuals values
1	3	30	40	0.2	0.335	0.336	−0.001
2	3	30	40	0.3	0.351	0.361	−0.010
3	3	50	40	0.2	0.371	0.362	0.009
4	3	50	40	0.3	0.411	0.394	0.017
5	3	30	60	0.2	0.511	0.494	0.017
6	3	30	60	0.3	0.552	0.516	0.036
7	3	50	60	0.2	0.581	0.592	−0.011
8	3	50	60	0.3	0.576	0.620	−0.044
9	5	30	40	0.2	0.456	0.421	0.035
10	5	30	40	0.3	0.459	0.442	0.017
11	5	50	40	0.2	0.446	0.475	−0.029
12	5	50	40	0.3	0.476	0.502	−0.026
13	5	30	60	0.2	0.423	0.433	−0.010
14	5	30	60	0.3	0.432	0.450	−0.018
15	5	50	60	0.2	0.561	0.558	0.003
16	5	50	60	0.3	0.587	0.582	0.005
17[a]	4	40	50	0.25	0.612	0.608	0.004
18[a]	4	40	50	0.25	0.602	0.608	−0.006
19[a]	4	40	50	0.25	0.609	0.608	0.001
20	2	40	50	0.2	0.361	0.369	−0.008
21	6	40	50	0.3	0.451	0.441	0.010
22	4	40	30	0.2	0.321	0.329	−0.008
23	4	40	70	0.3	0.601	0.591	0.010
24	4	20	50	0.2	0.308	0.342	−0.034
25	4	60	50	0.35	0.561	0.524	0.037
26	4	40	50	0.15	0.508	0.496	0.012
27	4	40	50	0.3	0.551	0.598	−0.047
28[a]	4	40	50	0.25	0.621	0.608	0.013
29[a]	4	40	50	0.25	0.632	0.608	0.024
30[a]	4	40	50	0.25	0.607	0.608	−0.001

[a] Central point.

temperature and pH have the greatest effect on the Cd(II) preconcentration. The correlation between experimental and predicted responses was also investigated. Experimental values were the measured response data for a particular run and the predicted values were estimated by the first order polynomial model Eq. (2). As in Fig. 1, the data points were well distributed close to a straight line (R^2_{square} = 0.948 and R^2_{adjusted} = 0.899), which suggested an excellent relationship between the experimental and predicted response.

The Pareto analysis (Fig. 2) was used for the selection of a minimum number of tasks that gives a significant overall effect. The Pareto chart used for the correlation effect of each variable on cadmium preconcentration in natural waters. After fixing the significant parameters; the CCD method used to find the effect of each significant parameter on the Cd–DT complex absorbance.

3.3. Effect of interactive variables and 3D response surface plot

The three dimensional (3D) response surfaces were used to examine the type of interaction between these chosen factors. Fig. 3 illustrates the mutual interactive effects of

Table 2
Analysis of variance (ANOVA) for CCD

Factor	Sum of squares	df[a]	Mean of squares	*F* value	*p*-value prob
(1) X_1 (L)	0.002886	1	0.002886	2.75296	0.117832
X_1 (Q)	0.043140	1	0.043140	41.15289	0.000012
(2) X_2 (L)	0.031663	1	0.031663	30.20449	0.000062
X_2 (Q)	0.026082	1	0.026082	24.88043	0.000162
(3) X_3(L)	0.081027	1	0.081027	77.29430	0.000000
X_3 (Q)	0.021309	1	0.021309	20.32737	0.000416
(4) X_4 (L)	0.006830	1	0.006830	6.51518	0.022089
X_4 (Q)	0.002409	1	0.002409	2.29809	0.150322
1L by 2L	0.000756	1	0.000756	0.72141	0.409033
1L by 3L	0.021462	1	0.021462	20.47355	0.000403
1L by 4L	0.000026	1	0.000026	0.02511	0.876198
2L by 3L	0.005041	1	0.005041	4.80878	0.044495
2L by 4L	0.000735	1	0.000735	0.70109	0.415560
3L by 4L	0.000013	1	0.000013	0.01221	0.913489
Error	0.015724			15	
Total SS	0.303121			29	

[a] df: degree of freedom.

