

A Microextraction Method Based on Ligandless Ion-Pair Formation for Measuring the Cadmium Cation in Real Samples by Flame Atomic Absorption Spectrometry

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Received: 28 November 2015 / Accepted: 10 March 2016
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Abstract A new, simple, and ligandless ion-pair microextraction method has been developed for preconcentration and determination of cadmium ion in saline solutions and food samples. This technique is based on using a double chain cationic surfactant called didodecyldimethylammonium bromide (DDAB) as an ion-pairing agent and extraction solvent combined with dispersive microextraction named supramolecule aggregate-based dispersive liquid-solid microextraction (SA-DLSME) prior to aspiration to flame atomic absorption spectrometer. The Cd²⁺ ion interacts with chloride ion in saline solution, and the resulting anionic complex is microextracted by cationic supramolecule aggregates of DDAB due to electrostatic interaction. This technique benefits the advantages of supramolecule aggregate properties and dispersive liquid-liquid microextraction technique without the use of any dispersing solvent. Phase separation behavior of DDAB and several effective parameters that have influence on extraction efficiency of cadmium ion such as pH, salt concentration, centrifugation time, and DDAB amount were thoroughly investigated and optimized. Under the optimized experimental conditions, the limit of detection (LOD) and linear range were 1.3 and 5–250 ng mL⁻¹, respectively, with relative standard deviations (RSD) in the range of 3.1–4.3 for interday analysis and 4.5–5.5 for intraday tests at different concentrations of cadmium. The proposed method was successfully applied for the determination of

cadmium ion in real samples, and its accuracy was confirmed by analysis of a certified reference material.

Keywords Didodecyldimethylammonium bromide · Cadmium · Ligandless · Supramolecule aggregate-based dispersive liquid-solid microextraction (SA-DLSME)

Introduction

Cadmium is one of the most hazardous heavy metals to human health. Bioaccumulation of cadmium occurs readily in aquatic and terrestrial food chains, specifically in plants and aquatic organisms, and its compounds with other elements can be potentially toxic to biota at low concentrations. This element can be transferred to animals and humans through the food chain systems. It has been suggested as a carcinogenic compound to humans, and long-term exposure to cadmium has been associated with a wide variety of problems in the kidneys, liver, and lungs (Agency for Toxic Substances and Disease Registry (ATSDR) 1998; Saryan and Zenz 1994). Therefore, determination of trace cadmium in water and food samples is very vital. A variety of analytical techniques such as atomic absorption spectrometry (AAS) (Rivas et al. 2009), inductively coupled plasma atomic emission spectroscopy (ICP-OES) (Cerutti et al. 2003) or mass spectrometry (ICP-MS) (D'Ilio et al. 2008), and voltammetry (Monticelli et al. 2007) have extensively been used for the determination of trace cadmium in different samples. Despite the good sensitivity of the analytical techniques, in many cases, the sensitivity of the analytical instrumentation is not good enough to determine low cadmium levels in a natural sample, and a preconcentration stage is often required.

In analytical procedures, the preconcentration of analytes and the elimination of sample matrix interferences are crucial for trace analysis. Conventional liquid-liquid extraction (LLE)

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and solid-phase extraction (SPE) methods are time-consuming and also require high volume of sample and toxic organic solvents (Sarafraz-Yazdi and Amiri 2010; Fang et al. 2005; Komjarova and Blust 2006; Xie et al. 2008). Therefore, from an analytical viewpoint, the development of miniaturized preconcentration systems was necessary to minimize sample amount and reagent consumption and also waste generation.

The dispersive liquid-liquid microextraction (DLLME) (Rezaee et al. 2006) is one of the most interesting techniques for analysts due to its rapidity, simplicity of operation, low cost, low volume consumption of organic solvents, and high enrichment factor (Anthemidis and Ioannou 2009; Zgoła-Grześkowiak and Grześkowiak 2011). Using this technique, a disperser solvent is used to disperse a water-immiscible extraction solvent into a sample solution which can be a mechanical barrier for analyte transmission into the extraction solvent. Elimination of disperser has been investigated using various techniques, e.g., by the help of a vortex (Chamsaz et al. 2012) or ionic liquids (Zhou et al. 2008).

