Green and Deep Eutectic Solvent Microextraction Method for FAAS Determination of Trace Level Cadmium in Water Samples Using Multivariate Strategic Approach

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INTRODUCTION

Cadmium (Cd) is one of the most toxic and carcinogenic metals which accumulates in different parts of the human body. It has a biological half-life of 10-30 years (1) and the contaminating level of Cd in sea and fresh water is in the range of 70–110 ng L⁻¹ and 2–960 ng L⁻¹, respectively (2), and dissolves easily in water. Even the lowest exposure level of Cd to the environment can become highly toxic to animals, plants, and humans. Cadmium can be easily absorbed in the soil, accumulates in plants and agricultural products, and can create toxic effects on some plant species (3, 4). Since Cd is naturally present in ores together with different metals, volcanic activity is one of the main exposure routes to the environment. It is also an important metal for use in industry with the potential risk of contributing to environmental pollution (5, 6). The metal is used as a stabilizer in PVC products, anti-corrosive mediator, color pigment, in nuclear power plants, and the manufacture of nickel-cadmium batteries. It is also used in phosphate fertilizers. The waste material contains high levels of Cd which can be recycled or dumped and incinerated (7). It was reported that the emission of Cd worldwide reaches 7000 tons/year (1). Cd can also inactivate the antioxidant enzymes, which leads to decreasing their levels in living cells, and can lead to the metabolic disorder of essential trace elements (8, 9). A prolonged

ABSTRACT

An innovative green, deep eutectic solvent microextraction (DES-ME) approach was developed for the preconcentration of trace level cadmium (Cd) in fresh canal and wastewater samples prior to flame atomic absorption spectrometry (FAAS) determination. The Cd was complexed with ammonium pyrolydine dithiocarbamate (APDC) to enhance the extraction capability in the deep eutectic solvent (DES). DES exhibits similar physico-chemical properties of the traditionally used ionic liquids, but is less costly, environmentally friendly, and offers a green alternative to conventional ionic liquid extraction. Separation of the metal-enriched DES from the aqueous medium can be induced by using the Triton X-114 surfactant. The metal-enriched phase was subjected to FAAS using conventional nebulization. The multivariate strategy was applied to estimate the optimum values of the experimental factors for the recovery of metal ions under study. The results showed that the pH, volume mixing ratios of the DES, and their interaction are the most statistically significant variables. Under the optimized experimental conditions, the limit of detection was found to be 0.504 µg L⁻¹ and the enhancement factor was 51. The validity and accuracy of proposed method were checked by the analysis of real water samples using the standard addition method and the TM-28.3 Fortified Water sample. The proposed method was successfully applied to the trace level determination of Cd in canal water and wastewater samples.

intake of Cd may create disturbance in the calcium metabolism in biological systems, which creates adverse effects on the cell structure. It also reduces the action of zinc-assisted enzymes by replacing its active site and is considered a teratogenic and carcinogenic agent (10).

Sample preparation plays an important role with regard to accuracy, precision, sensitivity of an analysis, and the number of steps required in the analytical process, especially when target analytes are present at trace levels (11, 12). The target analytes must be concentrated and separated from the real sample before instrumental analysis (13). The traditional liquid-liquid extraction (LLE), one of the most popular methods for sample preparation, is based on the miscibility of the analytes between the two water-immiscible media (14). However, LLE requires a large amount of solvents which are directly disposed into the environment, thus contributing to environmental problems (15-16).

The new era of modern analytical chemistry is towards miniaturization and an easy sample preparation approach, leading to reduced use of solvents and reagents, thus drastically reducing the disposition of laboratory waste into the environment (17). The use of room temperature ionic liquids (RTILs) is considered a green solvent and replaces conventional organic solvents. RTILs have found an extensive application in many fields, but are used as an extraction solvent in liquid-liquid microextraction (LLME) for the removal of heavy metal ions and other pollutants from different environmental

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samples. Therefore, finding a simple synthetic and greener alternative solvent is of great practical significance (18-22).