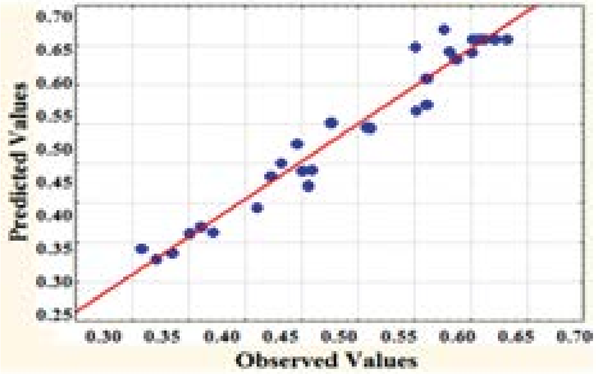

Fig. 1. Comparison of model predictions with the experimental data of Cd(II) preconcentration.

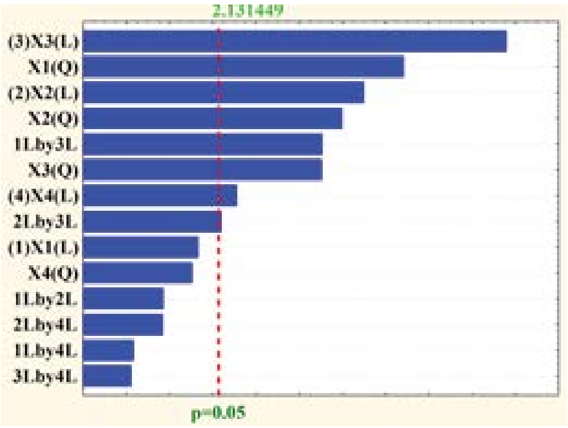

Fig. 2. Pareto chart obtained to study the effects of variables in the optimization of the system of extraction by cloud point.

the combinations variables on the response factor in the 3D plots. Fig. 4 give the interactions of initial pH with dithizone quantities, triton X-114 volume and temperature, respectively. Obtained results show that the maximum absorbance of complex was reached at a pH ranging from 3 to 5. The dominant species at pH < 4 is Cd(II), which leads to covalent attraction between chelating agent and positively charged cadmium species (Eq. (3)). The second important parameter is the dithizone, reacts with most heavy metals whose sulphides are sparingly soluble in water. Metal ions react with dithizone forming nonpolar coloured complexes whose colours differ significantly from dithizone [18]. Temperature seems to play an additional role in enhancing preconcentration efficiency and enhancement factors, as it is reported that applying elevated temperatures leads to dehydration of the micelle, increasing the phase–volume ratio. An important point, with regard to incubation time, is that, for metals, their reaction with chelating agents and their transportation inside the micelle are kinetically controlled (although thermodynamically favoured, simulating the shift of equilibrium towards precipitation). It is, therefore, essential to maintain the reaction time above a minimum threshold for quantitative extraction [19].

$$\mathrm{M}^{+n} + n\mathrm{HDz} \qquad \mathrm{M}\left(\mathrm{Dz}\right)_n + n\mathrm{H}^+ \tag{3}$$

3.4. Desirability function

The optimal conditions were tested by desirability function (DF) that is based on Derringer's DF [20]. The profile of predicted values and DF are presented in Fig. 4. The response desirability conception implicates specifying the DF for Cd–DT complex absorbance by attribution of predicted values. The range 0.0 to 1.0 is used to obtain the optimum design. The factorial matrix (Table 1) shows the maximum (0.63) and minimum (0.30) and 0.5 for the middle (0.47). The individual desirability scores used to calculate the removal percentage in the desirability of 1.0 are illustrated at the bottom of Fig. 4. For the desirability of 1.0, the global response obtained from these plots with the actual level of each variable is presented in the Fig. 4.

From the obtained results, we can notice that the variables simultaneously affect the response and its desirability. On the basis of this calculation and desirability result of 1.0, the optimal conditions are defined in Table 3.

