



Flotation/magnetic Stirring-assisted Liquid-liquid Microextraction Combined with Flame Atomic Absorption Spectrometry for the Preconcentration and Determination of Cadmium (II) after Optimization using Experimental Design

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(Received 19 Feb. 2019; Final revised received 15 May 2019)

Abstract

A rapid, highly sensitive and efficient flotation/magnetic stirring-assisted liquid-liquid microextraction combined with flame atomic absorption spectrometry has been proposed for the preconcentration and quantitative analysis of trace amounts of cadmium (II) in the presence of sodium diethyldithiocarbamate as complexing agent. Parameters including sample pH, concentration of the complexing agent, volume of extraction solvent, extraction time and aeration time were screened by a Plackett–Burman design and optimal conditions were obtained using a Box-Behnken design. At optimum conditions, the limit of detection and relative standard deviation ($n=7$, $C=20 \mu\text{g L}^{-1}$) were $0.16 \mu\text{g L}^{-1}$ and 1.39%, respectively. Furthermore, a linear dynamic range of $0.5\text{-}80 \mu\text{g L}^{-1}$ and enrichment factor of 152 was obtained. The accuracy of the method was evaluated using the analysis of certified reference material. Finally, the proposed technique was successfully used for the determination of trace amounts of cadmium (II) in water and cereal samples.

Keywords: cadmium (II), Flame atomic absorption spectrometry, flotation/magnetic stirring-assisted liquid-liquid microextraction, Multivariate optimization, Water and cereal samples.

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Introduction

In the recent years, the environmental pollution by heavy metals is one of the biggest concerns for human beings [1, 2]. Cadmium (Cd) is considered as an extremely toxic and dangerous metal even at low concentration level, which can cause damage to plants and animals and tends to accumulate in organs such as lungs, liver and kidneys [3-5]. Cadmium is extensively used in different fields of science and technology such as metallurgical alloying [6] and re-chargeable nickel-cadmium batteries [2]. Human exposure to Cd²⁺ may be the result of the consuming contaminated waters and foods [7]. For all the above reasons, the development of an effective and simple analytical technique for the extraction and determination of trace amounts of Cd²⁺ is necessary.

Various analytical techniques such as flame and graphite furnace atomic absorption spectrometry (FAAS and GFAAS) [8-10], inductively coupled plasma atomic emission spectrometry (ICP-AES) [11], inductively coupled plasma mass spectrometry (ICP-MS) [12, 13] and ultraviolet-visible spectrophotometry (UV-Vis) [2] have been applied for the determination of Cd²⁺ in various samples. However, due to the extremely low concentration of Cd²⁺ in different natural samples that are often less than limit of detection of these techniques and strong interference of the sample matrix, a preconcentration and separation step is usually required prior to determination. Therefore, several techniques such as solid phase extraction (SPE) [14, 15], liquid-liquid extraction (LLE) [16, 17] and cloud point extraction (CPE) [18, 19] have been the most commonly employed techniques for the enrichment/separation of Cd²⁺.

These methods are limited due to consumption of large volumes of organic solvents, unsatisfactory enrichment factors, high cost and long extraction time. In order to eliminate or decrease these disadvantages, an easy and rapid liquid phase microextraction (LPME) technique was introduced [20], which is called dispersive liquid-liquid microextraction (DLLME) by Rezaee et al., [21, 22]. Although DLLME technique is able to overcome most of the problems mentioned above, but some drawbacks of this method includes using toxic solvents that have higher density than water and the necessity of using the dispersive solvents. To alleviate these problems, various modified DLLME approaches such as vortex-assisted liquid-liquid microextraction (VALLME) [23, 24] ultrasound-assisted emulsification microextraction (USAEME) [25], air-assisted liquid-liquid microextraction (AALLME) [26] and magnetic stirring-assisted liquid-liquid microextraction (MSALLME) [27] have been developed.

In this work, flotation/magnetic stirring-assisted liquid-liquid microextraction (FMSA-LLME) method was performed for the separation and preconcentration of Cd²⁺ in water and cereal samples. In the present method, 1-octanol as extraction solvent was used instead of chlorinated solvents and dispersed in the aqueous phase by the use of magnetic stirrer instead of using dispersive solvents or

ultrasound bath. Then, the cloudy mixture was transferred into the homemade extraction vessel and after a few minutes, organic phase was collected on top of the solution by aeration (instead of centrifuging step). Finally, the collected extraction phase was injected to FAAS system.

