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Application of an *In-situ* Solvent Formation Microextraction Technique Using the Functionalized Ionic Liquids (FILs) as a Green Extractant for Cadmium Determination at Trace Levels in Real and Saline Samples

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An *in-situ* solvent formation microextraction technique, as an attractive mode of homogeneous liquid-liquid microextraction, was developed successfully for the sensitive extraction of cadmium ion. In this technique, green extracting solvents such as ionic liquids are used. Due to using ionic liquids, this technique is much safer than other extraction methods using toxic common organic solvents. Functionalized ionic liquid of 3-(2-(bis(2-(tert-butoxy)-2-oxoethyl)amino)ethyl)-1-methylimidazolium bromide was used as an extractant and organic phase which has a double role including complexing agent and extractant, so the extraction of cadmium ion does not need any complexing agent. To optimize the extraction conditions, several analytical parameters affected the microextraction efficiency including sample pH, functionalized ionic liquid dosage, counter-ion amount and centrifugation conditions were studied. To show abilities of the method, the figures of merits including limit of detection and quantification, relative standard deviation, linear dynamic range and enrichment factor were calculated which were found to be 0.23 $\mu\text{g l}^{-1}$, 0.76 $\mu\text{g l}^{-1}$, 1.8%, 10-1500 $\mu\text{g l}^{-1}$ and 75, respectively. It was found that the method could be successfully applied for the determination of Cd(II) ion in several real, and saline samples. Due to the use of environmental solvents, such as ionic liquids, and their small dosage, it can be said that the method has a low toxicity and classified as a green extraction/preconcentration technique. The proposed method opens a new window in the analytical applications due to its low cost, ease in experimental setup and use of non-toxic solvents as an extractant.

Keywords: *In-situ* solvent formation microextraction, Functionalized ionic liquids (FILs), Cadmium determination, Real and saline samples

INTRODUCTION

It has been proved that heavy metals, such as cadmium, copper, lead, arsenic and mercury, at trace levels are toxic, and can cause human health disorders such as damage to kidneys, liver, and lungs [1-3]. Several experimental, and epidemiological studies performed on long-term exposure to trace amounts of cadmium which could contribute to forming various cancers [4].

Due to the trace amount of cadmium ions in natural aqueous environments, which is generally lower than 5 $\mu\text{g l}^{-1}$, high sensitive analytical techniques for detecting cadmium ions are required. The analytical common direct measurement instruments including atomic absorption spectrometry (FAAS), electrothermal atomic absorption spectrometry (ETAAS), spectrophotometry (UV-Vis), and inductively coupled plasma-atomic emission spectrometry (ICP-AES) are not sensitive enough and have matrix interferences [5-7]. So, to address these, the

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sample preparation methods are widely suggested [8].

In analytical chemistry, sample preparation methods refer to the methods/techniques in which samples containing analytes are treated prior to be analyzed by various common analytical instruments. Sample preparation is a very important procedure in most analytical techniques, because the available techniques are often not responsive to the analyte in its present/*in-situ* form, or the results are distorted by interfering species, or the analytical instrument has low sensitivity, or there is a high limit of detection to determine trace or ultra-trace amounts of analytes [9]. Generally, the sample preparation methods often known by other names including separation, extraction or preconcentration methods.

A number of macro separation/preconcentration methods in frequent research studies have been proposed such as solvent extraction or liquid-liquid extraction [10], cloud-point extraction [11], membrane filtration [12], ion-exchange [13], co-precipitation [14], and solid-phase extraction [5-8]. Despite many advantages of macro separation/preconcentration methods, they have several disadvantages such as time-consuming, being slow, low sensitivity and high consumption of organic solvents. Nowadays, several researchers have made their efforts to adopt the appropriate measures and invent novel sample preparation methods to resolve the macro-extraction problems. These proposed replacement methods are micro-analytical sample preparation procedures such as solid-phase microextraction [15], stir-bar sorptive extraction [16], single drop microextraction [17], hollow fiber-liquid phase microextraction [18], dispersive liquid-liquid microextraction [19], micro-cloud point extraction [20], and cold-induced aggregation microextraction [21]. The main positive aspect of the microextraction methods are rapid and sensitive extraction, and low consumption of organic solvents.

