

Application of a Task-Specific Functionalized Ionic Liquid To Simultaneous Preconcentration of Cd and Pb As Toxic Pollutant in Real Water and Saline Samples By In-Situ Solvent Formation Microextraction Technique

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Abstract

In the present research, the application of a functionalized ionic liquid with a specific role to simultaneous extraction and preconcentration of cadmium and lead ions in aqueous media by in-situ solvent formation microextraction (ISFME) technique was developed. The task-specific functionalized ionic liquid of 3-(2-(bis(2-(tert-butoxy)-2-oxoethyl)amino)ethyl)-1-methylimidazolium chloride ([Tamim][Cl]) as a complexing agent utilized for the formation of metal chelates with Cd(II) and Pb(II) ions in aqueous solutions. Finally, determination of concentrated or separated metal ions contents after dilution step was carried out by flame atomic absorption spectrometry (FAAS). To obtain optimum extraction conditions, analytical parameters including the various range of sample solution pH, chelating agent amount, ionic strength of solution, solution temperature and counter ion dosage were investigated. Furthermore, parameters represent figures of merit of the method such as limit of detection (LOD), relative standard deviation (RSD), linear dynamic range (LDR) and the enhancement factor (EF) were 0.64;0.76 $\mu\text{g L}^{-1}$, 1.5;1.8%, 50-2500;50-2000 $\mu\text{g L}^{-1}$ and 85;80 for cadmium and lead, respectively. The ability of the method for analyzing of real water and saline samples were evaluated and good results were obtained.

Keywords

Task-Specific Functionalized Ionic Liquids; In-Situ Solvent Formation Microextraction Technique; Cd; Pb; Saline Samples.

1. INTRODUCTION

The trace heavy metals existing in water sources especially drinking water or reused wastewater as humans or animal's consumption caused to the changes of its physio-chemicals properties [1]. Among heavy metals, cadmium and lead as toxic agents not only cause to the environmental pollutions such as water, air and soil but also bring harm to human health and have been responsible for several deaths [2,3]. Determination of heavy metals amounts in foods and waters has become an important part of most studies concerned with environmental pollutions and occupational health hazards [4]. Direct determination of these heavy metals appears to be a complex problem as the concentration of them is close to or below the detection limit of most of the common analytical instruments such as flame atomic absorption spectrometer (FAAS). On the other hand, graphite furnace atomic absorption spectrometer (GF-AAS) or inductive coupled

plasma (ICP) have an appropriate detection limit for ppb levels but has several disadvantages such as low precision and high maintenance costs. Besides, the real sample matrix may cause serious interferences for their determination during detection by any atomic absorption spectrometers [5-7]. To overcome these problems, the separation or extraction and preconcentration methods have been suggested. In the last twenty years, several famous procedures have been used for the separation or extraction and preconcentration of inorganic and organic contaminants from environmental matrices such as liquid-liquid extraction [8], coprecipitation [9], solid-phase extraction [10] and cloud point extraction [11]. Besides a few advantages of these procedures, the main disadvantages are their slow, small concentration factor and large consumption of solvent [12]. Today, the significant requests for solving problems of old procedures and invent of novel methods have been caused to development

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of new micro-analytical procedures such as solid-phase microextraction [13], stir-bar sorptive extraction [14], single drop microextraction [15], hollow fiber-liquid phase microextraction [16], dispersive liquid-liquid microextraction [17], micro cloud point extraction [18], cold-induced aggregation microextraction [19] and in-situ solvent formation microextraction [20]. The main advantages of the all mentioned microextraction methods rather than old or macro extraction methods are their rapid and low consumption volume of solvent. Among them, in-situ solvent formation microextraction (ISFME) is another mode of dispersive liquid-liquid microextraction (DLLME) with minor differences in general but such DLLME has been some advantages such as high concentration factor, low solvent consumption, rapid, simple, costless and especially applicable for solutions containing high salt amounts [21]. Notably, the unique advantage of ISFME is its compatibility for the extraction of analytes containing high salt. In-situ solvent formation microextraction was proposed by authors in 2009, which is based on the use of ionic liquids for the microextraction of inorganic analytes [22]. First, in the ISFME method, there is no interface/boundary between aqueous and extracting phases because both phases are miscible together and the extraction process is complete with high efficiency after the formation of the droplets. On the other hand, mass transfer from the aqueous phase into the extracting phase has occurred rapidly and completely. After that, by adding a counter ion, water-miscible ionic liquid converted to the water-immiscible and then separation of phases was started [23]. Over the last decade, the in-situ solvent formation microextraction method rather than other microextraction methods was less developed because it needs a variable properties chemical such as ionic liquids. In this analytical technique, instead of toxic and hazardous organic solvents as the extracting phase, ionic liquids that are environmentally friendly were used. Ionic liquids are being considered as replacement of common and hazard solvents in the sample preparation and extraction systems because of their unique properties such as negligible vapor pressure, low melting point, high boiling point, wide liquid range, non-flammability, resistance to the thermal degradation, good extractability for various organic and inorganic species [24,25]. Developments of both synthesis and application of functionalized ionic liquids have been highlighted in several types of research. Ionic liquids are attracting attention as alternative solvents in green chemistry, but as more functionalized ILs are prepared, a greater number of applications in increasingly diverse fields are

