

Application of solvent-assisted dispersive solid phase extraction combined with flame atomic absorption spectroscopy for the determination of trace amounts of Cadmium

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Original Article

Abstract

Introduction: Cadmium is recognized worldwide as a toxic metal. In this study, Solvent-Assisted Dispersive Solid Phase Extraction (SA-DSPE) combined with Flame Atomic Absorption Spectrometry (FAAS), was used for determination of trace amounts of Cadmium (Cd-II) in drinking water samples.

Methods: In this approach, the dispersion of the sorbent was achieved by injecting a mixture of solution of the sorbent and dispersive solvent into the aqueous sample. Thereby, a cloudy solution formed. The cloudy solution was centrifuged and the enriched Cd (II) in the sediment phase dissolved in ethanol and determined by FAAS. Some effective parameters for SA-DSPE, such as: pH, concentration of chelating agent, type and amount of sorbent, type and volume of dispersive solvent and salt effect were investigated and optimized.

Results: Under the optimized conditions, the detection limit for Cd (II) ions was 0.6 ng mL⁻¹. Calibration curve was made in the range of 1-300 ng mL⁻¹, obtaining good linearity (R²=0.9930). Finally, SA-DSPE was successfully applied for trace determination of Cd (II) in drinking water samples.

Conclusion: SA-DSPE is environment friendly and strongly against high contents of salt. The other benefits of the method are its simplicity, ease of operation, good precision, short extraction time, low cost, and a good enrichment factor.

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Introduction:

Human health depends on safe and good quality of drinking water (1). According to a recent report by WHO/UNICEF, about 780 million people in the world is encountering to water microbiological and

chemical contaminations (2). Increased urbanization and industrialization are to be responsible for an increased level of heavy metals, in our waterways (3). Heavy metals are non-biodegradable and stable in environment and tend to accumulate in plants and

animals (4). Nowadays, the pollution of natural waters by heavy metals is a concern because of the adverse effects on living organisms (5). Some of heavy metals like copper, cobalt and zinc are essentially required for growth and functions of body organisms, while the high concentrations of other metals like Cd (II), are toxic and harmful for human health (6). The exposure to Cd (II) has been associated with nephrotoxicity, osteoporosis, neurotoxicity, carcinogenicity, teratogenicity and endocrine and reproductive effects (7).

Determination of Cd (II) in drinking water is very important because of the toxic effects on human health (8). The atomic absorption spectrometry is a significant instrument for the determination of heavy metals, but direct determination of these elements in water by atomic absorption spectrometry is very difficult because of low detection limit and matrix effects (9). Thus, in order to the determination of heavy metals, several pre-concentration procedures have been developed (8). Several methods have been used for these purposes such as dispersive liquid-liquid microextraction (DLLME) (10-13), co-precipitation (14-16), electrochemical methods (17-21) and solid phase extraction (SPE) (22-28). Although, disadvantages such as large amounts of sample and/or organic solvents, significant chemical additives and high time consumption, limit the application of these techniques (29). Recently, a novel extraction technique as a high performance and powerful preconcentration method termed as SA-DSPE was demonstrated by Jamali *et al.* (2013). Solvent-assisted dispersive solid phase extraction has been used for the pre-concentration and separation of trace amounts of metals from complex matrices (29-34). SA-DSPE can be considered as a new, fast, simple and reliable procedure for separation and detection of heavy metals (30).

In this method, an appropriate mixture of the sorbent and the dispersive solvent rapidly are injected into aqueous sample by a syringe and forms a cloudy solution. The cloudy state results from the formation of fine particles of the extraction solvent which disperse in the sample solution. The cloudy solution shall be centrifuged and the fine droplets sediment at the bottom of the conical test tube. Then the sediment phase was dissolved in

ethanol and the analyte were determined using FAAS.

In this study, FAAS coupled with the SA-DSPE method was used in order to determination of Cd (II). The applied method was very simple and rapid. The effect of various factors affecting extraction efficiency such as: pH, concentration of chelating agent, type and amount of sorbent, type and volume of dispersive solvent and salt effect were evaluated and optimized. Under optimum conditions, the developed method was used for the pre-concentration, separation, and the determination of Cd (II) in drinking water samples.