As a leading branch of homogeneous liquid-liquid microextraction (HLLME) method, *in-situ* solvent formation microextraction (ISFME) technique, based on the ionic liquids (ILs), has been recently the center of some research attention [4,22-24]. Another new and attractive mode of HLLME based on using common solvents is liquid-nitrogen-induced homogeneous liquid-liquid microextraction, in which a water-miscible extraction

solvent such as acetonitrile is mixed with an aqueous phase containing the analytes to form a homogeneous solution and next this phase was broken by the addition of a phase separation agent such as sugars, salts or cooling the solution [25].

However, for the first time, the ISFME was proposed by Baghdadi *et al.* in 2009 [26]. In this microextraction system, at first, there is no interface/boundary between aqueous and extractant phase because both of them are miscible together, and subsequently the extraction process is carried out very fast and complete with high efficiency. On the other hand, the mass transfer of the aqueous phase to the extractant phase carried out very fast and complete synthetically and thermodynamically, respectively. Lastly, after extraction process, by the addition of a counter-ion such as common bulky anions, miscible ionic liquid (or hydrophilic ionic liquid) is converted to the immiscible one (or hydrophobic ionic liquid), and then separation of phases starts [22]. In ISFME method, in the presence of high content of salts along analyte, the solubility of ILs would increase, and the phase separation can not happen. However, according to the common ion effect, the solubility of ILs decreases. So, because of the high density of ILs, even in the saturated solutions, the fine droplets of the organic phase could be settled. Due to the very low solubility of water in the hydrophobic ILs, residual salinity from the matrix is negligible. So, the main advantage of ISFME method is its compatibility with the high content of salts [23].

Room-temperature ionic liquids (RTILs) are considered as an alternative common and toxic solvents in the most sample preparation methods. This is because of ILs unique chemical and physical properties such as negligible vapor pressure, low melting point, wide liquid ranges, non-flammability, good extractability for various organic and inorganic compounds [27,28]. The unique properties of ionic liquids as solvents distinguish them from other non-conventional solvent options, enabling us to design and manipulate their architecture, making them suitable for specific applications. These ionic liquids, often referred to as the task specific or functionalized ionic liquids (TSILs or FILs), have been designed, synthesized and utilized in many applications such as electrochemistry, catalysis, reagents, supported phase, metal ion separation or extraction, *etc.* [29].

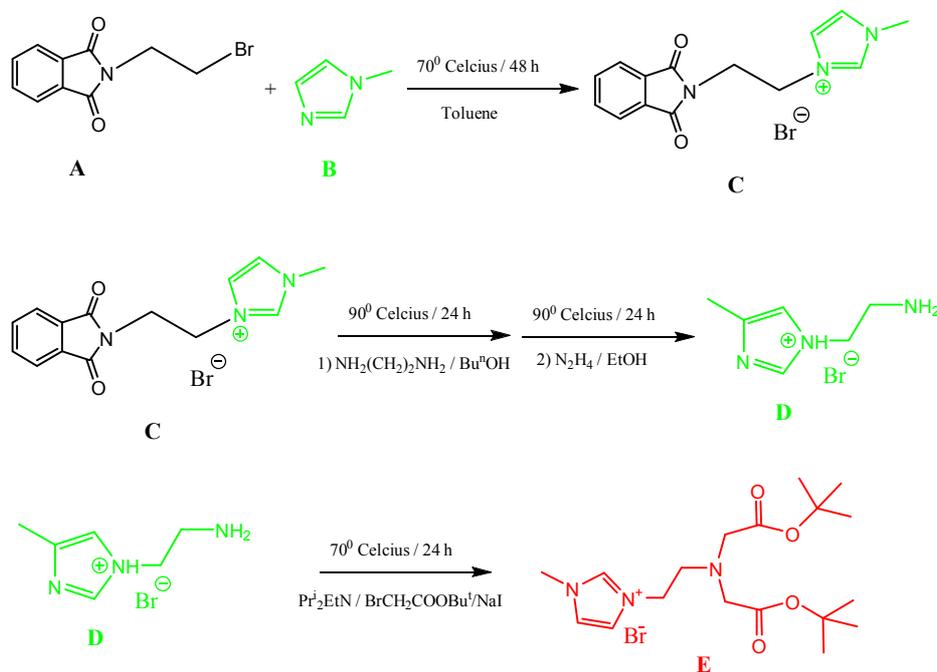


Fig. 1. Synthesis route of 3-(2-(bis(2-(tert-butoxy)-2-oxoethyl)amino)ethyl)-1-methylimidazolium bromide (FIL-Br).