A green solvent must contain the characteristics such as availability, low cost, biodegradability, non-toxicity, and easy recyclability. Deep eutectic solvents (DESs) are currently emerging as a green solvent and are considered a new family of ionic fluids. A DES is composed of two or three inexpensive and safe components which self-associate often through hydrogen bonding and form a eutectic mixture with a melting point lower than that of each individual component. DES is a liquid at less than 100 °C. The physico-chemical properties of these solvents are very similar to the traditionally used ionic liquids, but in addition are much less expensive and environmentally friendly. Since the introduction of DES, several papers have been published which highlight the general trends, key points, the outlook for DES development, and application of deep eutectic solvents in the extraction and separation of target compounds (23-27). A number of DESs are prepared by simply mixing and heating organic halide salts such as choline chloride (i.e., inexpensive, biodegradable and non-toxic quaternary ammonium salts) as the hydrogen bond acceptor with urea, organic acids, alcohols, amines or amide as the hydrogen bond donor (HBD). Compared with ILs, DESs can be produced from low cost, non-toxic, totally biodegradable and biocompatible materials and their preparation is very simple. They can be easily prepared from a certain molar ratio of zinc chloride salts and acetamide (as hydrogen-bond donors) by magnetic stirrer bars at 40 °C to form a homogeneous colorless liquid. The synthetic materials used with DES are inexpensive and abundantly available so this solvent could be successfully applied in

large-scale industrial productions (28). These DESs contain large, nonsymmetric ions that have low lattice energy and hence low melting points (29-32).

The aim of this research was to develop a green, deep eutectic solvent extraction method for Cd and to replace the classically used ionic liquid extraction techniques. A mixture of zinc chloride/acetamide was selected as the deep eutectic solvent for enrichment of trace level Cd complexed with ammonium pyrrolidine dithiocarbamate (APDC) from aqueous medium. The DES-ME method was fully characterized through optimization of the relevant variables influencing the extraction of trace levels of Cd. Optimization by using a multivariate strategy is a rigorous and simple method for finding the adequate experimental conditions to produce the best response of the applied procedure.

EXPERIMENTAL

Instrumentation

A PerkinElmer® Model AAnalyst™ 700 (PerkinElmer, Inc., Shelton, CT, USA) atomic absorption spectrometer, equipped with a flame burner, hollow cathode lamps, and an air-acetylene burner, was used for the analysis. A Metrohm 720 pH meter (Göttingen, Germany) was employed for pH adjustments and a Nuve NF 800 model centrifuge (Turkey) was used for centrifugation. The instrumental parameters are listed in Table I. A deuterium lamp and background correction were used.

Chemical Reagents, Standard Solutions, and Glassware

The chemicals used were of analytical reagent grade and all solutions were prepared with ultrapure water. A certified stock standard solution of 1000 µg mL⁻¹ Cd was obtained from E. Merck, Darmstadt, Germany. Working standard solutions were obtained by appropriate dilution of the stock standard solutions before analysis. ZnCl₂ and acetamide were purchased from Sigma, St. Louis, MO, USA, and used as obtained. Ammonium pyrrolidine dithiocarbamate (APDC) was obtained from Sigma, St. Louis, MO, USA and prepared by dissolving an appropriate amount in 10 mL ethanol and diluting to 100 mL with 0.01 mol L⁻¹ acetic acid. The 0.1 mol L⁻¹ acetate and 0.1 mol L⁻¹ borate buffers were used to control the pH of the solutions. The non-ionic surfactant Triton® X-114 was obtained from Sigma, St. Louis, MO, USA. The working standard solutions were obtained by appropriate dilution of the stock standard solutions before analysis. The pH of the samples was adjusted to the desired pH by the addition of 0.1 mol L⁻¹ HCl/NaOH solution to the buffer.

Sample Collection and Pretreatment

The fresh water samples (canal and industrial wastewater) were collected from various sample points in Turkey. All water samples were stored at 4 °C to avoid contamination and to reduce the loss of target analytes before analysis.