Recently, an increasing attempt has been made to apply green solvents instead of hazardous organic ones in laboratories. Surfactant aggregates known as supramolecular solvents have some excellent physicochemical properties which can be a great alternative to organic solvents. There are both hydrophilic and hydrophobic parts in the structure of surfactants which provide the possibility of various simultaneous interactions (including dispersive, dipole-dipole and dipole-induced dipole, hydrogen bond, ionic, and π -cation) with analytes. Therefore, they can extract a wide variety of compounds with different polarities. Moreover, multiple polar groups present in supramolecule aggregates of these solvents are ideal for solute binding in the same manner as multiligands. These aggregates are not volatile and, due to their high water content, are inflammable and safer than organic solvents (Ballesteros-Gómez et al. 2010).

Cloud point extraction (CPE) technique (Watanabe and Tanaka 1978) refers to phase transfer of nonionic surfactants from a homogeneous solution to a cloudy system by temperature increasing to a higher point than “cloud point temperature” (CPT) of the surfactant. Despite the good performance of CPE, this technique has limitations to extract thermally unstable compounds when the CPT is high, or maximum extraction efficiencies are obtained in much higher temperatures (Ballesteros-Gómez et al. 2010; Sarafraz Yazdi 2011). This problem is removed using ionic surfactants, and phase separation can be induced by adding common inorganic salts such as NaCl at high concentration (Kwok-Wai Man et al. 2002), an amphiphile with opposite charge (Nan et al. 2005), a co-surfactant such as 1-octanol (Jin et al. 1999), and an amphiphilic counterion (Kumar and Khan 2004), or by inducing pH changes (Jia et al. 2007).

Conventionally, supramolecule aggregates are formed in situ by adding surfactant and other required components in

sample solutions. Organization and phase separation of supramolecular solvents are improved and accelerated by stirring and centrifugation (Caballo et al. 2012). Shemirani et al. has coupled supramolecular solvent-based extraction with DLLME termed supramolecular-based dispersive liquid-liquid microextraction (SM-DLLME) to benefit the advantage of very short extraction time similar to DLLME (Jafarvand and Shemirani 2011a). They used decanoic acid dissolved in tetrahydrofuran (THF) to form reverse micelles of surfactant as a supramolecule which were stable in THF cage. When this solution was dispersed in a sample solution at pH lower than 3.5, water molecules trapped THF and reverse micelles started to aggregate. Consequently, a cloudy solution was formed, and after centrifugation, the supramolecular solvent and the extracted compounds were gathered on top of the solution which could be removed for analysis (Abadi et al. 2013; Jafarvand and Shemirani 2011b). However, there are two restrictions regarding the use of decanoic acid: firstly, the required pH to form the reverse micelles is lower than 3.5 to prevent deprotonating of decanoic acid and a different behavior appears at higher pH values due to the formation of decanoic acid/decanoate vesicles (Moradi and Yamini 2012). Therefore, this surfactant cannot be used in SM-DLLME technique above pH 3.5. Secondly, decanoic acid monomer and its supramolecules (reverse micelles) are not water soluble, and a disperser solvent (THF) is still required to dissolve and disperse them into the sample solution.

In the current study, a green cationic amphiphile (didodecyltrimethylammonium bromide (DDAB)) was used for the first time in the same strategy as SM-DLLME termed supramolecule aggregate-based dispersive liquid-solid microextraction (SA-DLSME) in saline solutions. No disperser solvent was needed for DDAB and good phase separation in the pH range of 1 to 13 was achieved. For assessing the technique, this surfactant was applied as an analytical technique for ion-pair ligandless determination of cadmium ion as a target, in saline solutions and food samples.

Experimental Instrumentation

The Shimadzu model AA-670 atomic absorption spectrometer, equipped with a 100-mm air-acetylene burner head with deuterium background correction and cadmium HCl (Hamamatsu Photonics, Shizuoka, Japan), was used for the determination of cadmium ion concentration in solutions. The wavelength of cadmium HCl was 228.8 nm and operated at 4 mA with a monochromator spectral bandpass of 0.3 nm. A Metrohm 632 pH meter with a glass combined electrode was employed for pH measurements. A vortex Gilson mixer (Villiers Le Bel, France) was applied in order to mix DDAB thoroughly in water. Also, a Centurion Scientific centrifuge

(Model Andreas Hettich D72, Tuttlingen, Germany) was used for phase separation.

