Original Article

GREEN VORTEX-ASSISTED IONIC LIQUID-BASED DISPERSIVE LIQUID-LIQUID MICROEXTRACTION FOR ENRICHMENT AND DETERMINATION OF CADMIUM AND LEAD IN WATER, VEGETABLES AND TOBACCO SAMPLES

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ABSTRACT

Objective: An eco-friendly, simple and sensitive vortex-assisted ionic liquid-based dispersive liquid-liquid microextraction method (VA-IL-DLLµE) has been proposed to enrich and determine trace levels of cadmium (Cd^{2+}) and lead (Pb^{2+}) ions in water, vegetables and tobacco samples, prior to its FAAS determination.

Methods: The proposed method based on utilization of ionic liquid (IL) (1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate [HMIM][FAP]) as an extraction solvent for both ions after the complexation with 4,5-dihydroxy-3-phenylazo-2,7-naphthalenedisulfonic acid, disodium salt (Chromotrope 2R) at pH 6.5. The impact of different analytical parameters on microextraction efficiency was optimized.

Results: In the ranges of 1.0–300 and 2.0-400 µg/ml, the calibration graphs were linear. The limits of detection were 0.3 and 0.6 µg/ml for Cd^{2+} and Pb^{2+} ions, respectively. The preconcentration factor was 100. The relative standard deviation (RSD %)<3.0%, which indicates the proposed method has high precision.

Conclusion: The proposed VA-IL-DLLµE method was developed and applied for the estimation of Cd^{2+} and Pb^{2+} ion content in various water, vegetables and tobacco samples, and satisfactory results were obtained. The obtained recovery values showed good agreement with the certified values.

Keywords: Cadmium, Lead, Vortex-assisted, Ionic liquid, Microextraction, Water, Vegetables and tobacco samples

INTRODUCTION

In the environment, heavy metals are considered to be hazardous materials due to their toxicity for humans, animals, and plants, even at low concentration levels [1]. Cadmium (Cd^{2+}) and lead (Pb^{2+}) have acute and chronic effects on humans and other living organisms due to their frequent industrial applications. Cd^{2+} and Pb^{2+} can be consumed through eating contaminated food, drinking water or breathing contaminated air. Both elements can cause harmful gastrointestinal, cardiovascular, hematological, renal disease, kidney and reproductive effects. Therefore, the accurate evaluation of trace levels of Cd^{2+} and Pb^{2+} as important heavy metals in environmental samples is a very significant goal for chemists working in the fields of analytical chemistry and environmental analytical chemistry [2-4]. The precise estimation of heavy metals in environmental samples at trace quantities requires the use of modern analytical measurement techniques with low detection limits such as flame atomic absorption spectrometry (FAAS) [5, 6] and spectrophotometry [7, 8]. A separation/enrichment step is necessary prior to the measurements to increase the sensitivity and enhances the accuracy of estimation.

Recently, the development of various analytical methods for the separation and enrichment of trace levels of Cd2+ and Pb2+ was reported in the literature, such as solid-phase extraction [9-13], dispersive liquid-liquid microextraction [14-19], cloud point extraction [20-22], co-precipitation [23-27], and membrane filtration [28].

This enrichment methodology effectively decreases the time duration, toxic solvent use and cost. Various instrumental methods such as electrothermal, electro-analytical, inductive coupled plasma joined with optical mass, flame atomic absorption spectroscopy and emission spectrometry are applicable to quantitatively analyze the toxic metals in different environmental samples as well as biological samples [29]. Flame atomic absorption spectroscopy is commonly applicable to use with the above-mentioned techniques to analyze toxic heavy metals

because of its capability to determine a very low level of metal ions with simple operating ability and low-cost applicability [30-32]. A simple FAAS has enhanced efficiency in term of calibration, accuracy, detection limit and results of the method couple with an enrichment step before the determination [33].

In developing countries, attentiveness of the public health impact due to exposure of toxic heavy metals is increasing; however, few of among these countries have introduced policies and regulations for significantly skirmishing the problems. To assess the toxic metal effect on environmental influence and human beings, measurement of Cd^{2+} and Pb^{2+} ion concentration in environmental samples done by using a highly sensitive or selective preconcentration method are extensively considered for the deliberation in recent years [34].

Dispersive liquid-liquid microextraction (DLLµE) is the most important and widespread method for the separation and preconcentration of trace quantities of different metal ions in environmental and biological samples with complex matrices because of its notable advantages, such as speed, simplicity, low cost, and environmentally-friendly and high enrichment factors.

The aim of the proposed work was to develop green and new VA-IL-DLLµE procedure in combination with FAAS for the enrichment and accurate determination of trace quantities of Cd^{2+} and Pb^{2+} ions in water, vegetables and tobacco samples. In the proposed technique, hydrophobic IL, (1-hexyl-3-methylimidazolium tris (penta-fluoroethyl) trifluoro-phosphate [HMIM] [FAP]) as an extraction solvent and 4,5-dihydroxy-3-phenylazo-2,7-naphthalenedisulfonic acid, disodium salt (chromotrope 2R) as a complexing agent were selected for the formation of the metal complex at a desirable pH. Vortex-assisted was utilized to accelerate the separation and preconcentration step. Different parameters such as (pH, ligand concentration, the volume of IL, sample volume, vortex time, temperature, disperser solvent, and matrix effect) were systematically evaluated. The method validity was examined by the

analysis of certified reference materials. The new method has been developed to estimate concentrations of Cd^{2+} and Pb^{2+} ions in water, vegetables and tobacco samples with satisfactory results.