TABLE I
FAAS Instrumental Parameters for Cd Determination
Using DES-ME Method

Spectral Bandwidth	Lamp Current	Wavelength	Oxidant (Air)	Gas (Acetylene)
0.7 nm	4 mA	228.8 nm	17.0 L min ⁻¹	2.0 L min ⁻¹

Preparation of Deep Eutectic Solvents

The deep eutectic solvent (DES) was synthesized in different molar ratios of ZnCl_2 and acetamide ($\text{ZnCl}_2/\text{acetamide}$ 1:1, 1:2, and 1:3) by using a stirring apparatus to mix the salt and the hydrogen bond donor. The DES mixture was prepared using a conical flask, then shaken in a stirring apparatus in the range of 200–600 rpm, and kept at 77 °C for a period of 1 hour until a homogenous transparent colorless liquid was formed.

Procedure for DES-ME

For the deep eutectic solvent microextraction (DES-ME) as shown in Figure 1, 15 mL each of the standard and the real sample containing the analyte ($20 \mu\text{g L}^{-1}$) and 400 mL (0.05 to 0.5% v/v) of ammonium pyrrolidine dithiocarbamate (APDC) were used. Then, 200 mL of acetate/ borate buffer was added to adjust the pH with HCl - NaOH ranging from 3–8. Synthesized DES of 200–500 μL was added to the aqueous medium (standard, certified sample, and real samples) as a dispersive and extractive medium to entrap the labile hydrophobic chelate of Cd -APDC. In this extrac-

tion method, 0.5 mL of Triton® X-114 (0.15% v/v) was added to induce phase separation. The contents of the flask were kept in a thermostatic bath at 55 °C for 2–10 minutes. Using different time intervals, the phase separation was accelerated by centrifuging for 5 minutes at 3500 rpm. After cooling in an ice bath, the metal-enriched phase became viscous, and the upper aqueous phase was decanted. To decrease the viscosity of the surfactant-rich phase, 100 mL of acidic ethyl alcohol ($0.1 \text{ Mol L}^{-1} \text{ HNO}_3$) was added and subjected to FAAS. A blank determination was simultaneously carried out in a matrix solution of standards ($0.1 \text{ mol L}^{-1} \text{ HNO}_3$) and samples using the same procedure and measurement conditions.

Optimization Strategy

The optimization process was carried using a Plackett–Burman design design and a central composite design (CCD), respectively. All experiments were performed in duplicates using a $20\text{-}\mu\text{g L}^{-1}$ Cd solution. Six variables, such as volume of DES, mixing ratio of the deep eutectic solvent, pH, surfactant concentration, concentration of complexing reagent, and extraction time were considered as the main factors (Table II). The experimental data were processed by using the Minitab 13.2 (Minitab Inc., State College, PA, USA) and STATISTICA (PA, USA) computer program 2007.

Experimental Design

Preliminary tests were performed to investigate the factors that could influence the extraction efficiency of Cd on the proposed DES-ME method. In this sense, the effect of the volume of the deep eutectic solvent on the efficiency of the proposed method was very important for Cd. The influence of the extraction behavior of Cd was studied from 200 μL to 500 μL . A quantitative recovery (>95%) was

Fig. 1. Graphical representation of the DES-ME method.

TABLE II
Variables and Levels Used for Plackett–Burman Designs
in the Factorial Design

Variables	Symbol	Low (–)	High (+)
DES Volume (μL)	DV	200	500
pH	pH	3	8
Mixing Ratio of DES Solvent (1:1, 1:2, and 1:3)	MR	1	3
Surfactant Concentration (% v/v)	SC	0.1	0.5
Extraction Time (min)	ET	2	12
Concentration of Complexing Reagent (% v/v)	CR	0.05	0.5

obtained at DES values between 250 and 400 μL . In addition, the extraction capability of the pH was obtained at pH 5.5. The mixing ratio of DES (1:2) also showed an important effect on the desired DES-ME method.

Therefore, in order to determine the influence of these factors and their interactions with the system, the Plackett-Burman design (PBD) was applied to screen out the multifactor in order to derive valid and robust statistically significant factors that influence the DES-ME method. The minimum and maximum levels of each factor are listed in (Table III). The merits of the application of the proposed design include reduced time, easy data interpretation, and less ambiguous extraction conditions. Two levels of the Plackett-Burman design with only 12 experiments in place of the $2^5=32$ were applied to estimate the optimum levels of the proposed variables. The analysis of variance (ANOVA) and the p-value were used to evaluate the significance of the effects on the preconcentration system. The main effects and their interactions can be seen in the Pareto chart shown in (Figure 2). The interpretation of the factorial design by the Pareto chart demonstrated that the volume of the deep solvent, pH, and the mixing ratio of the DES were statistically significant at the 95% confidence level.