Traditionally, in order to determine the optimum extraction conditions, a univariate method called one-factor-at-a-time was employed, which is time-consuming and requires a high number of trials, and also possible interactions between parameters are ignored. Therefore, in order to resolve these problems, experimental design is applied that allows the simultaneous variation of all variables. In this work, a Plackett–Burman design (PBD) was initially used to identify important factors and afterwards a Box-Behnken design (BBD) was performed to optimize the main factors.

Experimental

Apparatus and software

All experiments were done with the help of flame atomic absorption spectrophotometer (model AA-680, Shimadzu, Kyoto, Japan) equipped with an air-acetylene burner. A deuterium lamp was utilized as a background correction system. The radiation source was a cadmium hollow-cathode lamp from Hamamatsu, Photonic Co. Ltd, L233–series (Hamamatsu, Japan) and operated at a wavelength of 228.8 nm. Acetylene and air flow rates were 1.8 and 8 L min⁻¹, respectively. Adjustment of pH value of the solutions was done by a pH meter (MetrohmLab-827, Herisau, Switzerland) supplied with glass-calomel electrode. Experimental design was accomplished using Minitab version 16.

Reagents and solutions

All chemicals applied in this study were of analytical reagent grade. Analytical grade of cadmium (II) nitrate and nitrate salts of other cations were purchased from Merck (Darmstadt, Germany) and were of high purity without previous purification. Other chemicals such as 1-octanol, 1-dodecanol, 1-undecanol, 1-decanol, n-hexane, n-heptane, acetic acid (98%), hydrochloric acid (37%), nitric acid (65%) and phosphoric acid (85%) were provided from Merck. A stock standard solution of Cd²⁺ (1000 mg L⁻¹) was obtained by dissolving an appropriate amount of cadmium (II) nitrate in 1% (v/v) HNO₃, diluted with deionized water to a given volume and was used daily to prepare working standard solutions. A solution of sodium diethyldithiocarbamate (Na-DDTC) as chelating agent (Merck) was prepared by dissolving a proper amount of Na-DDTC in ethanol-deionized water (2:8). A CRM TMDW-500 drinking water was obtained from High-Purity Standards Inc, (Charleston, Sc, USA). For pH adjustment of Cd²⁺ solutions, a 0.2 mol L⁻¹ phosphate buffer solution (PBS) was applied.

FMSA-LLME procedure

The schematic procedure of the FMSA-LLME is illustrated in Figure 1. For this method, 45 mL of sample solution containing $20 \mu\text{g L}^{-1}$ of Cd^{2+} and 1 mL of Na-DDTC (0.005 mol L^{-1}) was placed into a cylindrical glass vial (13 cm height and 28 mm i.d.). Then, the pH of sample solution was adjusted to 7.25 via addition of 5.0 mL of 0.2 mol L^{-1} PBS (Figure 1a). Next, while the mixture was magnetically stirred slowly, 185 μL of 1-octanol was injected into the aqueous sample employing a 250 μL Hamilton syringe (Figure 1b) and then, the magnetic stirrer was set to 1200 rpm for 55 s (Figure 1c). The cloudy mixture was poured into the extraction vessel by a 250 mL syringe (Figure 1d) and subjected to aeration process using an air pump (Figure 1e). After about 6 min, the organic phase was accumulated on the top of the solution and aqueous phase became clear. After that, a floating layer on the surface of the solution was transferred to the narrow neck section by adding a small volume of deionized water (Figure 1f). Finally, the extraction phase was removed (Figure 1g), transferred into the Eppendorf tube, diluted to 300 μL using methanol and injected into the flame atomic absorption spectrometer for subsequent analysis.

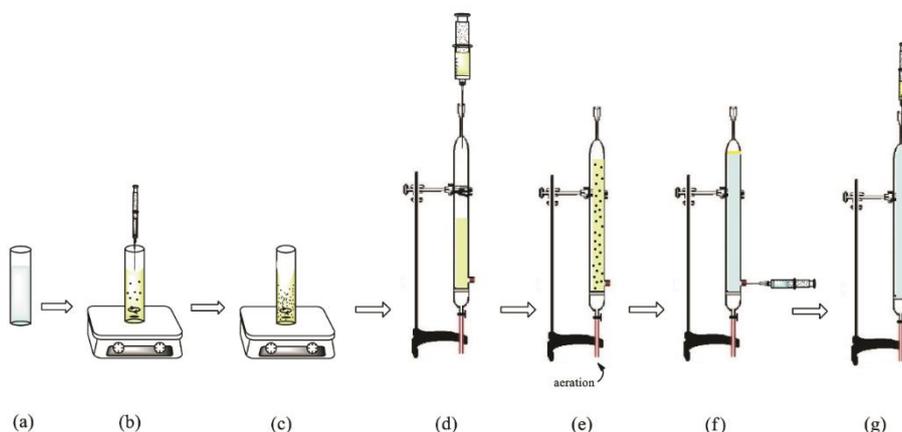


Figure 1. Schematic procedure of the proposed method. For (a)–(g), see text.