Reagents and Samples

All chemical reagents were of analytical grade and all aqueous solutions were prepared using deionized distilled water. For preparing a stock solution of 1000 mg L^{-1} cadmium ion, appropriate amounts of cadmium chloride (Merck, Darmstadt, Germany) were dissolved in 1 % (v/v) HNO_3 , and working standard solutions were prepared by stepwise dilution of the stock standard solution. Sodium diethyldithiocarbamate (NDDC) ($\geq 97\%$), ethanol (99 %), acetonitrile (99 %), methanol (99.8 %), sodium nitrate ($\geq 99\%$), sodium chloride (99.5 %), sodium sulfate (99 %), hydrochloric acid (35 %), and hydrogen peroxide (30 %) were purchased from Merck. Also, didodecyldimethylammonium bromide (98 %) was obtained from Sigma-Aldrich and applied without any further purification. All glasswares were soaked in 10 % HNO_3 for 24 h before use. The pH of the solutions was adjusted by adding 0.1 M sodium hydroxide or hydrochloric acid solutions.

A 5 % (w/v) homogeneous and stable jelly suspension of DDAB in deionized distilled water was prepared by adding appropriate amounts of DDAB in water and stored in a polypropylene tube. The tube was vigorously shaken for about 2 min and then vortexed for 1 min for homogenization. This jelly suspension remained stable at least for 4 weeks.

Water samples including tap water and Caspian Sea water were collected from local sources. After sampling, seawater was filtered through 0.45- μm filter paper for removal of suspended matters. Then, appropriate amounts of NaCl were added to the waters, and after pH adjustment, they were employed for the determination of Cd^{2+} ion concentration according to the present analytical procedure.

A certified reference material was purchased from Waters Company, and the method accuracy was confirmed by determination of its cadmium content according to real water samples.

To prepare food samples, 20 g of milled samples were weighed in a quartz dish and placed in a furnace. The furnace temperature was gradually raised from room temperature to 400 °C and remained at the temperature for 5 h. The dishes were then left to cool down to room temperature, and after the addition of 5 ml of concentrated H_2O_2 , they were heated on a hot plate to dryness. They were placed in a furnace for another 1 h, and after cooling, their contents were dissolved in 10 ml HCl/water (1:1) mixture on a hot plate at 90 °C and filtered using ashless filter paper in 50-mL volumetric flasks and diluted to volumes. These solutions were analyzed according to the proposed procedure for determining their cadmium content.

As cadmium is a volatile element and may be lost at high temperatures, the samples were spiked by enough amounts of Cd and, after preparation, were directly injected into the flame

atomic absorption spectrometer to check the performance of the preparation procedure. Recovery was calculated to be about 95 % (± 3) for the food samples which were considered in the final reported results.

Microextraction Method

Ten milliliters of cadmium ion standard solution or sample solution containing 5 % w/v sodium chloride at pH 9 was poured into a 15-mL centrifuge tube; 500- μL jelly suspension of 5 % w/v DDAB in water was then dispersed into the sample solution using a 2.00-mL syringe and was gently shaken for a few seconds. A cloudy solution of immiscible DDAB aggregates was formed which gradually started to separate out and move toward the top of the solution. The mixture was centrifuged at 4000 rpm for 2 min to accelerate the phase separation. The supramolecule aggregates of the cationic surfactant containing the extracted cadmium anionic complex were collected and formed as a flexible solid layer standing on top of the aqueous phase. The lower aqueous phase was withdrawn by a 10.00-mL syringe, and the remaining solid layer was dissolved in 300- μL ethanol and aspirated to the flame atomic absorption spectrometer for the determination of cadmium ion concentration in the solution.

Results and Discussion

Investigation of the Didodecyldimethylammonium Bromide Phase Separation Behavior

Didodecyldimethylammonium bromide (Fig. 1) is a double chain cationic amphiphile with a packing factor (p) equal to 0.62, and its dominant form at concentrations above the critical aggregation concentration (6.5×10^{-6} % w/v) is lamellar vesicles (Warr et al. 1988). Due to the strong hydrophobicity of alkyl chains, this surfactant is dissolved in water only 0.15 % w/v (3.2 mM) at 25 °C with a bluish isotropic appearance. Above 3 and up to 30 % w/v, a swollen lamellar phase is formed which has a mosaic texture and a gel appearance. In the range of 0.15–3 % w/v, there are two balanced phases (aqueous and lamellar) with similar densities which cannot be separated macroscopically even after ultracentrifugation (Marques et al. 2003; Regev and Khan 1994).