3.5. Interferences study

The effect of different cations and anions on the determination of 20 µg L^{-1} ion by the proposed method was studied. The effect of naturally occurring metal ions on the extraction of Cd^{2+} by DT reagent was also studied. DT forms stable binary complexes with various metal ions, including transition metal ions. Most of the cations and anions examined do not interfere with the extraction and determination of Cd^{2+}, and many of them are tolerated at very high levels. However, some of the species such as Zn^{2+}, Ni^{2+}, and Cu^{2+} interfered in the determination of Cd^{2+}. The interfering effect of these ions was completely eliminated up to 250 µg L^{-1} level in the presence of 1 mL of 10^{-2} mol L^{-1} of ethylenediamine

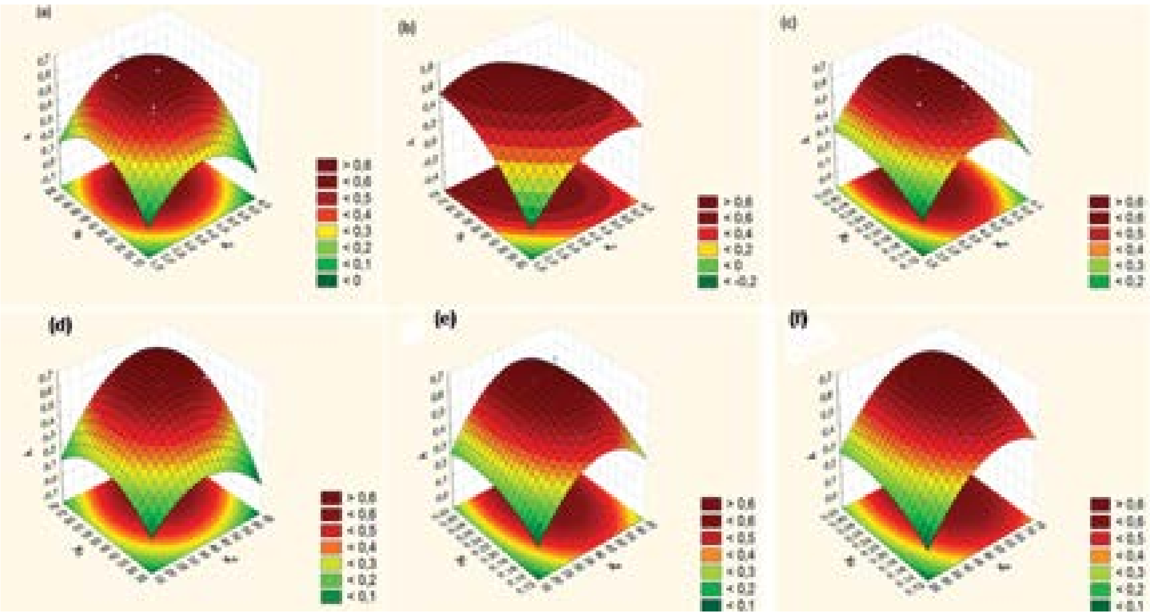

Fig. 3. Response surfaces for the Cd removal: (a) pH (X_1)–concentration of DT (X_2), (b) pH (X_1)–temperature (X_3), (c) pH (X_1)–triton X-114 volume (X_4), (d) concentration of DT (X_2)–temperature (X_3), (e) concentration of DT (X_2)–triton X-114 volume(X_4), and (f) temperature(X_3)–triton X-114 volume (X_4).

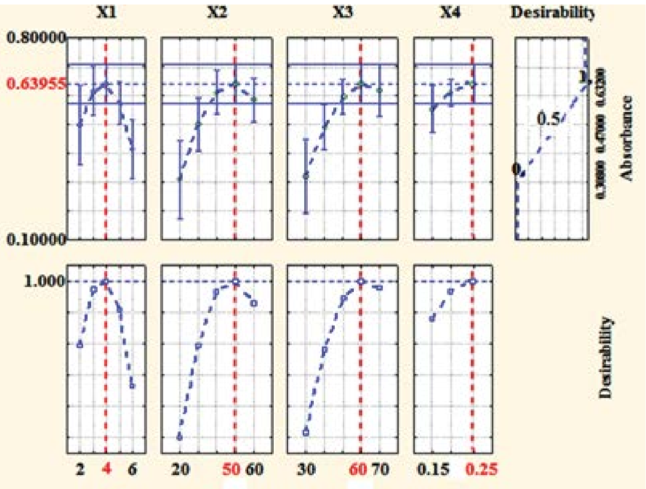

Fig. 4. Desirability function of parameters affect CPE.