*Sample preparation**Water sample*

Environmental water samples such as tap, well, mineral and river water as real samples were employed to test the proposed extraction method. All water samples were taken from local sources of Arak, Iran. These samples were filtered through a $0.45 \mu\text{m}$ pore size membrane filter to remove any suspended material, the pH of solution was adjusted to 7.25 and was treated according to the proposed method.

Cereal sample

Rice and wheat samples were purchased from local supermarket in Arak, Iran. 1.0 g of powdered of each sample was accurately weighed in porcelain crucible and transferred into the electric furnace. Then, the temperature was increased to 500 °C and maintained at this temperature for 4 h. After cooling the sample, 4 mL of concentrated nitric acid was added to the porcelain crucible. Next, the mixture was heated for 10 min on a hot plate. After cooling down to room temperature, the residue was diluted to 25 mL with deionized water. Finally, the solution was poured into the extraction vessel and then the proposed procedure was carried out.

Optimization strategy of FMSA-LLME

In order to find effective factors influencing the extraction efficiency of Cd²⁺ such as pH of sample solution, concentration of Na-DDTC, volume of extraction solvent, extraction time and aeration time, PBD as a screening approach was used. In the next step, based on the results obtained from the PBD, BBD was used to investigate the interactions between the significant parameters and obtain the optimal levels.

Results and discussion

Selection of extraction solvent

One of the most important factors in preconcentration and determination of Cd²⁺ in this work is type of extraction solvent. Lower density than water, compatibility with the FAAS system, low toxicity, immiscible with the aqueous phase, low cost and high extraction efficiency of the target analyte are desired properties in choosing a proper extraction solvent. According to these criteria, six solvents including 1-octanol, 1-decanol, 1-undecanol, 1-dodecanol, n-hexane and n-heptane were tested. Figure 2 depicts that 1-octanol presented the highest analytical signals and thus was chosen for the subsequent studies.

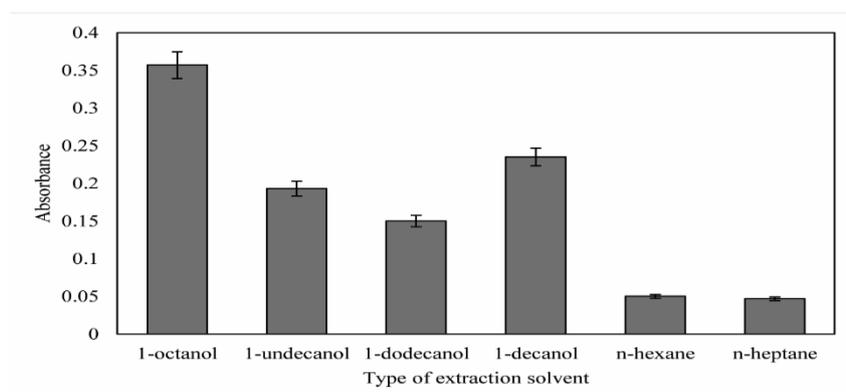


Figure 2. Effect of extraction solvent type on the extraction efficiency. Extraction conditions: sample volume, 50 mL; pH, 7.25; concentration of Na-DDTC, 0.005 mol L⁻¹; extraction solvent volume, 185 μL; aeration time, 6.47 min and extraction time, 55 s. The error bars represent standard deviations (n = 3).

Effect of ionic strength

In order to investigate influence of the ionic strength on performance of FMSA-LLME, various experiments were carried out using NaNO_3 in the range of 0-20% (w/v). The obtained results illustrated that the salt addition had no significant effect on the extraction efficiency (figure 3). Hence, subsequent experiments were performed without addition of salt.