found [26,27]. Functionalized ionic liquids (FILs), often referred to as the task-specific ionic liquids (TSILs), have been designed, synthesized and utilized in specialized applications such as catalysis, electrochemistry, catalyst anchoring, reagents, supported phase, metal ion separation, synthesis of nanomaterials and ion-conducting materials [28,29]. Both room-temperature ionic liquids (RTILs) and TSILs have been deemed useful for metal ion extraction. The extraction of metal ions such as U(VI) and Am(III) into an RTIL phase from aqueous solutions using agents that form complexes with them have been reported [30]. A few attempts have been made to splice the coordinating groups on the ionic liquid phase rendering them useful for extraction processes. These include anchoring thioether or thiourea, ethylene glycol, macrocyclic ethers and 2-hydroxybenzylamine moieties to the ionic liquid phase [31-34]. Although some physical evidence and spectroscopic data support the formation of complexes in some cases, no reports firmly establish the nature of bonding between the TSILs and metal ions. Harjani et al. described a method by which the amino acetic acid moiety that could be incorporated and utilized for the complex formation with the metal ions [35,36].

In this research, an attractive and efficient method for the extraction and determination of two toxic pollutants in water samples is presented. The analytical procedure is based on a chelating of the metal ions with TSFIL and then separated/preconcentrated by an in situ solvent formation microextraction. The separated ionic liquid phase is finally diluted by diluting agent and analyzed by FAAS. The proposed method has been successfully applied to the determination of cadmium and lead in lake, well, tap and saline waters.

2. EXPERIMENTAL

2.1. Reagents and chemicals

Custom-made pure task-specific functionalized ionic liquid of 3-(2-(bis(2-(tert-butoxy)-2-oxoethyl)amino)ethyl)-1-methylimidazolium chloride was purchased from Green compounds company (Zanjan, Iran) and so can be synthesized by instruction in this literature [30]. All consumable solvents such as acetone, methanol, ethanol and ethyl acetate and other inorganic salts with analytical grade were purchased from Merck (Darmstadt, Germany). Sodium hexafluorophosphate as counter ion, cadmium nitrate tetrahydrate and lead nitrate were purchased from Sigma-Aldrich (USA). Stock solutions of cadmium and lead (1000 mg L^{-1}) were prepared from the salts of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Pb}(\text{NO}_3)_2$, respectively. All aqueous solutions were prepared by dilution of stock solutions.

2.2 Apparatus

The measurement of cadmium and lead were performed with a precise Analytik-Jena Nov350 flame atomic absorption spectrometer equipped with a hollow cathode lamp and a deuterium background corrector (Darmstadt, German). The hollow cathode lamps of cadmium and lead were operated at 6 and 4 mA, wavelengths of 222.8 and 283.3 nm, slits of 0.6 and 0.7 nm, burner height of 8 mm and acetylene gas flow rate of 1.5 L min⁻¹. All measurements were carried out in peak area mode. To separation of phases, a centrifuge equipped with a swing-out rotor was used from Hettich (Kirchlengern, Germany). A Metrohm digital pH-meter (model 692, Herisau, Switzerland) equipped with a glass-combination electrode was used for pH adjustment.