Methods:

This research is descriptive and analytical. This study was conducted in laboratory of faculty of health in Bandar Abbas health college. 17 water samples were collected from local health centers and 2 samples from Damahy region, that is water distribution store. The samples were analyzed by SA-DSPE method.

Apparatus

A Younglin atomic absorption spectrometer model AAS 8020 was used for the analysis of Cd (II). The operating parameters were set as recommended by the manufacturer. Atomic absorption measurements were carried out in an air-acetylene flame. The pH was measured with a pH-meter AMTAST Model AMT12. Phase separation was achieved with a centrifuge (Behdad, Iran) in 10 mL conical tubes at 4000 rpm for 15 min.

Reagent and materials

All analytical grade reagents and solvents used in the experiments were purchased from Merck and used without further purification. A stock solution ($500.0 \mu\text{g mL}^{-1}$) of Cd (II) ions was prepared by dissolving an appropriate amount of Cd (II) nitrate salts in deionized water. The working standard solutions were daily prepared by appropriate stepwise dilution of the stock standard solution with deionized water. High purity water (resistivity $0.05 \mu\text{S/cm}$) obtained by a Millipore (Direct-Q S.A.S 67120 Molsheim) water purification system. The $500 \mu\text{g mL}^{-1}$ solution of APDC was prepared by dissolving the complex in pure methanol. The pH

of the extraction was adjusted with prepared 2.0 M NaOH and HCl solutions. Naphthalene, benzophenone, and 1, 4-dichlorobenzene solvents were utilized for selecting the sorbent and methanol, ethanol, acetone solvents were utilized for dispersive solvent. All laboratory glassware used for trace analysis were cleaned before use by soaking them in 15% nitric acid solution for at least 24 h and subsequently washed twice with deionized water.

Real sample pretreatment

In this study, to ensure from coverage of city for sampling, 17 samples of tap water were collected from health and treatment centers of Bandar Abbas city (Iran) as well as two samples from Damahy place that is the water distribution store. The polyethylene bottles were cleaned with detergent, water, 15% nitric acid and deionized water in sequence and then, filled with the samples. The samples were acidified to pH of 2.0 for storage, and were filtered through 0.45 μ m membranes. Sampling was carried out in a way that there is no air in the top of the bottle. Before the test, the water samples (50.0 mL) were adjusted to pH of 6.0 according to optimized experimental conditions.

Solvent-assisted dispersive solid phase extraction procedure

A solution (10mL) containing sample or standards of Cd (II) ion and APDC (7.5 μ g mL⁻¹) at pH of 6.0 was poured into a plastic screw-cap conical-bottom tube. Then 0.5 mL of methanol solution (as disperser solvent) containing benzophenone (4% (w/v)) (as sorbent) was rapidly injected into a sample solution by using 2.5mL Syringe. Thereby, cloudy solution formed in the test tube. This cloudy state resulted from the dispersion of fine particles of benzophenone in the bulk aqueous sample. Then, the mixture was centrifuged at 4000 rpm for 15 min. After that, the dispersed fine particles of benzophenone were gathered in the bottom of the conical tube.

The supernatant was poured away and the sediment phase was dissolved in ethanol and make up to 1.0 mL. The resulting solution was injected into the FAAS for determination of target ion. The simplified sketch of the above procedure was demonstrated in Figure 1.

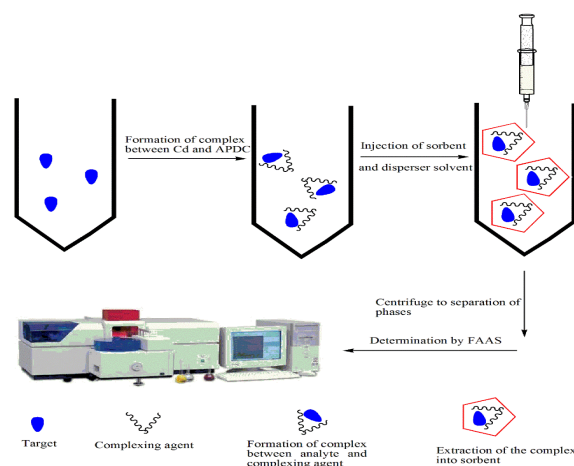


Figure 1. The simplified sketch for the SA-DSPE procedure

Results:

In this study, SA-DSPE was investigated for simultaneous preconcentration of Cd (II) ions from aqueous samples followed by their analysis by FAAS. The factors influencing the extraction procedure such as pH, concentration of chelating reagent, type and amount of sorbent, type and volume of dispersive solvent and salt effect were investigated and optimized.