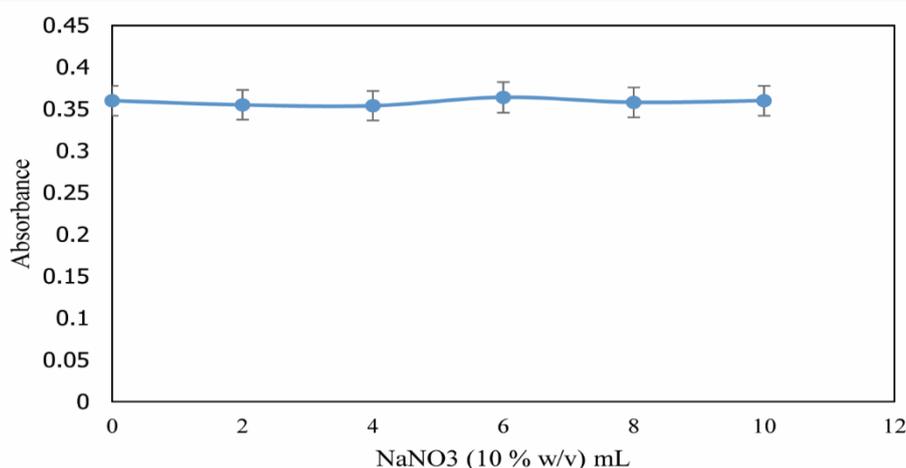


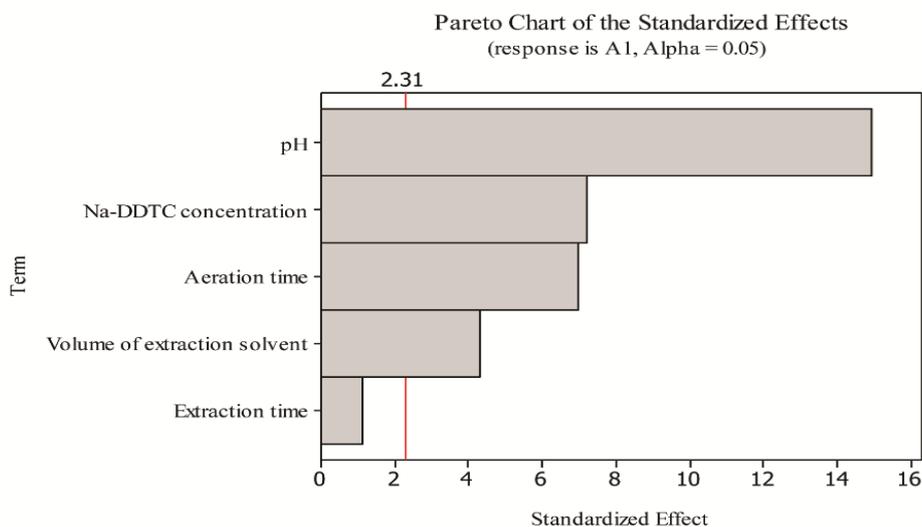
Figure 3. Effect of ionic strength on the extraction. Extraction conditions: sample volume, 50 mL; pH, 7.25; concentration of Na-DDTC, 0.005 mol L⁻¹; extraction solvent volume, 185 μL ; aeration time, 6.47 min and extraction time, 55 s. The error bars represent standard deviations (n = 3).

Plackett–Burman design (PBD)

In order to reduce the number of experiments and evaluate the main parameters that have an impact on the extraction efficiency of Cd^{2+} by FMSA-LLME method, the PBD was applied. In PBD, all interactions between factors that may be present are not considered, and only main effects are calculated [28, 29]. In this proposed method, the important effects of the five factors, namely pH of sample solution, concentration of Na-DDTC, volume of extraction solvent, extraction time and aeration time were assessed using the PBD which includes 15 experiments (12+3 center points). This design considers two levels for each factor that were selected based on the preliminary experiments. The factors, their levels, and the runs of PBD were depicted in Table 1. Analysis of variance (ANOVA) with a t-test at 95% probability was utilized in order to estimate the results obtained for determination of significant variables. The impact of the studied parameters in the PBD was described as Pareto chart with confidence level of 95% (Figure 4). Based on Pareto chart, pH of sample solution, concentration of Na-DDTC, aeration time and volume of extraction solvent were significant on the extraction process, while extraction time had no significant effect on the extraction recovery and so, was eliminated and kept constant in center point value (55 s) to optimize with BBD.

Table 1. The variables, their levels, design matrix and responses for the Plackett-Burman design.