In summary, in this research, instead of toxic and hazardous organic solvents, we used ionic liquids as the green solvents. A preconcentration method used in this study is an *in-situ* solvent formation microextraction method using a novel functionalized ionic liquid, 3-(2-(bis(2-(tert-butoxy)-2-oxoethyl)amino)ethyl)-1-methylimidazolium bromide (FIL-Br), with a double role as a complexing agent and an extractant phase for the determination of cadmium at trace levels in several real water and saline samples following FAAS measurement system. All analytical parameters affected on extraction system were studied and optimized.

EXPERIMENTAL

Apparatus

The measurement of Cd(II) amount was performed with a Analytik-jena Nov350 flame atomic absorption spectrometer equipped with a hollow cathode lamp and a D₂ background corrector (Darmstadt, German). The hollow cathode lamp of Cd(II) was operated at 6 mA, a wavelength of 222.8 nm, a slit of 0.6 nm, burner height of 8 mm, and acetylene gas flow rate of 1.5 l min⁻¹. A HERMLE

centrifuge equipped with a swing-out rotor was used (Hettich, Kirchlengern, Germany) for separation of phases. A Metrohm digital pH-meter (692-model, Herisau, Switzerland) equipped with a glass-combination electrode was used for pH adjustment.

Reagents

Functionalized ionic liquid of 3-(2-(bis(2-(tert-butoxy)-2-oxoethyl)amino)ethyl)-1-methylimidazolium bromide (FIL-Br) was synthesized in our laboratory as literature [30]. The other chemicals with analytical grade were purchased from Merck (Darmstadt, Germany). Potassium hexafluorophosphate [KPF₆] as bulky counter-ion supplier of PF₆⁻ was purchased from Sigma-Aldrich (USA). All aqueous solutions were prepared by dilution of Cd(II) stock solution (1000 mg l⁻¹).

Synthesis of Functionalized Ionic Liquid of 3-(2-(Bis(2-(tert-butoxy)-2-oxoethyl)amino)ethyl)-1-methylimidazolium Bromide (FIL-Br)

The procedure for the synthesis of FIL-Br involves the following steps (Fig. 1). First, the one pot phthaloylation and bromination of 2-aminoethanol to generate N-(2-

bromoethyl)phthalimide A was reproduced from the literature procedure [30]. The halide A can be used as a synthetic equivalent of b-haloamines to generate the FIL-Br (E) with the b-aminodiacetic acid groups.

Parameters Adjusting for Optimum Cd(II) Microextraction

pH. Generally, the pH of the sample solution has a considerable effect on extraction efficiency of metal ions. Furthermore, the amounts of complexation between Cd (II) ion and FIL is critically dependent on the free Cd(II) ions concentrations. To achieve the maximum Cd(II) complexation, the pH is adjusted between acidic to basic range of 2.0-10.0, in addition, it is possible the hydroxide and complex formation of cadmium ion in the various forms such as $\text{Cd}(\text{OH})_2$, $\text{Cd}(\text{OH})_3^-$ and $\text{Cd}(\text{OH})_4^{2-}$ in basic media.

Diluent type. The viscosity of most ionic liquids is high, leading to the difficulty in injection of organic phase (Cd-FIL complex after extraction step) into the atomic system, so, to decrease the viscosity of the Cd-FIL complex before injecting to the FAAS, some common diluents such as ethyl acetate, acetone, and ethanol were tested. Generally, diluents are solvents that completely dissolve the complex to inject them easily into the FAAS.

Salt content. The presence of high salt content in sample solution would increase the solubility of functionalized ionic liquid (based on Louis Le-Chatelier law). Generally, phase separation after the extraction process does not efficiently happen due to the common ion effect, and IL solubility would decrease, which would have negative impact on the extraction efficiency. To clarify the effect of salt anion type on Cd(II) extraction efficiency, the extraction was studied in the presence of the three common very soluble salts of Na_2SO_4 , NaCl , and Na_2CO_3 from 0 to 75% (w/v).

FIL dosage. FIL-Br performs as an extractant (complexing agent) and an organic phase in this extraction system. Theoretically, the extractant dosage has a considerable effect on the efficiency of the complexation amount between FIL-Br and Cd(II). So, the effect of the functionalized ionic liquid amount was studied in a range of 10-300 mg.

PF_6^- amount. This agent as a counter-ion is added to the system after extraction step, converting FIL-Br complex to

the FIL- PF_6 . The effect of the counter-ion agent amount was investigated in the range of 50-300 mg.