However, when a little amount of inorganic salts such as NaCl, Na_2SO_4 , or NaNO_3 is added into the two phase regions (0.15–3 % w/v), the phase separation could occur after 2 min

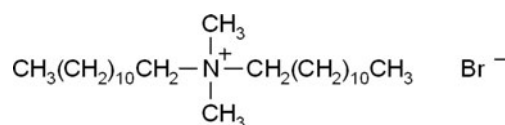


Fig. 1 The structure of didodecyldimethylammonium bromide (DDAB)

of centrifugation at a speed of 4000 rpm due to the salting out effect, and a supramolecule aggregate as a white integrated and flexible solid layer standing on top of the aqueous phase is formed. At a very low percentage of the inorganic salts, longer centrifugation times are required for phase separation, and at very high salt percentage, the phase separation was harder due to electrostatic interactions between the solvated ions with opposite charges of salts and DDAB. The experimental results are shown in Table 1.

The phase separation behavior of DDAB supramolecule aggregates in saline solutions was also investigated at different pH values in the range of 1–13 by adding HCl or NaOH to the solutions. The cationic part of DDAB is a quaternary amine whose charge does not vary with pH changes. Consequently, the phase separation behavior of DDAB is pH independent; this is an advantage for the extraction solvent because the extraction of analytes can be studied at all pH values without any variation in solvent phase separation behavior.

When the stable jelly suspension of 5 % w/v DDAB in water was prepared, an appropriate volume of DDAB could also be dispersed directly into the saline solution using a 2-mL syringe. After centrifugation, as before, the solid layer is separated on top of the aqueous phase and the lower aqueous phase could be removed by a 10-mL syringe. The solid layer was easily dissolved in about 100 μ L ethanol, methanol, or acetonitrile (see Fig. 2 for the steps).

The above strategy can be implemented as a very fast and simple microextraction technique for the preconcentration of organic and inorganic materials, and common toxic solvents in DLLME can be replaced by a green and suitable amphiphilic solvent. In comparison with SM-DLLME, no disperser solvent is used. Moreover, the extraction phase is solid and no solidification or designed centrifuged tubes with narrower aperture is required to remove the extraction phase. This technique is called supramolecule aggregate-based dispersive liquid-solid microextraction, and this was applied to preconcentrate cadmium (II) ion in a saline solution as a practical example of microextraction.

The effects of different factors, e.g., pH, chelating agent, disperser solvent, DDAB amount, NaCl concentration, centrifugation time, and interfering ions on the microextraction process, were thoroughly investigated and optimized. In this study, 300- μ L ethanol was used as a nontoxic solvent to

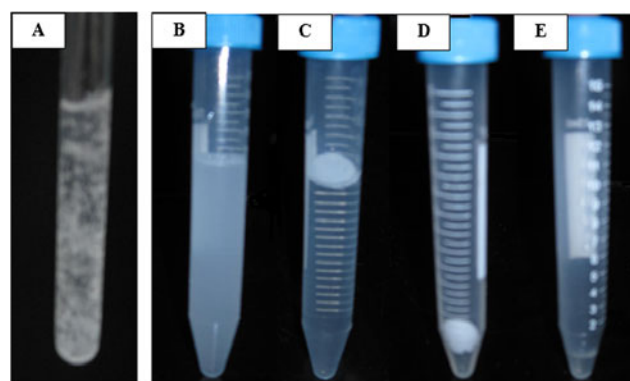


Fig. 2 a The stable jelly suspension of 5 % w/v DDAB in water. b After dispersing 500 μ L of the suspension in 5 % NaCl solution. c After centrifugation for 2 min in 4000 rpm. d After withdrawing the lower aqueous phase. e After dissolving the solid layer in 100 μ L of ethanol

dissolve the extraction phase to reach enough volume for aspiration into flame.

The Effect of NaCl Amount

It is known that cadmium ions in saline solutions containing chloride ions mainly exist in the forms of CdCl_3^- and CdCl_4^{2-} ; thereby, NaCl is selected as an inorganic salt that plays a dual role: (1) formation of anionic complexes with cadmium which can interact with the cationic supramolecule aggregates of DDAB due to electrostatic attraction and, simultaneously, (2) preconcentration of cadmium complexes into the formed solid extraction phase after centrifugation due to its salting out effect, as mentioned above. The effect of NaCl concentration on the extraction process was investigated in the range of 2.5–15 %, and the best results were obtained when NaCl remained between 5 and 12.5 % (Fig. 3).