	Factor	Symbol	Levels			
			Low	Central	High	
	pH	X ₁	4.5	7.25	10	
	Concentration of Na-DDTC (mol L ⁻¹)	X ₂	0.000150	0.005075	0.010000	
	Volume of extraction solvent (μL)	X ₃	70	185	300	
	Extraction time (s)	X ₄	20	55	90	
	Aeration time (min)	X ₅	2	6	10	
Runs	X ₁	X ₂	X ₃	X ₄	X ₅	Absorbance
1	10.0	0.010000	300	20	10	0.350
2	4.50	0.000150	70	20	2	0.035
3	10.0	0.000150	300	90	2	0.239
4	7.25	0.005075	185	55	6	0.402
5	10.0	0.010000	70	90	10	0.301
6	7.25	0.005075	185	55	6	0.411
7	10.0	0.000150	70	20	10	0.243
8	7.25	0.005075	185	55	6	0.403
9	10.0	0.010000	70	90	2	0.259
10	4.50	0.010000	70	20	2	0.079
11	4.50	0.000150	70	90	10	0.109
12	10.0	0.000150	300	20	2	0.189
13	4.50	0.010000	300	20	10	0.221
14	4.50	0.010000	300	90	2	0.148
15	4.50	0.000150	300	90	10	0.127

**Figure 4.** Pareto chart of the standardized effects at $P = 0.05$. The vertical line in the chart defines the 95% confidence interval.

Box–Behnken design (BBD)

In the next step, the response surface methodology (RSM) based on BBD was applied to determine the optimal conditions. Four variables (sample pH, concentration of Na-DDTC, aeration time and

volume of extraction solvent), interaction between them and quadratic effects were optimized and investigated in the BBD. The number of experimental points (N) is obtained using equation 1:

$$N = 2k(k-1) + C_0 \quad (1)$$

where k is the factor number and C_0 is the number of the center point [30]. In this study, k and C_0 were set at 4 and 3, respectively. By considering equation (1), 27 experiments were done randomly in the current BBD for minimizing the systematic error. The levels of factors and the design matrix with the responses were listed in Table 2.

Table 2: The variables, their levels, design matrix and responses for the Box-Behnken design.

	Factor	Symbol	Levels		
			Low	Central	High
	pH	X_1	4.50	7.25	10
	Concentration of Na-DDTC (mol L^{-1})	X_2	0.000150	0.005075	0.010000
	Volume of extraction solvent (μL)	X_3	70	185	300
	Aeration time (min)	X_4	20	6	10
Runs	X_1	X_2	X_3	X_4	Absorbance
1	4.50	0.010000	185	6	0.155
2	7.25	0.000150	300	6	0.181
3	7.25	0.000150	185	10	0.213
4	7.25	0.005075	300	10	0.278
5	10.0	0.005075	70	6	0.289
6	7.25	0.005075	70	2	0.167
7	7.25	0.000150	185	2	0.149
8	4.50	0.005075	70	6	0.146
9	7.25	0.010000	185	10	0.313
10	4.50	0.005075	185	2	0.109
11	7.25	0.010000	300	6	0.307
12	7.25	0.005075	185	6	0.401
13	10.0	0.005075	185	10	0.346
14	7.25	0.000150	70	6	0.167
15	7.25	0.005075	185	6	0.412
16	7.25	0.010000	70	6	0.239
17	10.0	0.005075	185	2	0.261
18	7.25	0.005075	185	6	0.406
19	7.25	0.010000	185	2	0.237
20	10.0	0.010000	185	6	0.341
21	7.25	0.005075	70	10	0.267
22	4.50	0.005075	300	6	0.169
23	7.25	0.005075	300	2	0.251
24	10.0	0.005075	300	6	0.348
25	4.50	0.005075	185	10	0.151
26	10.0	0.000150	185	6	0.267
27	4.50	0.000150	185	6	0.091

In order to evaluate the statistical significance of the model and the model terms, ANOVA was utilized (Table 3). According to the results shown in Table 3, if p-value with confidence level of 95% is less than 0.05, the model, variables and their interactions are significant. A good relationship

between the experimental data and fitted model was expressed by the coefficients of determination R^2 and adjusted R^2 . The value of R^2 is 99.32. In other words, this model can explain 99.32 of experimental results. The value of R^2 adjusted (98.53) emphasized that the model was highly significant. The lack of fit (LOF) illustrates the variation of signals around the fitted model and a particular investigative test for the adequacy of a model fit. The model's LOF was not significant because of p-value > 0.05 (0.186).

Table 3. Analysis of variance (ANOVA) for the Box-Behnken design.