The Pareto chart was used to screen out the most significant variable, while the remaining significant 3 variables (DES volume, pH, and DES mixing ratio) were optimized by the Central 2^3 star orthogonal composite design. The CCD was performed to optimize the significant variable having 16 new experiments within six degrees of freedom (Table III) and the volume of DES, pH, and mixing ratios of the deep eutectic solvent for the recovery of Cd.

RESULTS AND DISCUSSION

Optimization of Experimental Variables

Six variables were optimized: volume of DES, mixing ratio of DES, pH, surfactant concentration, concentration of complexing reagent, and extraction time to examine the efficiency of the developed procedure. While 20 mL of the sample/standard volume was used throughout the experiments, the analytical response was converted to % recovery by changing a factor value from low level to high level. The proposed design is listed in Table II and the Pareto chart was applied to screen out the standardized effect (Figure 2). Since a minimum *t*-value (95.0%) of 2.2 was obtained, it was concluded that above this value the factor will be highly significant.

Estimated Effects of Variables

The factors such as volume of DES, mixing ratio of DES, pH, surfactant concentration, concentration of complexing reagent, and extraction time were investigated by using the multivariate technique for the proposed DES-ME. It was found that they have a significant

effect on the analytical response of Cd. The results of the Plackett-Burman design are listed in Table III. In experiments 1 and 12, a 98% Cd recovery was achieved at optimum value of the DES volume (DV), pH, and mixing ratios of DES (MR). The combined effect of the above three variables is shown in experiments 15 and 16. The selected levels of surfactant concentration (SC), extraction time (ET), and complexing reagent (CR) did not show a good response at $p=0.315$. The important effects of the desired variable on the extraction capability of the proposed method were observed in the following order of $DV > pH > MR > SC > ET > CR$ as shown in Figure 2.

Final Optimization by Central Composite Designs

The significant variables (DV, pH, and MR) were optimized to achieve the highest extraction capability of Cd and remove the factors (SC, ET, and CR) that were not statistically significantly from the model. The CCD was conducted to optimize the variables (Table IV). The surface response methodology was used to calculate the response

Fig. 2. Pareto chart for the significance of response of the variables: volume of DES (DV), mixing ratio of deep eutectic solvent (MR), pH, surfactant concentration (SC), concentration of complexing reagent (CR), and extraction time (ET).

TABLE III
Plackett–Burman Design for Significant Variable Determination (n=6)

Experiment	(DV)	pH	(MR)	(SC)	(ET)	(CR)	(%) Recovery
1	+	+	+	-	+	-	38
2	+	+	-	+	+	-	30
3	-	+	+	-	+	-	32
4	+	-	+	+	-	+	65
5	+	+	-	+	+	-	28
6	+	+	+	-	+	+	55
7	-	+	+	+	-	+	38
8	-	-	+	+	+	-	27
9	-	-	-	+	+	+	32
10	+	-	-	-	+	-	26
11	-	+	-	-	-	+	24
12	-	-	-	-	-	-	18

DV = DES volume. pH (pH).
MR = mixing ratio of DES.
SC = Surfactant concentration.
ET = Extraction time.
CR = Concetration of complexing reagent.
Low (-) and High (+) values.