2.3. ISFME analytical procedure

A 5 mL of a sample solution containing metal ions following 150 mg of [Tamim][Cl] (Fig. 1a) as miscible-TSFIL ionic liquid (or organic phase) was transferred to a 10-mL screw-cap conical glass centrifuge tube. By vortexing for 1 min of the mixture, complexation of metal ions with a mole ratio of 2:1 for TSFIL-metal ion ([Tamim]₂-Cd][Cl] or [Tamim-Pb]₂][Cl]) (Fig. 1b) was started at largest possible amount because there is no any boundary/interface between aqueous and organic phase. Next, to separate phases, a 70 mg of sodium hexafluorophosphate ([NaPF₆]) as counter ion was added to the mixture, a cloudy solution was formed because the fine droplets of [Tamim][PF₆] as the immiscible task-specific ionic liquid was settled at the bottom of the tube and then phases separation could happen. By adding of NaPF₆ to [Tamim][Cl], the Cl⁻ as best leaving group leaves the [Tamim][Cl] and PF₆⁻ was replaced and finally, [Tamim][PF₆] was formed. Then, the final mixture was centrifuged for 2 min at 5000 rpm. The aqueous phase was discarded simply by inverting the tube and decanted. Subsequently, complexes of metal ions were dissolved in the acetone as a diluting agent and aspirate to FAAS for the determination of metals content.

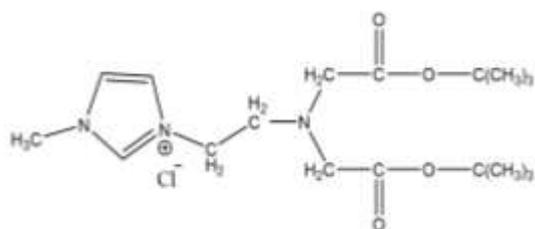


Fig. 1a. Chemical structure of TSIL of 3-(2-(bis(2-(tert-butoxy)-2-oxoethyl)amino)ethyl)-1-methyl imidazolium chloride abbreviated [Tamim][Cl].

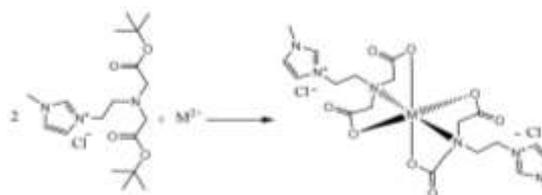


Fig. 1b. Complex formation mechanism between 3-(2-(bis(2-(tert-butoxy)-2-oxoethyl)amino)ethyl)-1-methyl imidazolium chloride and metal ions (M²⁺).

3. RESULT AND DISCUSSION

To attain higher sensitivity, selectivity and precision for metal ions preconcentration and determination, the effect of main analytical parameters affected the ISFME procedure such as pH of the sample solution, amounts of TSFIL, counter ion amount, salt concentration, centrifugation conditions and interfering effects were studied and optimized.

3.1. Selection of a diluting agent

A satisfactory diluting agent must dissolve the organic phase containing complexes of metal ions with TSFIL, completely. Ethanol, methanol, acetone and ethyl acetate were selected and examined. Results shown in Fig. 2 that in the presence of acetone and ethyl acetate, the maximum absorbance was obtained. On the other hand, the organic phase could not be dissolved in methanol and ethanol completely because it is a nonpolar compound. In the presence of acetone and ethyl acetate, the organic phase was completely dissolved and good absorbance was acquired. Therefore, these two diluting agents were chosen as the best diluents and finally acetone was used because it is of lower price.

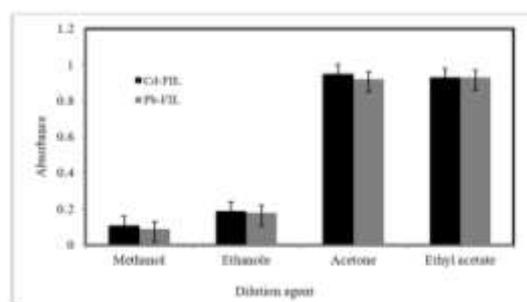


Fig. 2. Effect of diluting agent type on the absorbance performance. Conditions: 5 mL of sample solution with pH of 7, 150mg of TSFIL, 100 mg of counter ion of NaPF₆, vortexing time 1 min, diluting agents was variable, centrifugation rate and time were 4000 rpm and 1 min.