Source	DF ^a	Seq SS	Adj SS	Adj MS	F-value ^b	p-value
X ₁	1	0.088580	0.088580	0.088580	707.42	0.000
X ₂	1	0.022881	0.022881	0.022881	182.74	0.000
X ₃	1	0.005590	0.005590	0.005590	44.64	0.000
X ₄	1	0.012936	0.012936	0.012936	103.31	0.000
X ₁ ²	1	0.012394	0.048939	0.048939	390.84	0.000
X ₂ ²	1	0.020018	0.050613	0.050613	404.21	0.000
X ₃ ²	1	0.014842	0.033110	0.033110	264.42	0.000
X ₄ ²	1	0.040523	0.040523	0.040523	323.63	0.000
X ₁ X ₂	1	0.000025	0.000025	0.000025	0.20	0.663
X ₁ X ₃	1	0.000324	0.000324	0.000324	2.59	0.134
X ₁ X ₄	1	0.000462	0.000462	0.000462	3.69	0.079
X ₂ X ₃	1	0.000729	0.000729	0.000729	5.82	0.033
X ₂ X ₄	1	0.000036	0.000036	0.000036	0.29	0.602
X ₃ X ₄	1	0.001332	0.001332	0.001332	10.64	0.007
Lack of fit	10	0.001442	0.001442	0.000144	4.75	0.186
Pure Error	2	0.000061	0.000061	0.000030	-	
Total SS	26	0.222176				

^aDF: Degrees of freedom.

^bTest for comparing variance of model with variance of residual (error).

The mathematical relationship between the four variables and response obtained by the application of RSM is explained by the following equation:

$$A = 0.406333 + 0.085917 X_1 + 0.043667 X_2 + 0.021583 X_3 + 0.032833 X_4 - 0.095792 X_1^2 - 0.097417 X_2^2 - 0.078792 X_3^2 - 0.087167 X_4^2 + 0.002500 X_1X_2 + 0.009000 X_1X_3 + 0.010750 X_1X_4 + 0.013500 X_2X_3 + 0.003000 X_2X_4 - 0.0182500 X_3X_4 \quad (2)$$

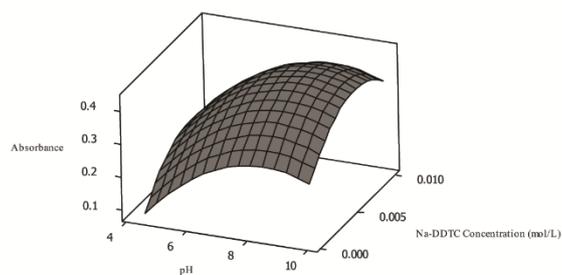
where A is the response and X₁, X₂, X₃ and X₄ are the coded values of pH, concentration of Na-DDTC, volume of extraction solvent and aeration time, respectively.

In the final step, three dimensional response surface plots were employed in order to investigate the relationship between the responses and experiment factors' levels, interaction effects and determine the optimum conditions for the four factors. (Figure 5a-5c). Figure 5a depicts the response surface obtained by plotting the pH versus concentration of Na-DDTC at the fix values of the other two

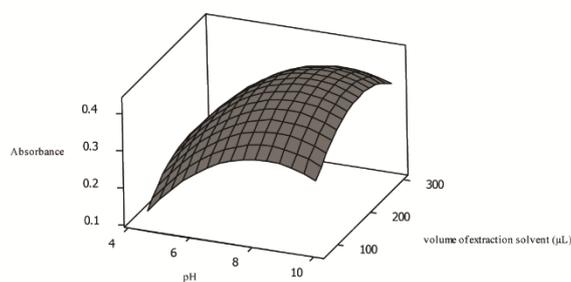
factors. As can be seen, the maximum extraction efficiency was obtained when the pH and concentration of Na-DDTC were about 8.5 and 0.0060 mol L⁻¹, respectively. The concentration of Na-DDTC has a significant impact on cadmium complex formation and extraction efficiency of analyte and so, increase of the analytical signal by increasing the concentration of chelating agent is well expected. Figure 5b shows the response surface obtained as a function of pH and volume of the extraction solvent while concentration of Na-DDTC and aeration time was kept constant at center point values. As can be seen, the absorbance reached a maximum value when pH and volume of extraction solvent were about 8.5 and 185 μL, respectively. The higher organic solvent volume causes to decrease the extraction efficiency due to dilution of the analyte. Figure 5C shows the effects of Na-DDTC concentration and aeration time on the extraction efficiency while pH and volume of extraction solvent were kept constant at center point values. The results indicate, absorbance increased with increasing Na-DDTC concentration and aeration time up to 0.0060 mol L⁻¹ and 6 min, respectively due to increasing mass transfer of cadmium complex into organic phase. According to the overall results of the optimization study, the optimum extraction conditions from "response optimizer" section were: pH = 7.25, concentration of Na-DDTC = 0.005 mol L⁻¹, extraction solvent volume = 185 μL and aeration time = 6.47 min.