Centrifugation conditions. To enhance the phases separation efficiency, the centrifugation conditions such as centrifugation rate and time were optimized. Effect of the centrifugation rate on the extraction of Cd(II) ion was studied in the range of 500-5000 rpm and the centrifugation time was studied between 1-5 min.

Analytical Procedure

Five ml of $20 \mu\text{g l}^{-1}$ Cd(II) solution with 150 mg of 3-(2-(bis(2-(tert-butoxy)-2-oxoethyl)amino)ethyl)-1-methylimidazolium bromide (FIL-Br) as the miscible ionic liquid was transferred to a 10-ml screw-cap conical bottom glass centrifuge tube. After manually shaking the mixture for a few minutes and formation of Cd-FIL-Br complex, 70 mg of potassium hexafluorophosphate was added to the mixture, immediately leading to a cloudy solution, because the immiscible ionic liquid 3-(2-(bis(2-(tert-butoxy)-2-oxoethyl)amino)ethyl)-1-methylimidazolium hexafluorophosphate containing cadmium complexed (Cd-FIL- PF_6) was formed (Fig. 2). Then, the mixture was centrifuged for 2 min at 4000 rpm. As a result, the immiscible fine droplets of Cd-FIL- PF_6 complex was settled at the bottom of the tube. The aqueous phase was removed simply by inverting the tube, and decanted. Subsequently, the complex of Cd-FIL- PF_6 was dissolved in the acetone and aspirated to FAAS for measurement of Cd(II) amount.

RESULTS AND DISCUSSION

Effect of pH

The line graph illustrates the extraction percentage of Cd (II) in pHs between 2.0 and 10.0 by FIL-Br extractant. As shown in Fig. 3, from pH, the extraction of Cd(II) increased sharply and peaked at almost 97% in pH 6.0. Then, the extraction percentage declined intensively to just over 65% in pH 8.0 and gradually decreased to 55% in pH 10.0. Based on the graph results, the maximum extraction occurred at a pH of 6.0. At acidic pHs, hydronium ion (H_3O^+) was as a serious competitor of Cd^{2+} to complexation with FIL-Br. Concerning the basic pHs, Cd(II) forms hydroxide ($\text{Cd}(\text{OH})_2$) or other soluble complexes such as $\text{Cd}(\text{OH})_3^-$, and $\text{Cd}(\text{OH})_4^{2-}$ leading to a decrease in the extraction percentage.

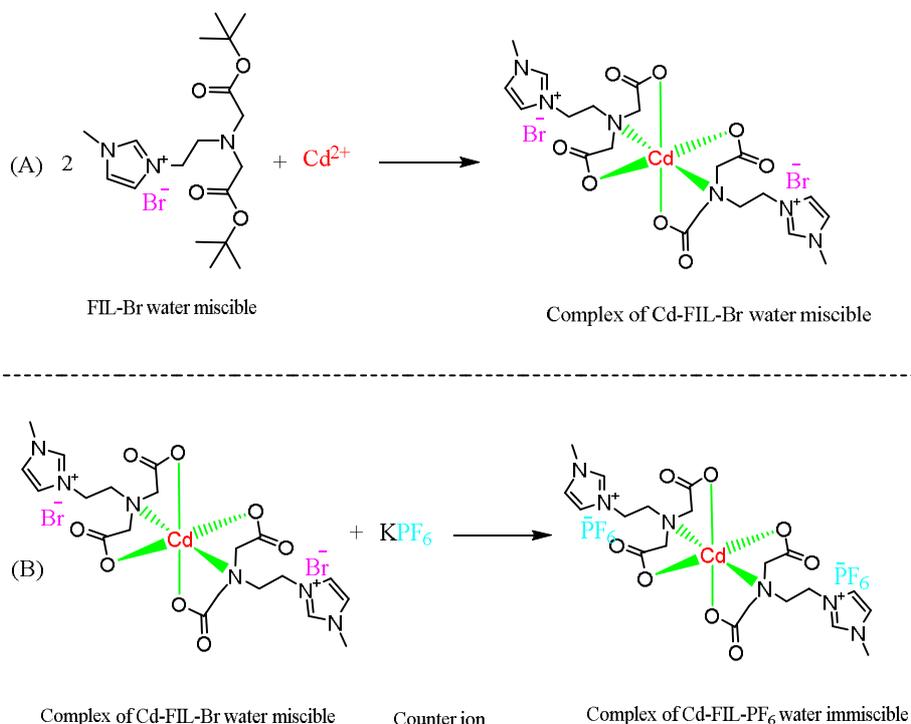


Fig. 2. Chemical mechanism of A) complexation of FIL-Br with Cd(II) ion in formation of Cd-FIL-Br, and B) converting the Cd-FIL-Br water miscible complex into Cd-FIL- PF_6 immiscible complex.