3.2. Effect of sample solution pH

The extraction of metal ions in the aqueous phase to the organic phase requires an increase in the hydrophobicity of ions. The formation of metal ion complex and its stability are the two important

factors to the extraction or separation of metal ions from aqueous media, and the sample solution pH containing metal ions plays a unique role in the metal-complex formation and then subsequent extraction or separation [37]. The effect of sample solution pH on the extraction of metal ions was studied in the range of 2.0–10.0. According to the obtained results in Fig. 3, the absorbance of metal ions was increased up to 7.0 and then was decreased. Thus, pH value of 7.0 was considered as the optimal value for further experiments. The K_{sp} constant for $Cd(OH)_2$ and $Pb(OH)_2$ is 7.2×10^{-15} and 1.43×10^{-20} respectively and represent that at low concentration of OH^- , the hydroxide form of metal ions immediately was formed and concentration of free metal ions was decreased. Thus low extraction of metal ions at basic pH is expected. At acidic pH because of the high concentration of hydronium ions, it would like to react with TSFIL and protonated it, so complexation amount between metal ions with TSFIL was decreased, significantly.

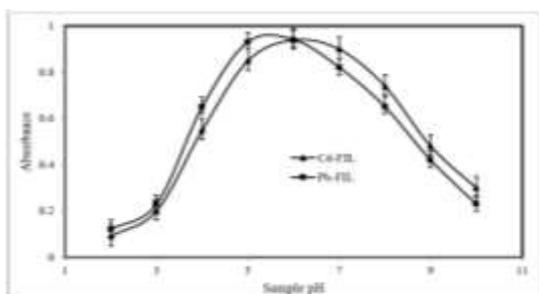


Fig. 3. Effect of sample solution pH on the absorbance performance. Conditions: 5 mL of sample solution with different pH, 150 mg of TSFIL, 100 mg of counter ion of $NaPF_6$, vortexing time 1 min, diluting agent was acetone, centrifugation rate and time were 4000 rpm and 1 min.

3.3. Effect of TSFIL dosage

The metal-complex formation is an important factor that influences on extraction or separation of metal ions from aqueous media, which is under the influence of complexing agents and free metal ions concentrations. TSFIL has two roles; the first role is act as complexing agent and next is as an organic phase. The effect of $[Tamim][Cl]$ or TSFIL dosage on the absorbance of metal ions was studied in the range of 25–250 mg. The absorbance increased by increasing in the TSFIL amount up to 150 mg. As can be seen in Fig. 4, by increasing the dosage of $[Tamim][Cl]$, the absorbance was increased and then decreased. Therefore, 150 mg was chosen as the optimum value.

By adding the TSFIL, the complex formation of both metal ions in the solution raised and subsequently the extraction efficiency factor was increased too.

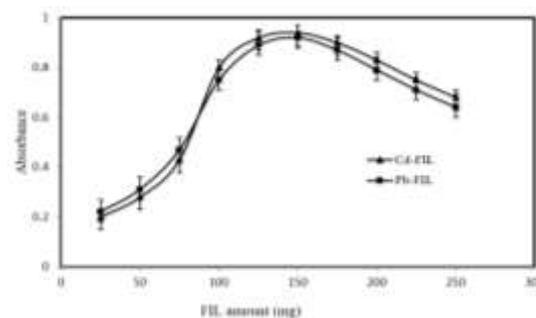


Fig. 4. Effect of organic phase (TSFIL) amount on the absorbance performance. Conditions: 5 mL of sample solution with pH of 7, TSFIL amount was variable, 100 mg of counter ion of $NaPF_6$, vortexing time 1 min, diluting agent was acetone, centrifugation rate and time were 4000 rpm and 1 min.

3.4. Effect of counter ion dosage

To decrease the solubility of the organic phase (soluble-TSFIL) in aqueous media and convert to insoluble-TSFIL, sodium hexafluorophosphate ($NaPF_6$) as counter ion was added to the sample solution. As a consequence of reaction between the water-miscible TSFIL ($[Tamim][Cl]$) and the counter ion (PF_6^-), a water-immiscible TSFIL ($[Tamim][PF_6]$) with very low solubility must be formed and so phase separation can be occurring successfully. Counter ion must have no interference in the extraction system. The effect of counter ion dosage was investigated in the range of 25–200 mg in the presence of 150 mg $[Tamim][Cl]$ and results are shown in Fig. 5. It is found that by adding of $NaPF_6$, $[Tamim][PF_6]$ was formed and according to common ion effect, the solubility of $[Tamim][PF_6]$ was decreased, so the absorbance or extraction efficiency was increased. At low amount of $NaPF_6$, the absorbance was insufficient because the phase separation was not complete and most of complex is soluble in the aqueous phase. Thus, 100 mg of $NaPF_6$ was chosen for the further experiments. The $[Tamim][Cl]$ and counter ion react in a stoichiometric ratio.