Interferences effects

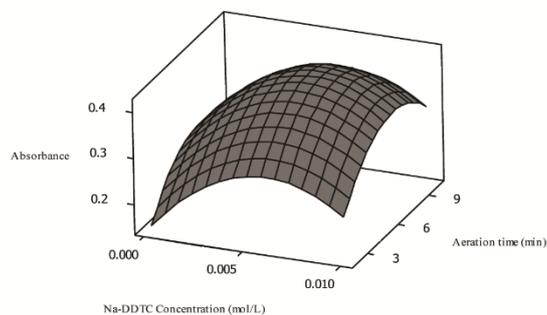
The effects of several ions on the extraction efficiency of Cd²⁺ using the FMAS-LLME procedure were examined in the natural water samples. For this purpose, sample solutions containing 20 μg L⁻¹ Cd²⁺ and different amounts of foreign ions were evaluated according to the recommended procedure. If variation in the absorbance was greater than ±5%, a compound was considered as an interfering ion. As Table 4 portrays, most of the cations and anions have no significant interference with the extraction and determination of Cd²⁺ using the FMAS-LLME method.



(a)



(b)



(c)

Figure 5. Response surface plots when optimizing the following pair of factors, while the other factors were kept constant at a central point (central level): (a) pH–concentration of Na-DDTC (extraction solvent, 185 μL and aeration time, 6 min); (b) pH–volume of extraction solvent (concentration of Na-DDTC, 0.005075 mol L^{-1} and aeration time, 6 min); (c) concentration of Na-DDTC–aeration time (pH, 7.25 and volume of extraction solvent, 185 μL).

Table 4. Effect of interfering ions.

Ion	Ion/Cd(II) mass ratio
Na ⁺ , K ⁺ , Al ³⁺ , Mg ²⁺ , Ca ²⁺ , Ba ²⁺ , Cr ³⁺ , NO ₃ ⁻ , Cl ⁻ , SO ₄ ²⁻	1000
Mn ²⁺	700
Ni ²⁺ , Bi ³⁺	500
Ag ⁺ , Pd ²⁺	100
Co ²⁺ , Cu ²⁺	50

Analytical figures of merit

The analytical characteristics including linear dynamic range (LDR), limit of detection (LOD), relative standard deviation (RSD) and enrichment factor (EF) were obtained to assess the developed technique. Under the optimized conditions, the linear dynamic range for calibration graph of cadmium was obtained from 0.5 to 80 $\mu\text{g L}^{-1}$ with $R^2 = 0.996$. The LOD calculated as the ratio of three times standard deviation of seven replicates of blank signals to the slope of the calibration curve after extraction was 0.16 $\mu\text{g L}^{-1}$. The RSD was 1.39%, which was achieved by performing seven replicate measurements. The enrichment factor (EF) was found to be about 152, which is defined as the ratio of the slope of the calibration curve obtained after and before preconcentration procedure [31, 32]. The equation of the calibration graph after the extraction procedure for Cd²⁺ is described in Equation (3). The equation of the calibration graph before the extraction procedure for the studied analyte is described by Equation (4):

$$A = 15.686 \times 10^{-3} [\text{Cd}] + 0.0679 \quad (r^2=0.996) \quad (3)$$

$$A = 0.1032 \times 10^{-3} [\text{Cd}] + 0.0344 \quad (r^2=0.999) \quad (4)$$

The validation and application of the method

The accuracy of the suggested method was evaluated by extraction and determination of Cd²⁺ in CRM TMDW-500 drinking water with a Cd²⁺ content of $10.00 \pm 0.05 \mu\text{g L}^{-1}$. The Cd²⁺ content found in CRM using this method was $9.81 \pm 0.31 \mu\text{g L}^{-1}$. The analytical result was in good agreement with the certified value of CRM. The applicability of the method was used to determination of Cd²⁺ in several water, rice and wheat samples as the real samples. Reliability was checked at optimum conditions by spiking 20 and 40 $\mu\text{g L}^{-1}$ of Cd²⁺ standard solution. The results are summarized in Table 5. According to the results, the relative recoveries of Cd²⁺ were in the acceptable range of 96.15-102.45% which demonstrated the FMSA-LLME method is suitable for the determination of Cd²⁺.