Effect of pH

In the other words, in the extraction of metal ions, the extraction efficiencies of metal complex are closely related to the pH of the system. Thus, in order to obtain the desired preconcentration efficiencies, the effect of pH on complex formation and the extraction of Cd (II) from samples was studied in the range of 3.0–9.0 by 2M HCl and NaOH. The results shown in Figure 2 indicates that the optimum pH for extraction of Cd (II) ions is 6.0.

Effect of chelating reagent (APDC) concentration

The effect of chelating reagent concentrations on the absorbance was investigated in the range of 1-10 μ g mL⁻¹. As can be seen in Fig. 3, the concentration of 7.5 μ g mL⁻¹ APDC was selected as the best choice in the experiments.

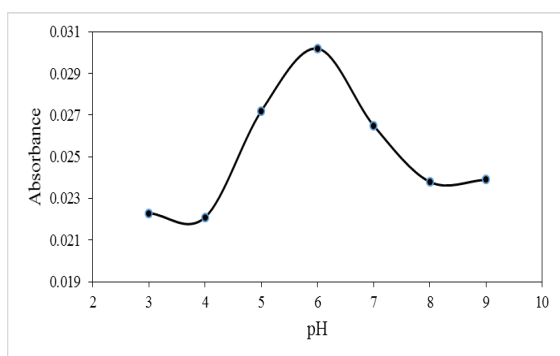


Figure 2. Effect of pH on the absorbance of Cd (II) obtained from SA-DSPE. Conditions: sample volume: 10 mL, Cd (II) concentration: 50.0 ng mL⁻¹, APDC concentration: 2.5 μg mL⁻¹, sorbent: benzophenone, 4%, dispersive solvent: methanol, 500 μL.

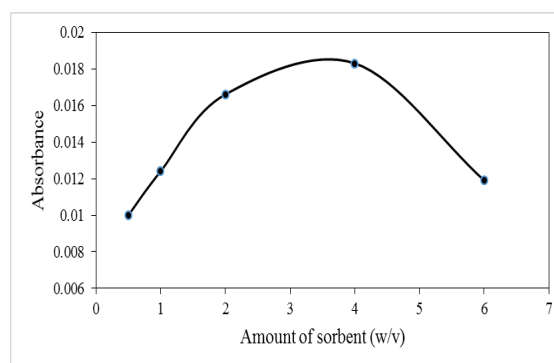


Figure 5. Effect of amount of sorbent on the absorbance of Cd (II) obtained from SA-DSPE. Conditions: sample volume: 50 mL, Cd (II) concentration: 50.0 ng mL⁻¹, APDC concentration: 7.5 μg mL⁻¹, sorbent: benzophenone, dispersive solvent: methanol, 500 μL, pH: 6.0

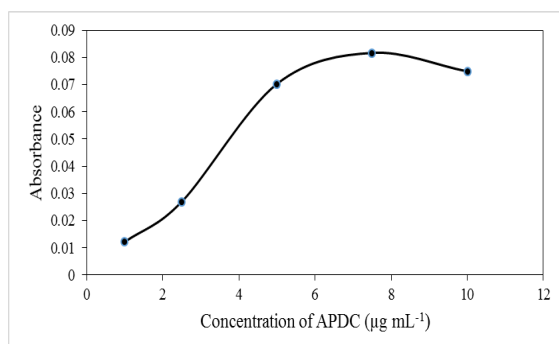


Figure 3. Effect of APDC concentration on the absorbance of Cd (II) obtained from SA-DSPE. Conditions: sample volume: 10 mL, Cd (II) concentration: 50.0 ng mL⁻¹, sorbent: benzophenone, 4%, dispersive solvent: methanol, 500 μL, pH: 6.0.