MATERIALS AND METHODS

Instruments

Agilent 55B AA spectrometer (Agilent Technologies Inc., Santa Clara, USA) equipped with a burner for an air-acetylene flame and a hollow cathode lamp of cadmium (228.8 nm) and lead (283.2 nm) were utilized to determine the analyte metals. The instrumental conditions were set in accordance with the instructions of the manufacturer. Microinjection method was utilized to introduce the sample to the nebulizer of the FAAS.

An AD1000 pH-meter (Adwa instruments Kft., Szeged, Hungary) was utilized to measure the pH-values of prepared buffer solutions. A centrifuge (Isolab, GmbH, Germany) was utilized to accelerate the separation of analyte from the sample solution. Vortex mixer (i S wix VT, Neuation Technologies Pvt. Ltd., India) was used to mix the sample solutions thoroughly and to assist the extraction of analyte from sample matrices. Milli-Q was utilized to obtain deionized/bidistilled water (Millipore, USA). Glassware's were kept in diluted HNO_3 (1:9 v/v) solution overnight, rinsed and cleaned many times with bidistilled water prior to use.

Chemicals and reagents

The chemicals and reagents used were obtained from Merck Co. (Darmstadt, Germany) and Sigma Aldrich (St. Louis, USA) companies. High-quality (65% v/v) HNO_3, (37% v/v) HCl and (25% v/v) NH_4OH solutions were used. Stock solutions (1000 µg/ml) of the studied Cd^{2+} and Pb^{2+} ions were prepared from nitrate salts of high purity (Fluka Chemie AG, Basel, Switzerland). Diluted standard solutions were prepared by appropriate dilution of aliquots of the standard stock solutions daily with HNO_3 (1.0 mol/l). A 0.2% (w/v) solution of chromotrope 2R was obtained by dissolving the proper weight of chromotrope 2R (Fluka Chemie AG, Basel, Switzerland) in bidistilled water. The IL, [HMIM] [FAP] (Sigma Aldrich St. Louis, USA), was selected as the extraction solvent. Triton X-114 (Sigma–Aldrich, USA), carbon tetrachloride (CCl₄), acetonitrile, tetrahydrofuran (THF), ethanol and methanol were inspected as dispersive solvents. Aqueous solution of Triton X-114 (0.05%, v/v) was prepared by dissolving 0.05 ml of Triton X-114 in 100 ml of bidistilled water in 100 ml volumetric flask with stirring. The pH values were adjusted using buffer solutions prepared according to the literature studies [35]. TMDA 51.3 and TMDA 53.3 fortified water (National Water Research Institute, Environment Canada, Burlington, Canada) and spinach leaves (SRM 1570A) (National Institute of Standard Technology, Gaithersburg, MD, USA) were utilized as certified reference materials to test the accuracy of the developed method.

Preconcentration VA-IL-DLLµE procedure

Aliquots of 25 ml of a sample solution containing 1.0-300 µg/l of Cd^{2+} or 2.0-400 µg/l of Pb^{2+} were placed in a conical-bottom glass centrifuge tube (50 ml) and mixed with 5.0 ml of phosphate buffer solution (pH 6.5). Subsequently, chromatrope 2R (0.2%, w/v) (2.0 ml), 200 µl of [HMIM][FAP] (extractant solvent) and 400 µl of Triton X-114 (0.05%, v/v) (disperser solvent) were added, respectively. Then the solution was completed to the mark with deionized water. After that, the tubes were stirred using a vortex mixer for 60 sec at 3000 rpm to complete dissolution of the IL The tubes were taken away and obscure in an ice bath for 5.0 min, and the cloudy turbid solution was formed. To speed up phase separation, the solution was centrifuged at 4000 rpm for 5.0 min. The IL-phase was subsequently sedimented at the bottom of the tube. Using a syringe, the aqueous phase was rejected. Finally, the remaining IL phase was diluted using acidic ethanol to 500 µl and aspirated into the conventional nebulizer of the FAAS using a microinjection system to estimate the concentrations of Cd^{2+} and Pb^{2+} ions in the final eluent solution.

Method validation

All the methods were validated as per ICH guidelines for parameters like linearity, the limit of detection and limit of quantification,

accuracy and precision by International Conference on Harmonization (ICH) guidelines [36].

Linearity

For linearity study, solutions at different concentrations were prepared using six different aliquots of the analyte, and the obtained data were used for the linearity calibration plot.

Limit of detection and limit of quantification

The limits of detection (LOD) and quantification (LOQ) were calculated using the following Eqn. 1 and Eqn. 2.

$$LOD = 3s/k \text{ Eqn ..... 1.}$$

$$LOQ = 10\,s/k \text{ Eqn ..... 2.}$$

Where, s is the standard deviation of ten replicate determinations values of the reagent blank and k is the slope of the calibration graph

Accuracy and precision

The accuracy studies were carried out by the analysis of Cd^{2+} and Pb^{2+} concentrations in certified reference materials (TMDA-51.3 fortified water, TMDA-53.3 fortified water, and spinach leaves SRM 1570a) and also by applying the standard addition method at different concentrations by spiking a known concentration of the standard analyte to the pre-analyzed sample and contents were reanalyzed by the developed method. Intra-day and inter-day precision were studied by analyzing three replicates of sample solutions.