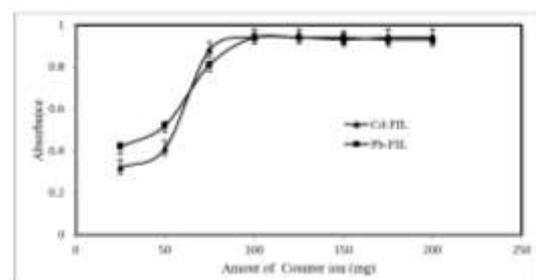


Fig. 5. Effect of counter ion amount ($NaPF_6$) on the absorbance performance. Conditions: 5 mL of sample solution with pH of 7, 150 mg of TSFIL, counter ion of $NaPF_6$ was variable, vortexing time 1 min, diluting agent was acetone, centrifugation rate and time were 4000 rpm and 1 min.

3.5. Effect of salt content

Notably, the main advantage of ISFME is compatibility for the extraction of analytes containing high amount of soluble salts. To investigate the influence of salt type and salt concentration on the microextraction performance, some experiments were designed and carried out. In these testes, different amounts of several soluble salts including sodium nitrate, sodium sulphate and sodium chloride from 5.0 to 40.0% w/v were added to the solution containing Cd ion. The amount of the absorbable metals was determined for each solution and reported. As shown in Fig. 6, the addition of 30% w/v of all the salts did not affect considerably the adsorption of Cd ion compared to the free salts solution. Besides, the addition of 30% w/v sodium nitrate, 10% w/v sodium sulphate and 15% w/v sodium chloride did not affect the adsorption of Pb ion. The results showed that the solution with higher salt amounts than above showed intense decreases in adsorption of both Cd and Pb. At the higher salts contents, the density of the solution matrix would become higher than the organic phase so that there is no settling complexes of metal ions in the solution. The results showed that the present method has a high ability to extract analyte from media containing salt.

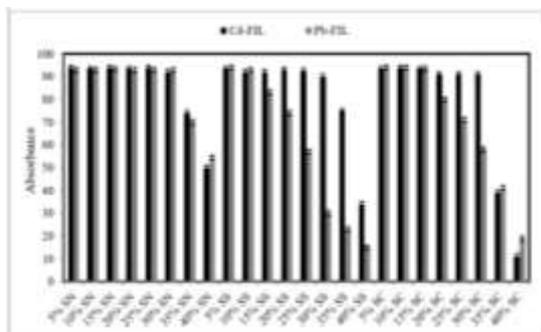


Fig. 6. Effect of type and concentration of salt on the absorbance performance (SN: Sodium nitrate, SS: Sodium sulphate and SC: Sodium chloride). Conditions: 5 mL of sample solution with pH of 7, 150 mg of TSFIL, 100 mg of counter ion of NaPF₆, vortexing time 1 min, diluting agent was acetone, centrifugation rate and time were 4000 rpm and 1 min.

3.6. Effect of centrifuge time and rate

The effect of main centrifugation conditions such as the rate on the absorbance was studied in the range of 1000–6000 rpm. It was found from Fig. 7a that over 3000 rpm, both organic phases containing metal ions completely settled, so to ensure complete separation, the maximum rate of 4000 rpm was applied. At the optimum rate, absorbance was investigated as a function of centrifugation time (Fig. 7b).

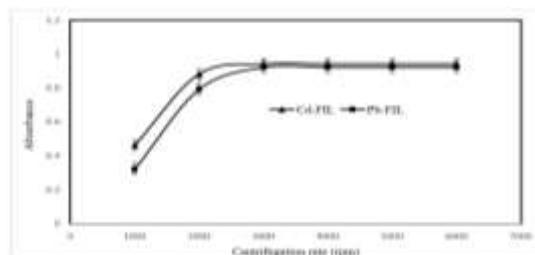


Fig. 7a. Effect of centrifugation rate on the absorbance performance. Conditions: 5 mL of sample solution with pH of 7, 150 mg of TSFIL, 100 mg of counter ion of NaPF₆, vortexing time 1 min, diluting agent was acetone, centrifugation rate was variable and time was 1 min.