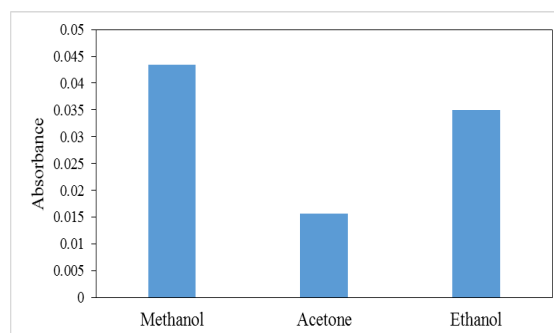


Figure 6. Effect of type of dispersive solvent on the absorbance of Cd (II) obtained from SA-DSPE. Conditions: sample volume: 10 mL, Cd (II) concentration: 50 ng mL⁻¹, APDC concentration: 7.5 μg mL⁻¹, sorbent: benzophenone, 4%, pH: 6.0.

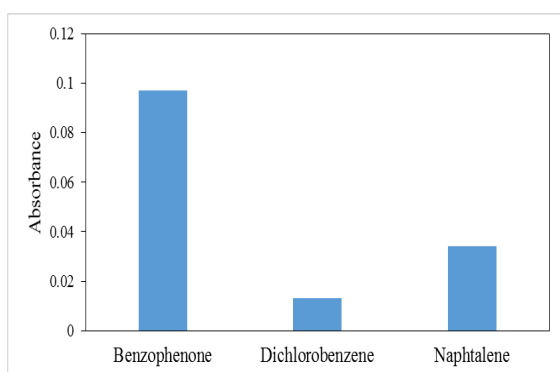


Fig. 4. Effect of type of sorbent on the absorbance of Cd (II) obtained from SA-DSPE. Conditions: sample volume: 10 mL, Cd (II) concentration: 50.0 ng mL⁻¹, APDC concentration: 7.5 μg mL⁻¹, dispersive solvent: methanol, 500 μL, pH: 6.0.

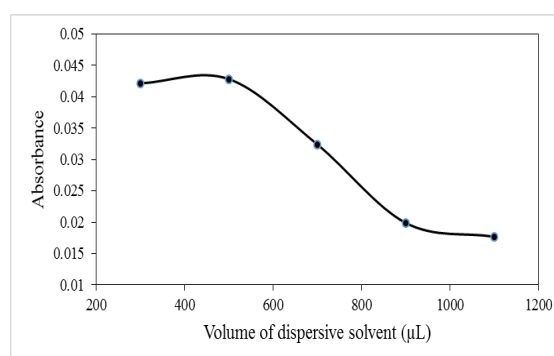


Figure 7. Effect of volume of dispersive solvent on the absorbance of Cd (II) obtained from SA-DSPE. Conditions: sample volume: 10 mL, Cd (II) concentration: 50.0 ng mL⁻¹, APDC concentration: 7.5 μg mL⁻¹, sorbent: benzophenone, 4%, dispersive solvent: methanol.

Table 1. The effect of foreign ions. Conditions: sample volume: 10 mL, Cd (II) concentration: 50.0 ng mL⁻¹, APDC concentration: 7.5 µg mL⁻¹, sorbent: benzophenone, 4%, disperser solvent: methanol, 500 µL, pH: 6.0

Foreign ion	Tolerable concentration ratio X/Cd (II)	Recovery (%)
Na ⁺	200.0	98.6
Mg ²⁺	200.0	95.7
K ⁺	200.0	95.4
Ca ²⁺	200.0	96
Ag ⁺	200.0	98.7
Fe ²⁺	100.0	95.4

Table 2. Determination of Cd (II) in drinking water samples with SA-DSPE procedure

drinking water samples	Real amount Cd (II) in water	Added (ng mL ⁻¹)	Recovery (%)
health center 1	–	50.0	98.6
health center 2	–	50.0	90.0
health center 3	–	50.0	90.6
health center 4	–	50.0	88.6
health center 5	–	50.0	88.7
health center 6	–	50.0	86.0
health center 7	–	50.0	104.6
health center 8	–	50.0	85.6
health center 9	–	50.0	94.2
health center 10	–	50.0	86.7
health center 11	–	50.0	86.6
health center 12	–	50.0	96.6
health center 13	–	50.0	89.3
health center 14	–	50.0	85.3
health center 15	–	50.0	98.6
health center 16	–	50.0	94.0
health center 17	–	50.0	87.3
Pipe before Damahy place	–	50.0	90.0
Pipe after Damahy place	–	50.0	87.3

Table 3. Comparison of different separating and analytical techniques with present method for the determination of Cd (II) in water samples.