Applications to real samples

Water samples

The proposed procedure was successfully applied to water samples (tap, mineral, well, sea, and wastewater" acquired from Egypt and stored in polyethylene bottles. All water samples are filtered through a cellulose membrane filter of 0.45-µm pore size (Millipore Corporation, Bedford, MA, USA) to eliminate hanging materials before being acidified with diluted HNO_3 and stored at 4 °C. To oxidize the organic content of water samples, H_2O_2 (1.0 % v/v) and HNO_3 (65 % m/m) were utilized. The same preconcentration VA-IL-DLLµE technique has been used to the CRM (TMDA-51.3 and TMDA 53.3 fortified water). The concentrations of Cd^{2+} and Pb^{2+} ions were evaluated by FAAS.

Vegetables and tobacco samples

The different vegetables (parsley, Mint, tomato, onion, potato, spinach, and cabbage) and tobacco samples were gained from local supermarkets of Egypt. For 24 h in an electric oven, the food samples are dried at 80 °C and homogenized by grinding in an agate mortar. For a wet acid digestion procedure, SRM 1570A spinach leaves, vegetable and tobacco samples (0.3 g) were treated with 5.0 ml of a mixture of concentrated HNO_3–H_2O_2 (2:1, v/v) into a beaker and kept at room temperature for 10 min, then heated on an electric hot plate until semi-dried mass was obtained. The digested semi-mass samples were dissolved in 10 ml of deionized water and filtered through a cellulose membrane filter of 0.45-µm pore size [37]. Then, the developed VA-IL-DLLµE procedure was satisfactorily applied to the samples. The concentrations of Cd^{2+} and Pb^{2+} ions in final solutions were determined using FAAS.

RESULTS AND DISCUSSION

Optimization of analytical, experimental conditions

In the present work, the preconcentration of trace quantities of Cd^{2+} and Pb^{2+} ions after chelation with chromotrope 2R was developed. To achieve high enrichment factors and recovery of both Cd^{2+} and Pb^{2+} ions, the following variables need to be optimized: pH, chelating agent concentration, the volume of IL and disperser solvent, sample volume, vortex time, centrifugation time and rate, and matrix effect.

Effect of pH

The pH has a crucial impact on the extraction yield and the formation of the metal-chelate complex [11, 12, 37]. Consequently, the influence of pH on the VA-IL-DLPµE microextraction technique

of Cd^{2+} or Pb^{2+}-chromotrope 2R complex was studied at a pH range of 3.0-10. At pH 6.0-7.0 with phosphate buffer solution as illustrated in fig. 1, the extraction recovery of Cd^{2+} or Pb^{2+} increased with

increasing pH and maximum quantitative values are accomplished. In subsequent studies, 5.0 ml of phosphate buffer solution (pH 6.5) was chosen.
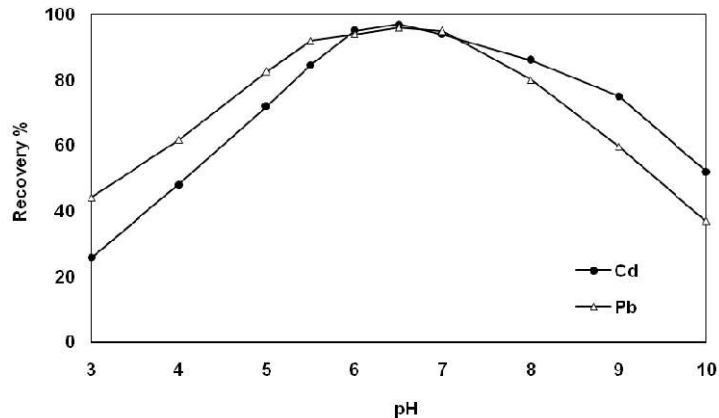

Fig. 1: Effect of pH on the recovery % of Cd^{2+} or Pb^{2+} through VA-IL-DLLµE method: Conditions: (Cd^{2+} or Pb^{2+} concentration, 300 µg/l; concentration of chromotrope 2R, (0.2%, w/v); [HMIM][FAP] volume, 200 µl; vortex time, 60 sec; Triton X-114 volume, 400 µl; the sample volume, 50 ml)

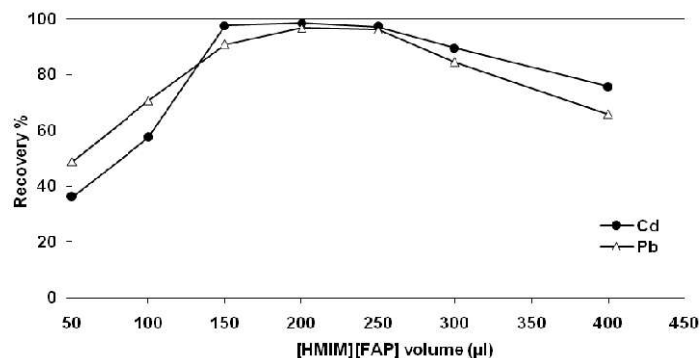**Effect of amount of chromotrope 2R**

The chromotrope 2R amount of has an important influence on the extraction recovery of Cd^{2+} and Pb^{2+} ions to give quantitative results. Various concentrations of chromotrope 2R were examined within the range of 0.05-0.5% (w/v) and results curvature is shown in fig.