Moreover, to investigate the impact of other influential inorganic salts on cadmium microextraction, different amounts of Na_2SO_4 and NaNO_3 (up to 15 %), which could have substantial effects on DDAB phase separation behavior, were applied in the presence of 5 % NaCl. No difference was found in the results at concentrations less than 6 % w/v in the solution above this value, the differences were significant, and the recovery was decreased gradually to about 70 % in 10 % Na_2SO_4 and NaNO_3 . However, there was a substantial decrement in recovery to lower than 50 % in 15 % Na_2SO_4 and NaNO_3 .

Table 1 Phase separation behavior of 0.25 % w/v DDAB dispersion in water in different pH values and different percentages of inorganic salts

Inorganic salt	pH of phase separation	Needed salt percentage (% w/v)	Required centrifugation time
NaCl	1–13	2.5–15	2 min
NaNO_3	1–13	2–30	10 min for 2–5, 25–30 % and 2 min for 5–25 %
Na_2SO_4	1–13	1–15	10 min for 1–2 % and 2 min for 5–15 %

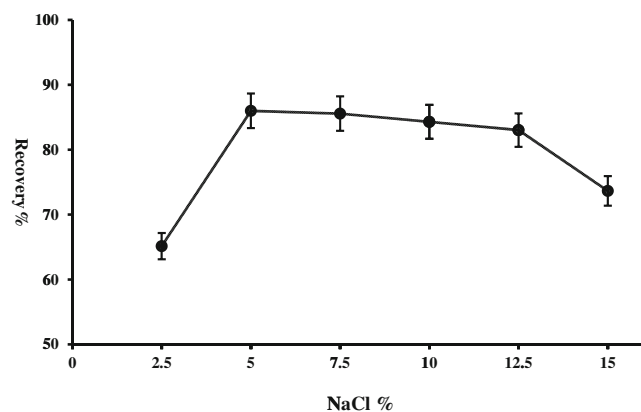


Fig. 3 Impact of NaCl concentration on preconcentration and determination of cadmium ion; conditions: pH=9.0, concentration of cadmium = $50 \mu\text{g L}^{-1}$, volume of 5 % w/v DDAB = 500 μL , and extraction time = 2 min. The experiments were performed in triplicate ($n=3$)

The Effect of DDAB Amount

The DDAB amount is a critical factor in the preconcentration of cadmium ion. The DDAB is a counterion for anionic complexes of cadmium ion; at high concentrations, it has a positive effect on cadmium preconcentration. However, in line with the increase in the amount of DDAB, the volume of the separated phase is also increased which has a negative effect on cadmium enrichment factor. These two inverse effects were investigated by adding different volumes of 5 % w/v DDAB to the saline solutions. The best result was obtained when 500- μL jelly suspension was dispersed into the aqueous phase (Fig. 4). There was about 25-mg DDAB in 500- μL jelly suspension of 5 % w/v DDAB which was dissolved and diluted in 300- μL ethanol for aspiration into FAAS. The final mean volume of the solution for five replications was 380 μL . As a result, the volume of the extraction solvent was 80 μL .

To check our results in the presence of the chelating agent, sodium diethyldithiocarbamate was also tested as a routine ligand for cadmium at all working pH values, and no

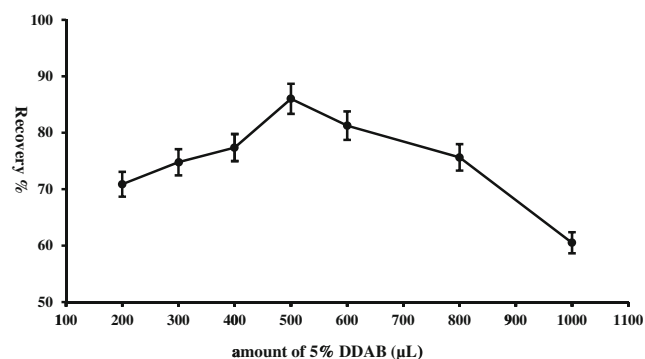


Fig. 4 Impact of the amount of 5 % w/v DDAB on preconcentration and determination of cadmium ion; conditions: pH=9.0, concentration of cadmium = $50 \mu\text{g L}^{-1}$, NaCl percentage = 5 %, and extraction time = 2 min. The experiments were performed in triplicate ($n=3$)

difference in the results was observed. Therefore, we have introduced a ligandless microextraction procedure for the extraction of cadmium ion in saline media.