Method	Instrument	pH	Dynamic range ng mL ⁻¹	LOD ng mL ⁻¹	Ref.
CoP; Aluminum hydroxide	FAAS	7	-	6	(35)
DLLME; APDC	ICP-OES	6	-	0.8	(36)
SPE; Diaion SP-207	FAAS	6.5	20-1500	1.1	(37)
DLLME; Dithizone	UV-Vis	12.8	10-100	8.5	(38)
DLLME; 1,5-bis(di-2-pyridinyl-methylene)-thiocarbohydrazone	FAAS	5.4	20-300	2	(7)
SA-DSPE; Dithizone	FAAS	7	0.5-110	0.2	(30)
SA-DSPE; APDC	FAAS	6	1-300	0.6	Presented work

Selection of type and amount of sorbent Naphthalene, benzophenone, and 1,4-dichlorobenzene were evaluated in the extraction of Cd (II) ions. A series of sample solutions were

studied using 0.5 mL methanol containing 4% (w/v %) of the sorbent. As illustrated in Fig.4 the highest absorbance was obtained with benzophenone. Effect of the sorbent amount, was studied using 0.5

mL methanol containing different amounts (0.5-6% (w/v %)) of benzophenone. Based on the findings and Figure 5, 4% of the benzophenone was selected as the optimum amount of the sorbent for experiments.

The effect of the type and volume of the dispersive solvent

In order to assess the effect of the type of dispersive solvent, acetone, methanol, and ethanol were evaluated. A series of sample solutions was studied using 500 μ L of each disperser solvent containing 4% of benzophenone. As shown in Figure 6, best absorbance for target ions was obtained with methanol as the dispersing solvent. Therefore, methanol was selected as the disperser solvent for further experiments. As shown in Figure 7, most of the absorbance occurred in 500 μ L of methanol. Therefore, 500 μ L of methanol was selected as optimum volume.

Effect of salt

Addition of salt often in conventional SADSPE due to the salting-out effect. To evaluate the possibility of salting-out effect and studying the impact of ionic strength on performance of SA-DSPE, several tests were done by addition of different amount of NaCl (0-5% (w/v)). Other experimental conditions were kept constant. The results showed that salt addition has no significant effect on the absorbance of FAAS. Hence, all the extraction experiments were performed without the addition of salt.

The effect of interfering ions

The optimized conditions was applied to assess the study of several ions on the efficiency of the presented work. In these experiments, solutions of 50 ng mL⁻¹ of the Cd (II) ion containing the interfering ions were treated. Table 1 shows tolerance limits of the interfering ions. Given species were considered to interfere if it resulted in a $\pm 5\%$ variation of the AAS signal. According to the results, the key ions in the real samples have no serious influence on the Cd (II) extraction under the selected conditions.

Figures of merit

Analytical figures of merit of the proposed SA-DSPE-FAAS method were obtained under optimal conditions. The calibration curve showed good linearity in the range of 1-300 ng mL⁻¹ at least 0.9930 of R² (correlation coefficient). The limit of detection, defined as C_{LOD} = 3 SB/m (where C_{LOD}, SB and m are the limit of detection, standard deviation of the blank and slope of the calibration curve, respectively), was 0.6 ng mL⁻¹.

The relative standard deviation (R.S.D.) for six replicate measurements of 50 ng mL⁻¹ Cd (II) was 2.5%.