2. The recovery was increased by increasing the chromotrope 2R concentration up to (0.2 %, w/v) and higher amounts of chromotrope 2R have no significant effect in the extraction recovery. Therefore, 0.2 % (w/v) of chromotrope 2R was utilized as the optimum amount for total complexation and maximum extraction recovery in further studies.
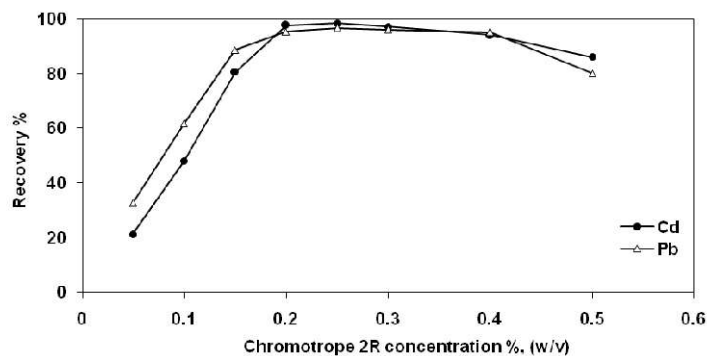
Fig. 2: Effect of the chromotrope 2R concentration on the Cd^{2+} and Pb^{2+} preconcentration using VA-IL-DLLµE method. Conditions: (Cd^{2+} or Pb^{2+} concentration, 300 µg/l; pH 6.5; [HMIM][FAP] volume, 200 µl; vortex time, 60 sec; Triton X-114 volume, 400 µl; sample volume, 50 ml)

Fig. 3: Effect of the IL volume on the Cd^{2+} and Pb^{2+} preconcentration using VA-IL-DLLµE method. Conditions: (Cd^{2+} or Pb^{2+} concentration, 300 µg/l; pH 6.5; concentration of chromotrope 2R, (0.2%, w/v); vortex time, 60 sec; Triton X-114 volume, 400 µl; sample volume, 50 ml)

Effect of ionic liquid

In the microextraction technique, the choice of the type and volume of ionic liquid was important, which has a large influence on the Cd^{2+} and Pb^{2+} extraction efficiency. In the present work, [HMIM] [FAP] was selected as the extraction solvent. This IL has some characteristics such as its good thermal stability, hydrophobicity and negligible vapor pressure. Consequently, the volume of IL was studied in the range of 50-400 µl, (fig. 3). The extraction competence of Cd^{2+} or Pb^{2+} was enhanced with IL volume in the range of 150-250 µl were used. At higher volume, no significant change in recovery was obtained. Hence, 200 µl of IL was chosen as an optimum volume for all the subsequent studies and to get a better enrichment factor.

Effect of dispersive solvent type and volume

In the microextraction technique, the choice of dispersive solvent is a significant parameter to form dispersed fine droplets of IL because of it must be miscible in both the aqueous and the IL phases. So, various dispersive solvents like (methanol, ethanol, acetonitrile,

nonionic surfactant Triton X-114 (0.05% v/v), and THF) were utilized. The high recovery and the best analytical signal were observed using Triton X-114 was as the dispersive solvent. The effect of Triton X-114 (0.05% v/v) volume of the analytical signal of Cd^{2+} or Pb^{2+} was tested in the range of 50–600 µl. In subsequent studies, the suitable volume of Triton X-114 (0.05%, v/v) (400 µl) was selected as optimal and provided the highest extraction efficiency.

Effect of sample volume

The Cd^{2+} or Pb^{2+} solution volume of is an important factor for achieving a high enrichment factor and maximum recoveries based on the VA-IL-DLLµE procedure. The sample volume effect was investigated using (5.0–100 ml) model solutions (fig. 4). Higher than 50 ml, Cd^{2+} or Pb^{2+} ion recoveries were not quantitative. Hence, Cd^{2+} or Pb^{2+} solution (50 ml) was chosen as the highest sample volume in all the subsequent studies. The preconcentration factor (PF) has been described as the sample volume ratio to the final dilute volume of IL phase (0.5 ml). Therefore, PF was attained as 100.
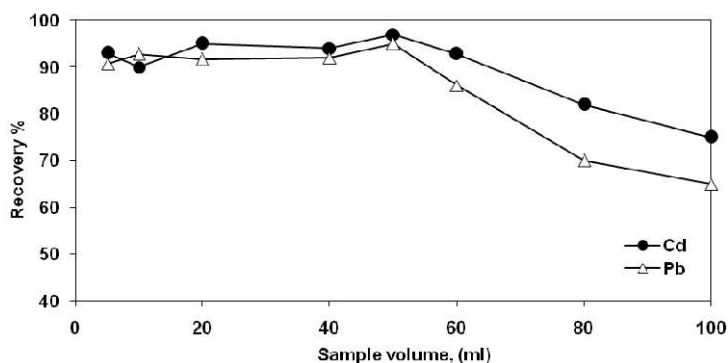