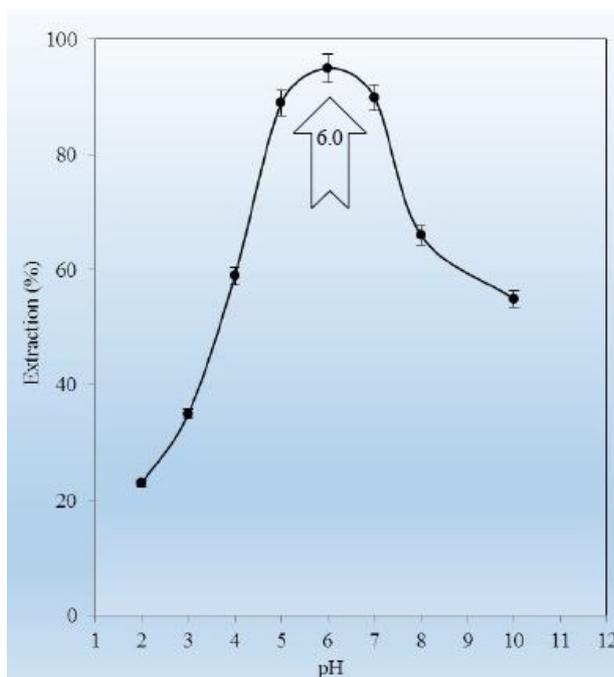


Fig. 3. Effect of the pH of sample solution on the extraction of Cd(II) ion.

Effect of Dilluent Type and its Volume

The line graph shows the Cd(II) extraction percentage by Cd-FIL- PF_6 , diluted by several common dilution agents such as ethyl acetate, acetone, and ethanol in the presence of various volume ratios of dilluents. As shown in Fig. , in the presence of ethylacetate and acetone, the maximum extraction percentage is obtained. The results also show the maximum extraction in 40% (v/v) of these two dilluents to the settled extractant phase, and then extraction amount remained constant. The main explanation for the same Cd(II) extraction percentage in the presence of ethylacetate and acetone could be that they have the same polarity with the Cd-FIL- PF_6 complex. Due to the lower cost of the acetone and its function as a fuel in FAAS, it was opted as the best diluting agent.

Effect of Salt Content

The line graph clearly illustrates the Cd(II) extraction performance in aqueous media in the presence of three common salts including Na_2SO_4 , NaCl , and Na_2CO_3 with a

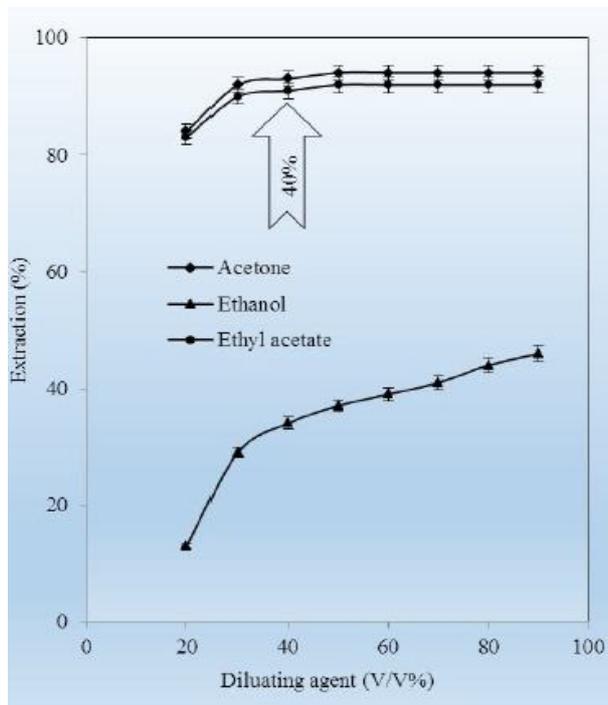


Fig. 4. Effect of diluent type and volume on the extraction of Cd(II) ion.