Table 3
Optimum values of variables for the removal of cadmium by cloud point extraction

Parameters		Optimum value	Predicted value
pH	X_1	4	0.639
Concentration of dithizone (10^{-6} mol L^{-1})	X_2	50	
Temperature (°C)	X_3	60	
Triton X-114 volume (mL)	X_4	0.25	

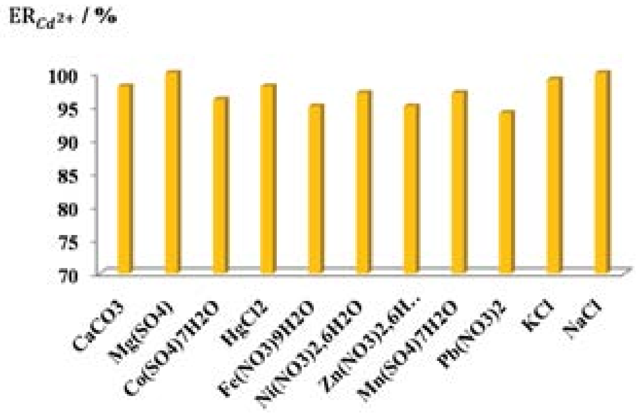

Fig. 5. Effect of different cations and anions on the extraction recovery (ER_{Cd}/%).

tetra-acetic acid (EDTA) as a proper masking agent. The test results are shown in Fig. 5.

In this study, analytical capabilities of the proposed method for Cd(II) were as follows: the calibration curve was obtained in range of 5–60 µg L^{-1} with a regression coefficient of 0.991 for Cd(II) after preconcentration with CPE. After optimization studies for Cd(II) selected for analyte, the limit of detection (LOD) using standard solutions was obtained from LOD = $3S(b_0)/b_1$, this values was 2.85 µg L^{-1}. For the accuracy and precision of the method, a statistical study based on five replicate measurements of samples containing: 5–60 µg L^{-1} Cd^{+2} at 510 nm was conducted to the equation: $Y_{Cd^{+2}} = 0.016 [Cd^{+2}] + 0.197$, the relative standard deviation was calculated for five replicate measurements of 20 µg L^{-1} of cadmium with

Table 4
Addition recovery test for water samples (N = 5 repetitions)

Added (μg L^{-1})	Found (μg L^{-1})	Recovery (%)
Tap water		
0.0	ND	<LOD
5.0	5.45 ± 0.30	109
10	10.25 ± 0.50	102.5
River water		
0.0	3.45 ± 0.05	–
5	8.12 ± 0.32	96
10	13.31 ± 0.42	99
Seawater		
0.0	3.80 ± 0.05	–
5	9.80 ± 0.32	111
10	14.71 ± 0.42	106

dithizone was 3.25%. The amount of cadmium in 10 mL of sample solution is measured after preconcentration by CPE in a final volume of 0.3 mL, the preconcentration factor was calculated by a factor of 33.3.

3.6. Removal of cadmium from simulated natural waters

The preconcentration potential of Cd(II) by CPE was evaluated with natural water samples. The optimum values of variables obtained from DF (Table 3) were applied and the results are summarized in Table 4. Moreover, it is necessary to mention that the CPE can be used for preconcentration of other pollutants from real natural waters. These results suggested that the CPE has an excellent potential application for the speciation of Cd(II) from water samples highly and rapidly.

4. Conclusion

The objective of this study was to estimate, optimize, and model the preconcentration of Cd(II) from aqueous solution using CPE. Then the RSM was successfully applied to examine the influences of pH, dithizone volume, temperature, and triton X-114 volume. Polynomial model was developed for process optimization. The significant main and interaction effects of factors affecting the removal efficiency were tested with ANOVA. Temperature ($p \leq 0.000001$; $F = 77.29$) was found to be the most significant parameter for cadmium preconcentration followed by the pH ($p = 0.000062$; $F = 41.15$). Response surface contour plots were investigated to understand the combined effect of process variables on percentage removal. The DF indicated that 100.24% preconcentration of cadmium can be possible by using the optimal conditions of initial pH 4, concentration of dithizone 50×10^{-6} mol L^{-1}, triton X-114 dose 0.25 mL and temperature 60°C. Subsequently, the experiments demonstrated that green, efficient CPE had a good potential in the efficient preconcentration of Cd^{2+} from natural waters.

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