Analysis of drinking water samples

The proposed SA-DSPE methodology was applied to the determination of Cd (II) in 17 water samples from health and treatment centers and 2 samples from Damahy place in Bandar Abbas city. The real samples were analyzed by spiked samples of Cd (II) (50 ng mL⁻¹ Cd (II)). The water samples were extracted using the proposed method and analyzed by FAAS. The analytical results are given in Table 2. As can be seen, these results demonstrated that the real water samples matrices, in our present context, had little effect on SA-DSPE of Cd (II) and the recoveries ranged from 85.3% to 104.6%.

Conclusion:

The sample pH, plays an important role in SA-DSPE procedure. The separation of Cadmium ions by solvent-assisted dispersive solid phase extraction involves prior formation of a complex with sufficient hydrophobicity interacting and adsorbing with the fine particles of the sorbent. Therefore pH of solution is a key parameters that needs to evaluated and optimized (Figure 2).

The decrease in the absorbance at pH < 6.0 is due to the electrostatic repulsion of the protonated active sites on the chelating agent with the positively charged Cadmium species. As can be seen, a further increase in pH values, absorbance decreased probably due to Cd (II) hydroxide formation. Hereby, pH 6.0 was selected for Cd (II) experiments.

As shown in Figure 3 the absorbance was amplified by increasing the APDC amount. It looks that by arising the concentration of APDC the

extraction efficiency was declined and this phenomena could be attributed to the saturation of sorbent in small amount. Reason of the low extraction efficiency at low concentrations of complex could be inadequate amounts of APDC in solution to form the complexation of Cadmium ions.

Careful attention must be regarded to in the choice of the sorbent, and it should have extraction ability for concerning compounds, high solubility in disperser solvent and low solubility in water (29) (Figure 4). The Simple structure of benzophenone and the complex of APDC with Cd (II) and their proper interaction could due to the higher absorbance of benzophenone (30). Therefore, benzophenone was selected as the sorbent.

The obtained results (Figure 5) showed that by increasing the adsorbent amounts from 0.5-4% (w/v %), extraction efficiency increased due to the increase in accessible sites. A further rise of the amount of benzophenone to 6% lead to decrease absorbance. It seems Clogging of Nebulizers pipe due to reducing efficiency was occurred.

In SA-DSPE, the selection of disperser solvent is critical and it affects the efficiency of extraction. Dispersive solvent should be miscible with the sample matrix in order to release the sorbent easily; also it should be able to dissolve the sorbent (29). In this section methanol was the best dispersing solvent probably because of better dispersing strength of methanol (Figure 6).

The effects of the volumes of methanol on the extraction efficiency were investigated in the range of 300-1100 μ L with 4% of benzophenone as the sorbent. The extraction efficiency decreased clearly when the volume of methanol exceeded 500 μ L (Figure 7).

It could be stated that by increasing in the volume of methanol an increase in the solubility of the complex can occurred and consequently, extraction recovery decreases (30). The extraction efficiency decreased in amounts of less than 500 μ L, because of benzophenone cannot well dispersed by methanol. A comparison of the proposed method with others reported in preconcentration method for Cd (II) determination is shown in Table 3. In comparison with other reported methods, the proposed method has lower LOD except the work presented by Behbahani et.al. However, the

proposed method has better linear dynamic range than reported Behbahani et al. work. The outcome of this varying shows that the present work is a simple, rapid and low-cost technique and could be applied for the preconcentration and determination of Cd (II) in water samples.

As a final conclusion, the recommended SA-DSPE technique combined with FAAS was successfully used for preconcentration of Cd (II) from drinking water samples. The proposed method is very simple, fast, inexpensive, effective, sensitive, high-selective and suitable. In this method, sample preparation time and consumption of toxic organic solvents was reduced without affecting the sensitivity of the system. The SA-DSPE permits the quick extraction of Cd (II) ions using a low amount of sorbent. This method is environment friendly and strong against high contents of salt. In addition, the proposed method has good linear dynamic range and low LOD. The suggested method has the extraction time lower comparable to the previously reported methods including LLE, SPE and DLLME. Although the results obtained in this research were primarily focused on Cd (II) determination, the system may be readily applied for the determination of other metals with the help of various chelating agents and organic solvents.

Limitations: Preparation of standard samples and clogging of Nebulizer pipe in atomic absorption spectrometer is from Limitations of this study.

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