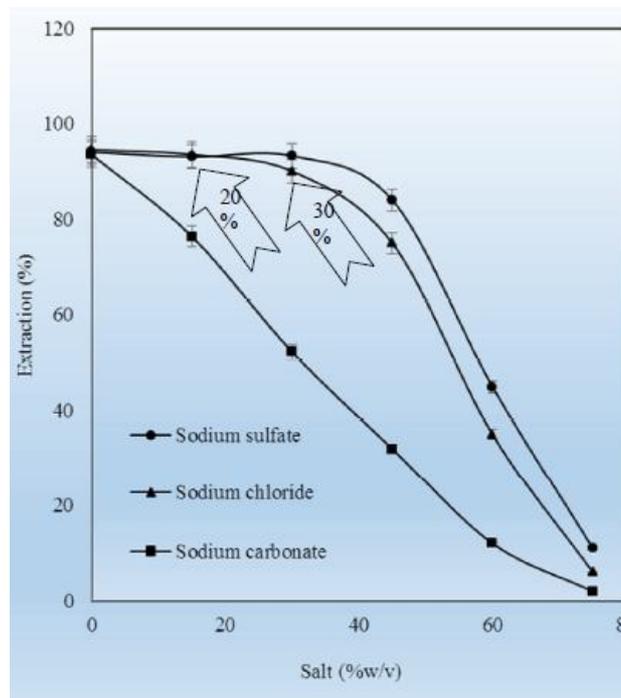


Fig. 5. Effect of salt type and amounts on the extraction of Cd(II) ion.

concentration from 0 to 75% (w/v) (Fig. 5). On the one hand, the extraction amount of cadmium in the presence of Na_2SO_4 and NaCl stood at about 94% in 20% (w/v) of sodium sulfate and sodium chloride salts and then remained unchanged. At high salt amounts, the extraction of cadmium was still constant about 94% in presence of 30% (w/v) Na_2SO_4 and 20% (w/v) of NaCl , respectively. Subsequently, with more increase in the amounts of salts up to 75% (w/v) the Cd(II) extraction amount witnessed a sharp decrease in the presence of both salts and extraction amount fell to about 10%. The Cd(II) extraction began at about 92% in a free any salt solution and then dramatically went down to 76% in the presence of 15% (w/v) Na_2CO_3 . Toward the end of the graph, the Cd(II) extraction continuously experienced a significant decline of 1% in Cd(II) extraction at 75% (w/v) Na_2CO_3 concentration.

Overall, it was found that the extraction percentage decreases by increasing the salts' content. The main reason for the decrease of Cd(II) extraction in the presence of Na_2CO_3 might be the formation of insoluble CdCO_3 , while

in the presence of Na_2SO_4 and NaCl the more soluble salts of CdCl_2 and CdSO_4 are formed. It should be noted that the K_{sp} value for cadmium sulfate, cadmium chloride, and cadmium carbonate are 1.25, and 0.2, and 1.0×10^{-12} , respectively. Accordingly, more soluble Cd-salts could be more detected, showing higher Cd(II) extraction percentages. Interestingly, at any amount of sodium carbonate, immediately cadmium carbonate was precipitated. In summary, at more elevated amounts of all salts, the density of aqueous solution was more than the organic phase (Cd-FIL-PF), and the saline aqueous phase was located under the organic phase. Owing to this difference in density of phases, Cd-FIL-PF₆ phase did not settle at the bottom of the tube and separation of phases will be hard and incomplete. So, the method is robust in the presence of certain salts concentrations.

Effect of FIL-Br Dosage

Figure 6 illustrates the Cd(II) extraction by the various amounts of FIL-Br from 10 to 300 mg. The Cd(II) extraction percentage stood at 12% at 10 mg of FIL-Br. The