The Effect of Disperser Solvent

In the conventional DLLME procedure, disperser solvents such as methanol, ethanol, and acetonitrile are required to disperse organic solvents into aqueous solutions. To investigate the effect of the disperser solvents, DDAB was dissolved in them and then injected into the saline solutions. As shown in Fig. 5, the maximum signal was obtained when no disperser solvent was used. This might have occurred due to the direct contact between anionic complexes and cationic amphiphile. Furthermore, the disperser solvent could dissolve some DDAB in the aqueous phase; thus, the separation phase of the cadmium complex-supramolecule aggregate was not completed, and hence, no disperser solvent was used for further studies.

The Effect of pH

In order to investigate the effect of pH, saline solutions of cadmium ion were prepared at different pH values and subjected according to the microextraction procedure. As shown in Fig. 6, changes in pH in the range of 1 to 10 did not change the recovery, but it decreased at higher pH values. As it was mentioned earlier, the DDAB phase separation behavior was not affected by pH change, and consequently, the interaction between cationic amphiphile and anionic complexes was similar in all pH values. Nevertheless, at pH values higher than 10, the cadmium ion is precipitated due to its interaction with hydroxide ion and would not be extracted into the supramolecule aggregates.

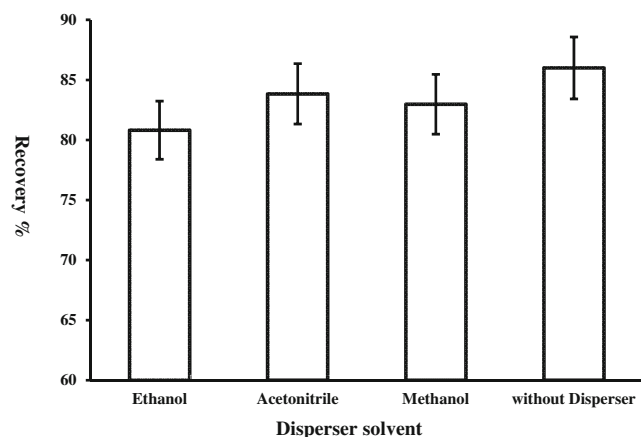


Fig. 5 Impact of disperser solvents. Conditions: pH=9.0, concentration of cadmium = $50 \mu\text{g L}^{-1}$, volume of 5 % w/v DDAB with or without disperser solvent = 500 μL , percentage of NaCl = 5 %, and extraction time = 2 min. Experiments were performed in triplicates ($n=3$)

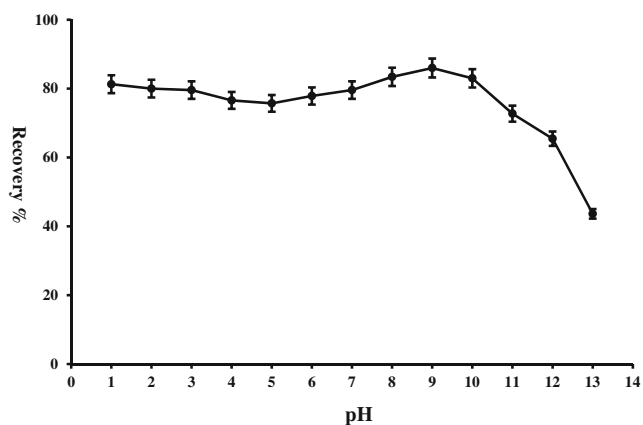


Fig. 6 Impact of pH on preconcentration and determination of cadmium ion. Conditions: concentration of cadmium = $50 \mu\text{g L}^{-1}$, volume of 5 % w/v DDAB solvent = $500 \mu\text{L}$, percentage of NaCl = 5 %, and extraction time = 2 min. Experiments were performed in triplicates ($n=3$)

The Effect of Centrifugation Time

The impact of centrifugation time on cadmium absorbance was studied in the range of 0.5–20 min. The results showed that the phase separation would be completed after 2 min of centrifugation at 4000 rpm. Therefore, 2-min centrifugation time was chosen as the optimum value.