Fig. 4: Effect of sample volume on the Cd^{2+} or Pb^{2+} preconcentration using VA-IL-DLLµE method. Conditions: (Cd^{2+} or Pb^{2+} concentration, 300 µg/l; pH 6.5; concentration of chromotrope 2R, (0.2%, w/v); [HMIM][FAP] volume, 200 µl; vortex time, 60 sec; Triton X-114 volume, 400 µl; N = 3.0)

Effect of vortex time

In the microextraction technique, vortex time has a significant effect on the dispersion of IL phase into the aqueous phase and improves the extraction efficiency. The impact of vortex time was investigated

between 10-120 sec at a constant rate 3000 rpm (fig. 5). The results indicate that the extraction efficiency was increased up to 60 sec. After this time, no significant improvement in analytical signals was obtained. As a result, 60 sec was chosen as the optimum vortex time, which was adequate to fully dissolve the IL in the aqueous phase.
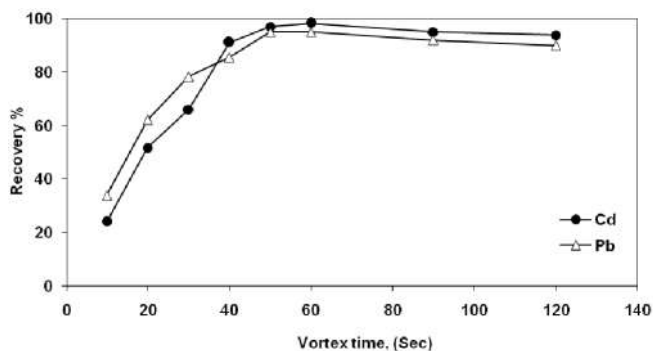

Fig. 5: Effect of vortex time on the Cd^{2+} or Pb^{2+} preconcentration using VA-IL-DLLµE method. Conditions: (Cd^{2+} or Pb^{2+} concentration, 300 µg/l; pH 6.5; concentration of chromotrope 2R, (0.2%, w/v); [HMIM][FAP] volume, 200 µl; Triton X-114 volume, 400 µl; sample volume, 50 ml)

Effect of centrifugation conditions

Centrifuge rate and time have an important impact on the separation of IL and an aqueous phase. The centrifugation rate was tested in the range 1000 and 5000 rpm. The centrifugation rate was increased up to 4000 rpm, which was chosen as the optimum rate. Also, the centrifugation time effect on the analytical signals was evaluated between 2.0 and 20 min. The maximum recovery was obtained at 5.0

min to ensure complete phase separation. When the centrifugation time was up to 5.0 min. So, 4000 rpm and 5.0 min were chosen as optimum centrifuge rates and time, respectively, for further studies.

Effect of matrix ions

The possible effect of the commonly present matrix constituents on the preconcentration and determination of the Cd^{2+} and Pb^{2+} ions in

different real samples were examined. The results obtained are shown in table 1. The tolerance limit is defined as the highest quantity of interfering ions, creating a relative error ≤±5 %. An advantage of this method was that the Cd^{2+} and Pb^{2+} ions recovered from the multi-element real samples were quantitative (>95%) at

the level of tolerance provided in table 1. No obvious interference effect of matrix ions was observed in the determination of Cd^{2+} and Pb^{2+} ions under the experimental conditions, which confirm the applicability of the VA-IL-DLLµE method for Cd^{2+} and Pb^{2+} determination in various real samples.

Table 1: Influence of various coexisting matrix ions on the recovery of Cd^{2+} and Pb^{2+} ions using the proposed VA-IL-DLLµE method.

Ions	Added as	Concentration (mg/l)	Recovery (%)[a]	
			Cd^{2+}	Pb^{2+}
Na^+	NaCl	4000	96.0±2.0	96.0±1.0
K^+	KCl	4000	97.0±1.0	98.0±3.0
Ca^{2+}	$CaCl_2$	2000	99.0±2.0	95.0±2.0
Mg^{2+}	$MgCl_2$	2000	98.0±2.0	98.0±2.0
Cl^-	KCl	4000	97.0±2.0	95.0±2.0
SO_4^{2-}	Na_2SO_4	2000	97.0±1.0	96.0±3.0
NO_3^-	$NaNO_3$	2000	100.0±3.0	97.0±3.0
Al^{3+}	$Al(NO_3)_3.9H_2O$	500	97.0±1.0	98.0±1.0
Fe^{3+}	$FeCl_3$	500	98.0±3.0	99.0±2.0
Mn^{2+}	$MnSO_4. H_2O$	400	99.0±2.0	95.0±3.0
Cr^{3+}	$Cr(NO_3)_3.9H_2O$	400	95.0±2.0	98.0±2.0
Co^{2+}	$Co(NO_3)_2.6H_2O$	200	98.0±3.0	95.0±2.0
Cu^{2+}	$Cu(NO_3)_2.3H_2O$	150	100.0±2.0	97.0±3.0
Ni^{2+}	$Ni(NO_3)_2.6H_2O$	100	96.0±3.0	98.0±2.0
Zn^{2+}	$Zn(NO_3)_2.6H_2O$	100	95.0±2.0	98.0±3.0

[a]mean±standard deviation (N=3.0).