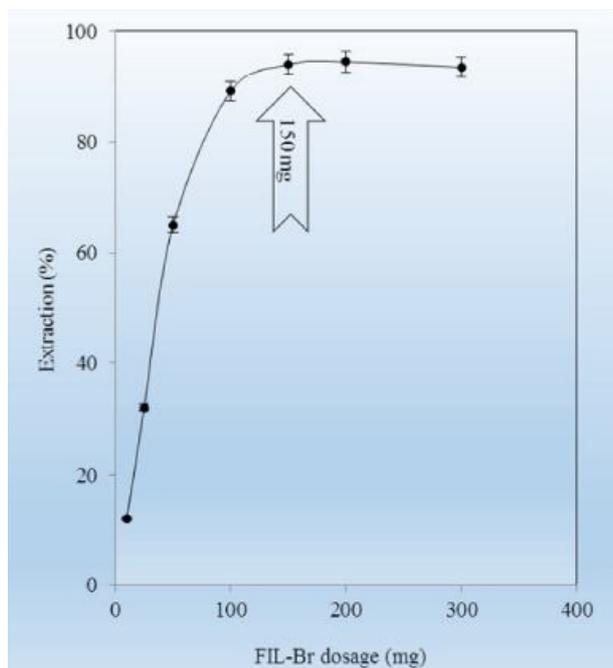


Fig. 6. Effect of functionalized ionic liquid (FIL-Br) or extractant phase dosage on the extraction of Cd(II) ion.

following dosage of FIL-Br experienced a dramatic rise in extraction percentage. Finally, the extraction remained virtually unchanged at 93% between 150 to 300 mg. It is noticeable that the rapid increase in the extraction is due to a rise in the number of contacts between two species to form complex. Accordingly, the dosage of 150 mg of FIL-Br was chosen as the optimum amount.

Effect of PF_6^- Amount as the Counter-ion

The bulky counter-ion of PF_6^- was added to the extraction system containing FIL-Br to be replaced with Br^- to form FIL- PF_6^- . There are some stark differences between the chemical properties of FIL-Br and FIL- PF_6^- . The electrostatic bond between cation FIL [3-(2-(bis(2-(tert-butoxy)-2-oxoethyl)amino)ethyl)-1-methylimidazolium] $^+$ and anion PF_6^- is strong, and FIL- PF_6^- is efficient in phase separation. The main reasons could be: First, Br^- is one of the best leaving groups, and second, the electrostatic attraction between $[\text{FIL}]^+$ and $[\text{Br}]^-$ as the result of significant difference in their size is poor.

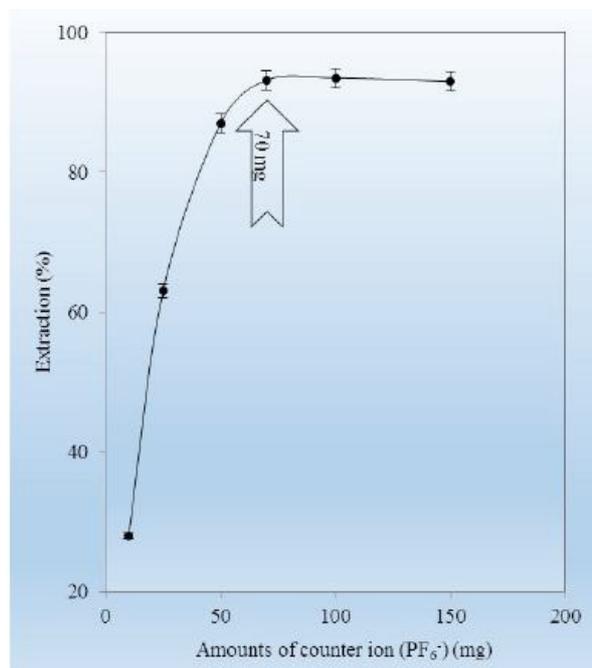


Fig. 7. Effect of counter ion dosage on the extraction of Cd(II) ion.

FIL-Br is water-miscible while FIL- PF_6^- is water-immiscible. The explanation for this change is that the replaced $[\text{FIL}]^+$ and $[\text{PF}_6^-]$ in FIL- PF_6^- have a strong chemical bond. So, the solubility of FIL- PF_6^- is much lower than that of FIL-Br in aqueous media. Consequently, FIL- PF_6^- is more effective in phase separation. Figure 7 shows the Cd(II) extraction percentage in various PF_6^- amounts from 10 to 150 mg. In 10 mg of PF_6^- , the extraction percentage stood at 28%. However, extraction rose sharply over the next 50 mg PF_6^- , and finally, remained constant from 70 to 150 mg. Based on the results, 70 mg was opted as the optimum dosage.