Table 5. Determination of Cd in water, rice and wheat samples.

Sample	Cd(II) added ($\mu\text{g L}^{-1}$)	Cd(II) found ^a ($\mu\text{g L}^{-1}$)	Recovery (%)
Tap water (Arak, Iran)	0.0	N.D ^b	-
	20.0	19.55 ± 0.32	97.75
	40.0	39.92 ± 0.39	99.80
Well water (Arak, Iran)	0.0	N.D	-
	20.0	20.49 ± 0.30	102.45
	40.0	40.07 ± 0.37	100.17
Mineral water (Sarband mountain, Arak, Iran)	0.0	N.D	-
	20.0	19.60 ± 0.25	98.00
	40.0	40.05 ± 0.31	100.12
Bolagh river (Arak, Iran)	0.0	5.61 ± 0.29	-
	20.0	25.25 ± 0.21	98.20
	40.0	45.33 ± 0.35	99.30
Rice	0.0	14.15 ± 0.28	-
	20.0	33.38 ± 0.31	96.15
	40.0	52.85 ± 0.33	96.75
Wheat	0.0	8.70 ± 0.32	-
	20.0	28.06 ± 0.29	96.80
	40.0	47.78 ± 0.22	97.70

^aMean value of three replicate determination \pm standard deviation (n = 3).

^bNot detected.

Comparison of FMSA-LLME with other methods

The main analytical characteristics of the FMSA-LLME method were compared with others reported in the literature (Table 6). As can be seen, the developed method illustrated several improvements including low LDR, high EF and good RSD, which are comparable or even better than the results of the other methods. As is obvious, the FMSA-LLME technique is simple, rapid, reproducible and sensitive that can be applied for the preconcentration and determination of Cd²⁺ with FAAS.

Table 6: Comparison of proposed method with other preconcentration methods for cadmium.

Method	LOD ($\mu\text{g L}^{-1}$)	RSD (%) EF/PF		LDR ($\mu\text{g L}^{-1}$)	References
IL-DLLME/FAAS ^a	0.06	2.4	100	0.2-60	[33]
CPE/FAAS ^b	0.2	2.4	20.7	1.25-50	[34]
VSLLME-SFO/FAAS ^c	0.16	3.2	37.68	0.5-30	[35]
SPE-SD-DLLME/FAAS ^d	0.03	5.1	165	0.1-50	[36]
IL-UA-DMME/FAAS ^e	0.4	4.29	100	10-500	[37]
VALLME/FAAS ^f	0.5	4.2	20	10-200	[38]
TC-IL-DLPME/FAAS ^g	0.2	1.5	25	0.6-20	[39]
FMSA-LLME/FAAS	0.16	1.39	152	0.5-80	This work

^aIL-DLLME: Ionic liquid-based dispersive liquid-liquid microextraction.

^bCPE: Cloud point extraction.

^cVSLLME-SFO: Vortex-assisted surfactant-enhanced-emulsification liquid-liquid microextraction with solidification of floating organic droplet.

^dSPE-SD-DLLME: Solid phase extraction- solvent-based de-emulsification-dispersive liquid-liquid microextraction. ^eIL-UA-DMME: Ionic liquid-based ultrasound- assisted dual magnetic microextraction.

^fVALLME: Vortex-assisted liquid-liquid microextraction.

^gTC-IL-DLPME: temperature-controlled ionic liquid dispersive liquid phase microextraction.

Conclusion

In the present study, a simple and fast determination of Cd^{2+} in different real samples was successfully carried out via the flotation/magnetic stirring assisted liquid-liquid microextraction method coupled with flame atomic absorption spectrometry. The PBD was used to obtain the main factors and a BBD was applied to determine the optimal conditions for significant factors. This methodology has benefits such as low cost, requires no sophisticated procedure, high sensitivity, short extraction time, less consumption of the organic solvent, low LOD, excellent enrichment factor, as well as good precision. Due to the above mentioned advantages, this method was successfully performed for the determination of Cd^{2+} in various water, rice and wheat samples.

Acknowledgement

The support provided by Islamic Azad University of Arak (Arak, Iran) is highly appreciated.

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