Analytical features of the proposed method

Using the optimized experimental conditions described above, a satisfactory linear relationship was obtained in the range of 1.0-300 and 2.0-400 µg/l for Cd^{2+} and Pb^{2+}, respectively, with the following linear regression equation, $A = 5.0 \times 10^{-4}C+1.0 \times 10^{-3}$ and $A = 5.0 \times 10^{-4}C+5.0 \times 10^{-4}$ with a correlation coefficient ($r^2= 0.9997$ and 0.9994, n=5) for Cd^{2+} and Pb^{2+}, respectively, where A is the absorbance and C is the Cd^{2+} concentration (µg/l). The LOD were 0.3 and 0.6 µg/l and LOQ were 1.0 and 2.0 µg/l, respectively for Cd^{2+} and Pb^{2+}, respectively. The lower detection limit of the present VA-IL-DLLµE method indicates high sensitivity and suggests its efficient application for the determination of very low concentrations of Cd^{2+} and Pb^{2+} in water, vegetables and tobacco samples. The performance of the proposed VA-IL-DLLµE procedure was assessed by calculating two parameters, including; the enrichment factor (EF) and the consumptive index (CI). The enrichment factor (EF), defined as the ratio between the calibration graph slopes with and without

preconcentration procedure (EF= 25 and 17 for Cd^{2+} and Pb^{2+}, respectively). The consumptive index (CI) was determined using the expression CI = Vs/EF, where Vs is the analyte solution volume and CI are 1.0 and 1.47 for Cd^{2+} and Pb^{2+}, respectively.

Validation studies

Additionally, the applicability of the developed VA-IL-DLLµE method was checked and validated for the estimation of Cd^{2+} and Pb^{2+} concentrations in certified reference materials (TMDA-51.3 fortified water, TMDA-53.3 fortified water, and spinach leaves SRM 1570a). Also, by applying the standard addition method at three concentrations. The resulting concordant values of recoveries levels derived from the method developed were in good agreement with the CRMs certified values (table 2). The application of the proposed method to the real samples and CRMs show that this method is highly accurate and reliable, is free of interference and validates the estimation of Cd^{2+} and Pb^{2+} ions at trace levels in real samples (table 2).

Table 2: The analysis results for certified reference materials after the application of the proposed VA-IL-DLLµE procedure

Certified reference materials	Cd^{2+}				Pb^{2+}			
	Certified value (µg/l)	Found [a] (µg/l)	RSD (%)	Recovery (%)	Certified value(µg/l)	Found [a] (µg/l)	RSD (%)	Recovery (%)
TMDA-53.3 fortified water	118	113±1.70	1.50	95.76	350	340±3.20	0.94	97.14
TMDA-51.3 fortified water	25.8	25.03±0.30	1.20	97.0	73.3	70.0±0.80	1.14	95.50
	(µg/g)	(µg/g)						
NIST 1570a Spinach Leaves	2.89±0.07	2.75±0.10	3.64	95.20	-	<LOD[b]	-	-

[a]mean±standard deviation based on three replicate determinations (N=3.0). [b]LOD: limit of detection.

Another study for validation of the proposed method, recovery check for spiked samples, was performed intra-day and inter-day analysis. Five duplicate extractions and analysis of three concentrations of Cd^{2+} and Pb^{2+} solutions (100, 200 and 300 µg/l) was performed on the same day to assess the RSD% for the intra-day precision. Furthermore, for analyzing the same Cd^{2+} and Pb^{2+} concentrations, the precision (as RSD%) for inter-day analysis was determined by extractions on five consecutive days. The RSD% ranged from 1.39-2.87% and 1.70-2.50% (Cd^{2+}) and from 1.26-2.14% and 1.44-1.94% (Pb^{2+}) for intra-day and inter-day precisions, respectively. The method's reliability (as recovery %) was reached in the range of 95.0–97.50% and 95.0–98.0% for Cd^{2+} and Pb^{2+}, respectively (table 3).

Analytical applications

The potential application of the developed VA-IL-DLLµE preconcentration method for the identify and separate of Cd^{2+} and Pb^{2+} ions in in real environmental water (tap, mineral, well, sea and wastewater), different real acid digested samples, including vegetables (parsley, Mint, tomato, onion, potato, spinach, and cabbage) samples and tobacco samples were tested. The sample solutions were spiked with known quantities of Cd^{2+} and Pb^{2+} ions using the standard addition method to verify the reliability and accuracy of the developmental process. Tables 4 and 5 shows the percentage of the analyte recovered from the real spiked sample

and the RSD%. The quantitative recoveries for the Cd^{2+} and Pb^{2+} analytes were great, in the range of 95.0–100 % for Cd^{2+} or Pb^{2+} with RSD<3.0 %. Such results show that the approach is accurate and could, therefore, be used into separate, preconcentrate and evaluate trace amounts of Cd^{2+} and Pb^{2+} in water, vegetables and tobacco samples.