The Effect of Interfering Ions

To examine the selectivity of the proposed method, the effects of different common cations and anions were tested. These were considered as interfering ions when cadmium absorbance changed more than $\pm 5\%$. The obtained results (Table 2) revealed that most of the added ions have no significant interference at the concentration range of 100–1500

Table 2 The effect of different ions on the determination of $50 \mu\text{g L}^{-1}$ of cadmium by the developed method

Interfering ion	Concentration ($\mu\text{g L}^{-1}$)	Recovery (%)
CO_3^{2-}	150,000	84
SO_3^{2-}		83.3
$\text{CH}_3\text{CO}_3^{2-}$		87.4
Sn^{2+}	10,000	82.5
Fe^{3+}		84.5
Cu^{2+}		88.1
Mn^{2+}		89.3
Pb^{2+}		84.8
Zn^{2+}		85
Hg^{2+}		83.7
Ni^{2+}		82.9
Co^{2+}	8000	82.8
NO_2^-	5000	89.6
Fe^{2+}		83.1

times of cadmium amount. The process was performed at pH 9 at which many of the metal ions are precipitated and therefore could not be extracted into the supramolecule aggregates.

Analytical Application

Analytical Figures of Merit

The analytical performance of the developed procedure was evaluated at optimal conditions. The linearity was investigated by the standard addition method at eight concentration levels in the range of 5–250 ng mL^{-1} . The calibration equation and square of correlation coefficient (R^2) are shown in Table 3. This method showed good precision at different concentrations. Moreover, for better validation of the proposed methodology, intraday experiments at different concentrations were also implemented using the obtained results in three consecutive days. The limit of detection (LOD) of the method is 1.3 ng mL^{-1} based on the ratio of signal to noise of 3. The enhancement factor of the method was 37 and the cadmium recovery was equal to 86 % which was considered in the calculation of cadmium amount in the real sample analysis.

Analysis of the Real Samples

In order to evaluate the accuracy of the proposed method, a certified reference material (CRM) of Waters Company (WatR™ Supply Metals), Lot No S198-697, was tested; using three replication analysis, its cadmium content was determined to be $37.9 \pm 2.1 \mu\text{g L}^{-1}$ which was in good agreement with the certified value of $39.8 \pm 2.36 \mu\text{g L}^{-1}$. Moreover, the proposed method was applied to determine cadmium content in tap water, seawater, rice, wheat, and vetch to demonstrate the applicability of this method. The LOD values established

Table 3 Analytical characteristics of the microextraction method for the determination of cadmium

Parameter	Analytical feature		
Linear range ($\mu\text{g L}^{-1}$)	5–250		
Calibration equation	$A = 0.0037C + 0.00188$		
Correlation coefficient (R^2)	0.9984		
Limit of detection ($\mu\text{g L}^{-1}$) (3σ , $n=5$)	1.3		
Enhancement factor	37		
Sample volume (mL)	10		
RSD (%)	Concentrations ($\mu\text{g L}^{-1}$)	Interday (5 replicates)	Intraday (3 days)
	25	4.3	5.5
	50	3.1	4.7
	150	3.2	4.5

Table 4 Determination of cadmium ion in real sample. Results (mean \pm standard deviation based on three replication analysis)

Sample	Spiked ($\mu\text{g L}^{-1}$)	Found ^a ($\mu\text{g L}^{-1}$)	Recovery (%)	RSD (%)
Tap water ^b	0	ND	–	–
	50	52.1 \pm 1.8	104.2	4.5
	100	103.6 \pm 2.6	103.6	3.7
Seawater ^c	0	ND	–	–
	50	50.6 \pm 2.2	101.2	5.2
	100	99.6 \pm 3.2	99.6	4.9
Rice	0	17.2 \pm 1.5	–	7.3
	50	66.2 \pm 2.4	98	5.9
	100	113.3 \pm 3.7	96.1	5.2
Wheat	0	10.7 \pm 1.4	–	9.2
	50	59.2 \pm 2.5	96.8	6.2
	100	106.3 \pm 3.9	95.6	5.5
Vetch	0	21.8 \pm 2.2	–	6.9
	50	69.7 \pm 2.9	95.8	5.4
	100	118.2 \pm 3.9	96.4	4.7

ND not detected

^a After considering the microextraction method recovery (86 %)

^b Obtained from Mashhad City, Iran

^c Obtained from Caspian Sea, Iran

according to the matrixes were equal to 1.3 and 3.25 $\mu\text{g L}^{-1}$ for water and food samples, respectively. The recovery tests were also carried out by spiking the samples with different amounts of cadmium ions.