TABLE IV
Central 2³+star Orthogonal Composite Design (n = 16)
for DES Volume, pH, and Mixing Ratio of DES

Experiments	DES Volume	pH	Mixing Ratio of DES (MR)	(%) Recovery
1	aDVo	bpHo	cMRo	98.6
2	-	-	-	25
3	+	-	-	32
4	-	+	-	38
5	+	+	-	35
6	-	-	+	24
7	+	-	+	32
8	-	+	+	32
9	+DV1	bpHo	cMRo	43
10	+DV2	bpHo	cMRo	23
11	aEVo	+pH1	cMRo	55
12	aDVo	+pH2	cMRo	10
13	aDVo	+pH2	-MR1	17
14	aDVo	bpHo	+MR1	68
15	+	+	-	26
16	aDVo	bpHo	cMRo	98.8

aDVo, bpHo, and cMRo, where a, b, and c represent variable category a, b, and c.
Low (-) and high (+) values.
DV1 = 0.097. DV2 = 0.60. DVo = 0.35.
pH1 = 1.3. pH2 = 9.7. pHo = 5.5.
MR1 = 0.1. MR2 = 65. MRo = 0.275.
Minimum values = DV1, pH1, MR1,
Maximum values = DV2, pH2, MR2.
Optimum values = DVo, pHo, MRo.

surface between [DV]/[MR] and [pH]/[DV] of Cd (see Figures 3A and 3B). In experiments 1 and 16, at optimized levels of all three variables (aDVo, bpHo, and cMRo), the recovery of Cd was >98%.

After plotting the three-dimensional (3D) response surfaces, a calculation was made by using the quadratic equation. The results indicated that the recoveries were quantitative at 350 µL of DV and at pH 5.5 (see Figure 3A). The DV is the prime advantage, with a significant effect on the proposed method, while on the other side to low volume it creates a negative effect on the proposed method. The pH also plays a key role through the metal-chelate complex formation and subsequent extraction (Figure 3B).

Interferences

Environmentally polluted fresh canal and wastewater contains many coexisting ions which might be responsible for forming stable chelating complexes with APDC and which are co-extracted along with the analyte at the desired pH range. This viable co-extracted condition would influence the chelating degree between Cd and APDC and decrease the extraction efficiency of the proposed method. A series of experiments were designed to investigate the effect of foreign ions. To carry out this study, 25-mL solutions (50 µg L⁻¹) of Cd at different interfering to analyte ratio was subjected to the proposed procedures. The effect of the potential interfering species were tested. Thus, Fe³⁺, Pb²⁺, Cu²⁺, Mn²⁺, Ni²⁺, and Zn²⁺ were tolerated up to 50 mg L⁻¹, and Al³⁺ and Cr³⁺ were tolerated up to 25 mg L⁻¹. Commonly encountered matrix components such as alkali and alkaline earth elements have a negligible effect on the preconcentration of Cd (Na⁺ is tolerated up to 10.000 mg L⁻¹, Ca²⁺ and Mg²⁺ tolerated up to 3.000 mg L⁻¹, Cl⁻ tolerated up to

Fig. 3A. Three dimension (3D) surface response for % recovery of Cd by DES-ME. Interaction b/w [DV]/[MR].

Fig. 3B. Three dimension (3D) surface response for % recovery of Cd by DES-ME. Interaction b/w [pH]/[DV].

30.000 mg L⁻¹, nitrate, sulphate, and phosphate up to 1.000 mg L⁻¹. An ion was considered as interfering when it caused a variation in the absorbance of the analyte greater than 5%. Since the % recovery is greater than 95%, there is no interference of coexisting ions in the natural water samples for the determination of Cd. A high concentration of APDC reagent was added in order to ensure the complete chelation of the analyte, even in the presence of interferents.

Analytical Figures of Merit

The calibration graph using the proposed method at optimum values for Cd was linear at the concentration range of 1.5–50 µg L⁻¹ with a correlation coefficient (r^2) of 0.9948. The limits of detection (LOD) were calculated as the ratio between three times the standard deviation of 10 blank readings, the slope of the calibration curve after preconcentration was found to be 0.504 µg L⁻¹. The enhancement factor of the proposed DES-ME method was 51, which was calculated from the ratio slope of the calibration graph with and without extraction (Table V). The validity of the proposed method was also

TABLE V
Analytical Figures of Merit of the DES-ME Method

Concentration Range	1.5–50 µg L ⁻¹
Slope	1.54×10^{-2}
Intercept	0.00324
R ² (correlation coefficient)	0.9948
LOD ^a	0.504 µg L ⁻¹
LOQ ^b	1.7 µg L ⁻¹
Repeatability (RSD%) ^c (n=10)	4.5 (20 µg L ⁻¹)
Enrichment Factor ^d	51

^a Limit of detection (LOD) = calculated as three times the S.D. (3σ) of the blank signal.