Table 3: The reproducibility and repeatability for the replicate measurements of Cd^{2+} and Pb^{2+} in quality control samples spiked with 100, 200, and 300 μg/l (*N=3*)

Spiked level (μg/l)	Intra-day precision (repeatability)			Inter-day precision (reproducibility)		
	Found±SD[a]	Recovery[b] (%)	RSD (%)	Found±SD[a]	Recovery[b] (%)	RSD (%)
Cd2+						
100	97.50±2.80	97.50	2.87	96.0±2.40	96.0	2.50
200	190.0±3.70	95.0	1.95	194.0±3.30	97.0	1.70
300	288.0±4.0	96.0	1.39	290.0±5.0	96.70	1.72
Pb²⁺						
100	98.0±2.10	98.0	2.14	95.0±1.80	95.0	1.89
200	192.0±3.0	96.0	1.56	196.0±3.80	98.0	1.94
300	285.0±3.60	95.0	1.26	292.0±4.20	97.30	1.44

[a]Mean value±standard deviation (N=3.0). [b]Recovery% =[Observed value of analyte/Expected value of analyte] × 100

Table 4: The results for the standard addiction-recovery method for the preconcentration of Cd^{2+} and Pb^{2+} ions in water samples using the proposed VA-IL-DLLμE method

Samples	Added (μg/l)	Cd^{2+}			Pb^{2+}		
		Found[a]±SD (μg/l)	Recovery [b] (%)	RSD%	Found[a]±SD (μg/l)	Recovery [b] (%)	RSD%
Tape water	-	<LOD[c]	-	-	<LOD[c]	-	-
	100	96.0±0.71	96.0	0.74	98.0±1.35	98.0	1.38
	200	190.0±2.40	95.0	1.26	195.0±3.80	97.50	1.95
Mineral water	-	<LOD[c]	-	-	<LOD[c]	-	-
	100	99.0±0.87	99.0	0.88	95.50±1.10	95.50	1.15
	200	192.0±4.20	96.0	2.14	196.0±4.60	98.0	2.35
Well water	-	3.60±0.11	-	-	<LOD[c]	-	-
	100	99.50±1.30	96.05	1.30	97.0±1.50	97.0	1.55
	200	197.0±3.70	96.76	1.88	190.0±4.10	95.0	2.16
Sea water	-	23.0±0.70	-	-	16.0±0.48	-	-
	100	118.0±1.80	96.0	1.53	111.0±2.50	95.70	2.25
	200	220.0±3.80	98.65	1.73	216.0±5.50	100.0	2.55
Wastewater	-	18.0±0.60	-	-	9.0±0.30	-	-
	100	113.0±2.30	95.75	2.04	107.0±1.95	98.17	1.82
	200	216.0±5.80	99.0	2.69	205.0±4.90	98.0	2.39

[a]mean±standard deviation (N=3.0). [b]Recovery% =[Observed value of analyte/Expected value of analyte] × 100, [c]LOD: limit of detection.

Table 5: The results for the standard addition-recovery method for the preconcentration of Cd^{2+} and Pb^{2+} ions in vegetables and tobacco samples using the proposed VA-IL-DLLμE method

Samples	Added (μg/g)	Cd^{2+}			Pb^{2+}		
		Found[a]±SD (μg/g)	Recovery[b] (%)	RSD%	Found[a]±SD (μg/g)	Recovery[b] (%)	RSD%
Parsley	0	4.0±0.21	-	-	<LOD[c]	-	
	100	102.0±1.70	98.0	1.67	95.0±2.60	95.0	2.74
	200	198.0±4.10	97.0	2.07	196.0±4.60	98.0	2.35
Mint	0	<LOD[c]	-		<LOD[c]	-	
	100	96.50±1.50	96.5	1.55	98.50±1.40	98.50	1.42
	200	190.0±3.80	95.0	2.0	194.0±4.50	97.0	2.32
Tomato	0	<LOD[c]	-	-	<LOD[c]	-	-
	100	100.0±1.20	100.0	1.20	95.70±1.50	95.70	1.57
	200	196.0±2.70	98.0	1.38	198.0±3.50	99.0	1.77
Onion	0	<LOD[c]	-	-	<LOD[c]	-	-
	100	96.80±1.90	96.80	1.96	98.0±2.50	98.0	2.55
	200	195.0±2.20	97.50	1.13	200.0±4.60	100.0	2.30
Potato	0	<LOD[c]	-	-	<LOD[c]	-	-
	100	98.0±1.30	98.0	1.33	96.0±1.80	96.0	1.88
	200	191.0±3.30	95.60	1.73	194.0±4.20	97.0	2.16
Spinach	0	<LOD[c]		-	<LOD[c]	-	-
	100	99.0±0.90	99.0	0.91	95.80±1.40	95.80	1.46
	200	195.0±5.10	97.50	2.62	196.0±4.10	98.0	2.09
Cabbage	0	<LOD[c]		-	<LOD[c]	-	-
	100	96.40±1.60	96.40	1.66	100.0±1.30	100.0	1.30
	200	196.0±4.70	98.0	2.40	190.0±4.0	95.0	2.11
Tobacco	0	12.0±0.30	-	-	15.0±0.42	-	-
	100	107.0±1.80	95.54	1.68	112.0±1.30	97.40	1.16
	200	206.0±5.70	97.17	2.77	207.0±2.80	96.28	1.35

[a]mean±standard deviation (N=3.0). [b]Recovery% =[Observed value of analyte/Expectedvalueof analyte]× 100, [c]LOD: limit of detection.