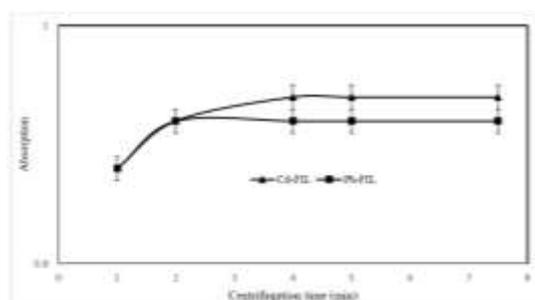


Fig. 7b. Effect of centrifugation time on the absorbance performance. Conditions: 5 mL of sample solution with pH of 7, 150 mg of TSFIL, 100 mg of counter ion of NaPF₆, vortexing time 1 min, diluting agent was acetone, centrifugation rate was 4000 rpm and time was variable.

Over 1 min, the absorbance of metal ions was constant and indicating complete transfer of each organic phase to the bottom of the centrifugation tube occurred. Therefore, to decrease general extraction time, 2 min was chosen as an optimum value.

3.7. Effect of centrifugation temperature

It is a fact that if the temperature of the sample solution increases during the centrifugation process, ionic liquids may be dissolved in aqueous phase before separate it and therefore the absorbance of metal ions will be decrease. So, it is necessary to study and investigate the effect of centrifugation temperature. Centrifugation temperature was studied at the range of 0–40 °C. It was found that the centrifugation temperature in this range does not affect the extraction process of studied metal ions especially the separation of phases step.

3.8. Effect of sample temperature and mixing time

The influences of sample solution temperature and mixing contact time of two phases on extraction performance are necessary to study and understand the complete reaction between metal

ions in aqueous phase with TSFIL as an organic phase, and to achieve phase separation. Therefore, the effect of the sample solution temperature was investigated from (ice bath) 1.5 to 70 °C. It was found that the increase of temperature up to 60 °C has no considerable effect on the absorbance (extraction performance) but above it, a cloudy solution cannot be formed immediately and it is necessary to cool the solution at the equilibrium amount. Thus, the room temperature (23-25 °C) was chosen as the optimum value in which the effect of mixing time on the absorbance was studied in the range of 1-10 min by the vortex. It was found that the mixing time before centrifugation has not considerable effect on the absorbance of both complexes. So, from one side to keep extraction time as short as possible and on the other hand to ensure from maximum mixing, the mixed sample solution was vortexed for a 1 minute.

3.9. Effect of interferer ions

To assess the selectivity of the present procedure for the simultaneous extraction and determination of Cd and Pb ions, the effect of other metal ions as interference was studied. The interferences were studied by analyzing sample solution containing 50 µg L⁻¹ of both metal ions and other interferer ions at different concentrations, according to the recommend microextraction procedure at the optimum conditions. It is found be that from Table 1, all ions such as alkali and alkaline metal ions, famous anions and some same transitional metal ions at certain concentrations do not interfere effectively.

Table 1. Tolerance limits of interfering ions in the simultaneous determination of Cd and Pb ions.

Ions	Interfering ion to Cd or Pb ion ratio
Na ⁺ , K ⁺ , Ca ²⁺ , Mg ²⁺ , Ba ²⁺	100000
Fe ²⁺ , Co ²⁺ , Zn ²⁺ , Ni ²⁺ , Mn ²⁺ , Cu ²⁺	400
NO ₃ ⁻	1000
Cl ⁻ , SO ₄ ²⁻ , PO ₄ ³⁻	200
Fe ³⁺ , As ³⁺ , Cr ³⁺ , V ³⁺	500

3.10. Figures of merit

Under the optimum conditions, figures of merit including a limit of detection, linear dynamic range, relative standard deviation and enhancement factor were calculated for two metal ions and the results are shown in Table 2. Based on the obtained results, the ISFME method has satisfying characteristics to simultaneous

concentration and determination of cadmium and lead in aqueous samples.

Table 2. Analytical characteristics of the method.