^b Limit of quantification LOQ = calculated as 10 times the S.D. (3σ) of the blank signal.

^c Cd concentration was 20 µg L⁻¹ for which the R.S.D. was obtained.

^d Calculated as the ratio of the slope of the preconcentrated samples to that obtained without preconcentration.

checked by the standard addition method of Cd in a fresh canal and wastewater sample and analysis of the standard reference material TM-28.3 Fortified Water (National Institute of Standards and Technology, Gaithersburg, MD, USA) as shown in Table VII. The recovery was greater than 95%, which confirms the capability and the validity of the proposed method. The analytical features such as enrichment factor, limit of detection, and accuracy were satisfactory and comparable

to other methods reported in the literature (see Table VI) (33–38). The high enrichment factor and low detection limits suggest that the method is efficient and sensitive for the determination of very low concentrations of the Cd ion in various complex samples.

Application

The proposed procedure was optimized and successfully applied for the determination of Cd in 20 fresh canal and wastewater samples

from Tokat, Turkey (see Table VII). The standard addition method was also applied to 20 fresh canal and wastewater samples, and quantitative recovery values were obtained.

CONCLUSION

Application of a two-level full factorial and central composite design allowed the efficient optimization of the variables involved

in the green, deep eutectic solvent microextraction (DES-ME)-based procedure for the preconcentration of Cd in fresh canal and wastewater samples using flame atomic absorption spectrometry (FAAS) detection. The proposed system is simple, rapid, and user-friendly for the determination of Cd in water samples. The DES method exhibits similar physico-chemical properties to the traditionally used ionic liquids,

but is low cost as well as environmentally friendly and a green alternative to using conventional ionic liquid. The high enrichment factor and low detection limits of the present DES-ME method suggest that the method is efficient and sensitive for the determination of Cd ions in various complex samples.

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TABLE VI
Comparative Study for Cd With Previously Reported Methods

Preconcentration Method/Technique	Concentr. Range ($\mu\text{g L}^{-1}$)	RSD (%)	Enhancement Factor	LOD ($\mu\text{g L}^{-1}$)	Reference
SPE / FAAS	1.0–30.0	5.1	50	0.25	(33)
SFO-DME / FAAS	0.08–30	5.4	365	0.0079	(34)
CPE / FAAS	0.003–0.30	1.67	22	0.62	(35)
FI-LLE / FAAS	0.06–6.0	3.2	155	0.02	(36)
USA-EME / FAAS	10–600	2.56	95	0.91	(37)
LLME / FAAS	0.53–157	5.4	28.2	0.16	(38)
DES-ME / FAAS	1.5–50	4.5	51	0.504	Present work

SPE = Solid phase extraction.

SFO-DME = Solidified floating organic drop microextraction.

CPE = Cloud point extraction.

FI-LLE = Flow injection liquid-liquid extraction.

USA-EME = Ultrasound-assisted emulsification microextraction.

LLME = Liquid Liquid microextraction.

DES-ME = Deep eutectic solvent micro extraction.

FAAS = Flame atomic absorption spectrometry.

TABLE VII
Determination of Cd in Real Water Samples Using DES-ME Method (N=4)

SRM	Certified ($\mu\text{g L}^{-1}$)	Measured ($\mu\text{g L}^{-1}$)	Recovery (%)
TM-28.3 Fortified Water	1.91	1.89 $\pm$ 0.10	98.9

Samples	Added ($\mu\text{g L}^{-1}$)	Measured ($\mu\text{g L}^{-1}$)	Recovery (%)
Canal Water	0	12.5 $\pm$ 2.22 ^a	—
	10	22.3 $\pm$ 3.12	98.0
	20	32.0 $\pm$ 3.98	97.5
Wastewater	0	14.2 $\pm$ 2.42	—
	10	23.9 $\pm$ 3.35	97.0
	20	33.5 $\pm$ 3.55	96.5

^a Mean $\pm$ S.D. (n = 3).

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