Comparison of the proposed method with other preconcentration methods

The proposed VA-IL-DLLµE method was compared to the other extraction procedure documented in the literature. The comparison allows better analysis, relative to other approaches, of the positive aspects of the proposed method. The main advantages of the process were low detection limits, better reliability (as recovery %) and repeatability/reproducibility (as RSDs %) and high PF, as well as the use of green chemicals. As can be seen in table 6, the preconcentration factor and the limits of detection found in this work is superior to other preconcentration techniques [7–12, 16, 18, 24-26]. According to these properties, using conventional ILs and toxic organic solvents, the VA-IL-DLLµE technique has the potential to be a good alternative to the extraction methods. Such results showed that the proposed VA-IL-DLLµE protocol could be implemented successfully without any systematic error to analyse different real samples.

Table 6: Comparison between the proposed VA-IL-DLLµE procedure and other reported extraction methods for preconcentration and determination of Cd^{2+} and Pb^{2+} in various samples

Preconcentration method	Detection system	Linear range (µg/l)	LOD[a] (µg/l)	PF/EF[b]	Samples matrix	Reference
SPE	FAAS	Cd^{2+} (20-3000) Pb^{2+} (500-8000)	Cd^{2+} 0.8 Pb^{2+} 6.6	40	Water and food samples	[9]
SPE	FAAS	-	Cd^{2+} 2.8 Pb^{2+} 7.2	15	Food samples	[10]
SPE	FAAS	-	Cd^{2+} 0.7 Pb^{2+} 2.6	100	Food and water samples	[11]
VA-MSPE	FAAS	-	Cd^{2+} 1.4 Pb^{2+} 1.5	15	Food, water and environmental samples	[12]
SPE	FAAS	Cd^{2+} (100-3000) Pb^{2+} (500-10000)	Cd^{2+} 1.7 Pb^{2+} 9.1	5.0	Environmental samples	[13]
DLLME	ICP-OES	-	Cd^{2} 0.3 Pb^{2+} 0.6	Cd^{2+} 13 Pb^{2+} 11	Water samples	[14]
DLLME	FAAS	5.0-250	Cd^{2+} 0.55		Water and food samples	[18]
CPE	FAAS	10-500	Cd^{2+} 0.28 Pb^{2+} 0.5	Cd^{2+} 63 Pb^{2+} 57	Water samples	[20]
Co-precipitation	FAAS	-	Cd^{2+} 0.58 Pb^{2+} 3.4	Cd^{2+} 25 Pb^{2+} 50	Environmental samples	[26]
Coprecipitation	FAAS	-	Cd^{2+} 2.0 Pb^{2+} 7.0	100	Environmental samples	[27]
Membrane filtration	FAAS	5.0-20	Cd^{2+} 0.08 Pb^{2+} 0.93	50	Environmental samples	[28]
VA-IL-DLLµE	FAAS	Cd^{2+} (1.0-300) Pb^{2+} (2.0-400)	Cd^{2+} 0.3 Pb^{2+} 0.6	100	Water, vegetables and tobacco samples	Proposed work

[a]LOD: Limit of detection. [b]PF: Preconcentration factor and EF: Enrichment factor. [c]SPE: solid-phase extraction; VA-MSPE: Vortex-assisted magnetic solid-phase extraction; DLLME: dispersive liquid-liquid microextraction; CPE: cloud point extraction; VA-IL-DLLµE: vortex assisted ionic-liquid dispersive liquid-liquid microextraction; FAAS: flame atomic absorption spectrometry; ICP-OES: inductively coupled plasma optical emission spectrometry.

CONCLUSION

In the present study, green, efficient, simple, fast and environmentally friendly VA-IL-DLLµE technique was developed and validated to preconcentrate Cd^{2+} and Pb^{2+} ions in water, vegetables and tobacco samples prior to FAAS determination. Good characteristics of the proposed method such as extremely high sensitivity with low LODs, high preconcentration factors, simplicity, and green. Moreover, the developed procedures were successfully applied to preconcentrate and determine trace amounts of Cd^{2+} and Pb^{2+} ions from real sample solutions without significant interference. Low values of RSD% of Cd^{2+} and Pb^{2+} (<3.0%) show that's the method has satisfactory reproducibility. The new method was successfully applied to certified reference materials for trace Cd^{2+} and Pb^{2+} determination.

AUTHORS CONTRIBUTIONS

Prof. Dr. Ragaa El Sheikh has generated the research idea and interpreted the data and helped to draft the manuscript. Prof. Dr. Wafaa El Sayed Hassan has suggested the research idea and participated in the design of the study. Miss. Sara H. Ibrahim and Amira M. Youssef were prepared the solutions, carried out the experiments, interpreted the data and helped to draft the manuscript. Prof. Dr. Ayman A. Gouda helped in check spelling, reducing plagiarism, interpreting the data, reviewed the manuscript and submit the manuscript for publication.

CONFLICTS OF INTERESTS

The authors confirm that this article content has no conflict of interest.

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