Approximately, all organic parts of the milled food samples were destroyed to ash on a hot plate and in an electrical furnace. Thus, the sample matrix left no significant impact on cadmium determination. The results presented in Table 4 confirm that this method can be used successfully for the analysis of real samples.

A Comparison Between the Proposed Method and Other Techniques

Table 5 shows a comparison between the performance of SA-DLSME and some other techniques for the determination of Cd^{2+} in solutions. This method has a wide dynamic range with precision and LOD comparable to other methods. However, HF-RLM (Luciano et al. 2010) and SPE (Bianchin et al. 2009) are more expensive and time-consuming than SA-DLSME. The proposed technique has various advantages over DLLME (Rojas et al. 2011), ultrasound (Ma et al. 2009), and vortex-assisted (Chamsaz et al. 2012) LLME methods, and indeed, it does not require any disperser solvent or ultrasound tools for dispersing the extraction solvent. In addition, DDAB is a green solvent compared with CPE (Baliza et al. 2012) and does not require temperature control tools and can be used at room temperature.

Compared to SM-DLLME (Jafarvand and Shemirani 2011c), neither disperser solvent nor glass centrifuge tube with a narrow neck is required. Moreover, the simple preconcentration of cadmium ion without any need for ligand, the possibility of implementing the experiment in a wide range of pH values, and saline solutions are the other excellent properties of this method.

Conclusion

Applying this method, didodecyldimethylammonium bromide stable jelly suspension was used for the first time as a green solvent in combination with dispersive microextraction technique termed SA-DLSME to determine cadmium ion in saline media and some food samples.

This technique does not need a disperser solvent for dispersing DDAB in aqueous solution, and it is possible to have a

Table 5 Comparison of SA-DLSME with others for the determination of cadmium

Method	Sample volume (mL)	LOD ($\mu\text{g L}^{-1}$)	RSD (%)	Dynamic range ($\mu\text{g L}^{-1}$)	Ref
Ultrasound-assisted microextraction	5	0.91	1.6–2.6	10–600	Ma et al. (2009)
Solid-phase extraction-in flow injection system	10	1.7	2.4	5–50	Bianchin et al. (2009)
Hollow fiber renewal liquid membrane procedure	20	1.50	4.0	5–30	Luciano et al. (2010)
Cloud point extraction	7	0.5	3.4	1.7–20	Baliza et al. (2012)
Dispersive liquid-liquid microextraction	10	0.4	1.9–2.7	5–100	Rojas et al. (2011)
Vortex-assisted ionic liquid based liquid-liquid microextraction	25	1.1	4.3	5–150	Chamsaz et al. (2012)
Supramolecular-based dispersive liquid-liquid microextraction	5	0.3	2.5–4.2	5–180	Jafarvand and Shemirani (2011c)
SA-DLSME	10	1.3	3.1	5–250	This work

direct contact between the analyte and extraction solvent for better interaction. Moreover, phase separation behavior of the solvent is the same in a wide range of pH values (1–13); this applicability in all pH values is an excellent attribute for this method. In addition, no ligand was required for interaction with cadmium ions. Other advantages of this technique are fast analysis, low cost, and simplicity of operation.

DDAB aggregates have both hydrophilic and hydrophobic sites for interaction with a wide variety of compounds in solution, and we recommend DDAB to be used as a green solvent instead of routine toxic organic solvent for extraction and preconcentration of organic and inorganic compounds, similar to the strategies employed in the SA-DLSME procedure.

Acknowledgments The authors would like to thank Ferdowsi University of Mashhad for financial support of this work.

Funding This study was funded by Ferdowsi University of Mashhad.

Compliance with Ethical Standards

Conflict of Interest Hadi Kahe, Mahmoud Chamsaz, and Gholam Hossein Rounaghi declare that they have no conflict of interest.

Ethical Approval This article does not contain any studies with human participants or animals performed by any of the authors.

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