Analytical parameter	Value	
	Cd	Pb
Limit of detection (µg L ⁻¹)	0.64	0.76
Relative standard deviation (%)	1.5	1.8
Linear dynamic range (µg L ⁻¹)	50-2500	50-2000
Enhancement factor	85	80

3.11. Real sample analysis

To demonstrate the ability of the ISFME method to analyzing of real samples, the method was applied for the determination of cadmium and lead in several water samples and saline samples such as lake water, well water, tap water and real and synthesized saline samples and the results are shown in Table 3. As can be seen, the relative recoveries for Cd and Pb at the spiked values were in the range of 98.2–104.0% and 98.0–101.3%, respectively. The results indicated that the present ISFME method could be reliably applied for the simultaneous determination of Cd and Pb in real water and saline samples. The presented ISFME method was compared with the other analytical microextraction methods used for the determination of cadmium or lead separately [38-49] and the results are presented in Table 4. As can be seen, the present ISFME method shows a comparative and satisfactory data such as low RSD, good detection limit and high enhancement factor.

4. CONCLUSION

The in situ solvent formation microextraction (ISFME) method was successfully used for the simultaneous preconcentration and determination of cadmium and lead metal ions in some real water and saline samples. For the first time, use a [Tamim][PF₆] as task-specific functionalized ionic liquid (TSFIL) as an alternative to traditional volatile organic solvents, complexing agents or organic phase. Also, the present ISFME method is free of volatile organic solvent using the ionic liquid. In this extraction system, there is no any complexing agent because the TSFIL can complex with metal ions at certain analytical conditions. The result shows that this method is robust against a very high content of salt (up to 30% w/v) in comparison with other microextraction methods. These characteristics are of key interest for laboratories doing routine trace metal ion analysis. Finally, the ISFME method was successfully applied to the simultaneous determination of cadmium and lead in real water and saline samples, with good accuracy and reproducibility.

Table 3. Simultaneous determination of Cd and Pb in real and saline samples.

Ion	Lake water			Well water		Tap water		Saline sample ^a		Saline sea water	
	Added ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	R ^b (%)	Found ($\mu\text{g L}^{-1}$)	R(%)	Found ($\mu\text{g L}^{-1}$)	R (%)	Found ($\mu\text{g L}^{-1}$)	R(%)	Found ($\mu\text{g L}^{-1}$)	R(%)
Cd	0	23	-	^c ND	-	ND	-	ND	-	260	-
	75	99	101.0	78	104.0	75	100.0	78	104.0	340	101.4
	150	170	98.2	152	101.3	147	98.0	153	102.0	410	100.0
Pb	0	43	-	ND	-	ND	-	ND	-	196	-
	75	117	99.1	75	100.0	76	101.3	75	100.0	270	99.6
	150	195	101.0	148	98.7	150	100.0	147	98.0	350	101.1

^aSample containing 30% (w/v) of sodium nitrate salt; ^bRecovery; ^cNot detected.

Table 4. Characteristic performance data of present ISFME and other microextraction methods for the determination of Cd and Pb.

Microextraction method	Analyte	LOD ($\mu\text{g L}^{-1}$)	RSD (%)	EF ⁱ	Ref.
DLLME ^a	Cd	0.07	4.2	50	[38]
DLLME	Cd	0.2	-	87	[39]
DLLME	Cd	0.4	1.9	55	[40]
DLLME-SQT ^b	Cd	0.5	8.2	-	[41]
DLLME	Cd	1.2	2.1	34.5	[42]
DLLME-VALLME ^c	Cd	2.9	4.1	35	[43]
ISFME	Cd	0.07	2.4	78	[37]
UA-DLLME-SFO-BE ^d	Pb	1.9	3.4	81	[44]
VAM ^e	Pb	0.02	5.6	70	[45]
DLLME	Pb	0.0095	2.12	-	[46]
DLLME	Pb	0.5	2.0	50	[47]
SPME/GC ^f	Pb	3-4	2.9	-	[48]
AA-LLME ^g	Pb	1.36	5.2	-	[49]
ISFME-FIL ^h	Cd, Pb	0.64, 0.76	1.5, 1.8	85, 80	Present work

^aDispersive liquid-liquid microextraction;

^bDispersive liquid-liquid microextraction-slotted quartz tube;

^cDispersive liquid-liquid microextraction-Vortex-assisted liquid-liquid microextraction;

^dUltrasound-Assisted dispersive liquid-liquid microextraction based on solidification of Floating organic drop and back-extraction;

^eVortex-assisted microextraction;

^fSolid phase microextraction-gas chromatography;

^gAir-assisted liquid-liquid microextraction;

^hIn situ solvent formation microextraction based on functionalized ionic liquid;

ⁱEnhancement factor.

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