Effect of Centrifugation Rate and Time

Based on the obtained results, it was found that at the highest possible rate (4000 rpm), the functionalized ionic liquid phase (FIL- PF_6^-) could be completely separated from the aqueous phase. So, 4000 rpm was selected as the optimum centrifugation rate. It is clear that with increasing the centrifugation rate, the separation of phases was

Table 1. Tolerance Limit for Determination of 50 µg l⁻¹ of Cd(II) in Presence of some Interferences

Interferer	Tolerance limit	Recovery of cadmium (%)
Na ⁺ , K ⁺ , Ca ²⁺ , Mg ²⁺ , Ba ²⁺	>10000	100.0
Fe ²⁺	200	99.3
Fe ³⁺	500	100.1
Mn ²⁺	300	100.0
Pb ²⁺	100	99.5
Ni ²⁺	100	99.2
Zn ²⁺	200	100.9
Co ²⁺	200	99.4
NO ₃ ⁻ , Cl ⁻ , SO ₄ ²⁻ , PO ₄ ³⁻	1000	98.4
Cu ²⁺	50	100.3

faster and simpler. By increasing the centrifugation time, extraction percentage was increased, and up to 2 min, sedimentation of the ionic liquid phase of FIL-PF₆ containing cadmium to the bottom of the tube was completed.

Effect of Interferences on the Cd(II) Extraction

An analytical selective extraction or preconcentration method is performed in the presence of various interfering agents with any concentration, detecting analytes in the lowest amounts. Therefore, this method can quantify the analytes in real samples containing complicated matrices. In order to study the selectivity of the present ISFME method to determine the cadmium ion concentrations in the presence of various interference agents, the highest tolerability of several common interfering metal ions was evaluated. Interferences may occur due to competition of metal ions with cadmium ions to complexation with FIL. So, the tolerable limits of various interfering agents were studied. The effect of interferences of various metal ions on Cd(II) extraction was explored by analyzing the several real water sample being added to 50 µg l⁻¹ of Cd(II) ion. The optimum experiment parameters were calculated in previous sections and were adjusted in this part. The tolerance limit of the some interfering ions on Cd(II) extraction is shown in Table 1. It is worth noting that a species is considered as an

interferer when it changes the extraction of analyte more than 5%. Commonly, metal ions such as alkali and alkaline ions do not form a stable complex with FIL-Br. It is seen that Cu(II) ion can be as interferer at a higher ratio of 50, which was eliminated by using an excess of ionic liquid or by masking it with thiourea.

Characterization of Method

Table 3 summarizes the analytical characteristics (figures of merit) of the optimized method including the limit of detection (LOD), limit of quantification (LOQ), linear dynamic range (LDR), relative standard deviation (RSD), and enrichment factor (EF). The limit of detection was calculated using 3S_b/m equation and was 0.23 µg l⁻¹. The precision of the method at a concentration of 50 µg l⁻¹ of Cd(II) ion for seven replicated (n = 7) measurements, represented by the relative standard deviation, was 1.8%. A range of 10-1500 µg l⁻¹ was obtained as a linear dynamic range with regression of R² = 0.998. The enrichment factor, representing the ability of the method to concentrate on the analyte, was 75. The intra-day precision of ISFME method was calculated from standard deviation (SD%) and average concentration results of three replicate analyses of each real sample in one day (Eq. (1)). The inter-day precision was calculated as the same equation from results of each real sample analysis in three consecutive days. Basically, the

Table 3. Analytical Figures of Merit for the Method

Parameter	Value (unit)
Limit of detection (LOD) ^a	0.23 ($\mu\text{g l}^{-1}$)
Limit of quantification (LOQ) ^b	0.76 ($\mu\text{g l}^{-1}$)
Relative standard deviation (RSD) ^c	1.8 %
Linear dynamic range (LDR)	10-1500 ($\mu\text{g l}^{-1}$)
Enhancement factor (EF) ^c	75

^aDetermined as $3S_b/m$ (where S_b and m are the standard deviations of the blank signal and the calibration graph's slope, respectively). ^bDetermined as $10S_b/m$ (where S_b and m are the standard deviations of the blank signal and the calibration graph's slope, respectively). ^cCalculate as the standard deviation for seven ($n = 7$) replicate measurements of Cd(II) concentration. ^dCalculated as the slope ratio of the calibration graph obtained with and without concentration.

difference between these two parameters is in the SD value.

$$\text{RSD}_{\text{Intra-day}} (\%) = (\text{SD}_{\text{Standard deviation}} / \text{Average concentration}) \times 100 \quad (1)$$

Determination of Cd(II) in Real Water Samples

The ability of ISFME method for the determination of Cd(II) ion at various amounts in several real water and two saline water samples were tested by the standard addition method. The obtained results are shown in Table 3, and recovery percent for any sample was calculated, which indicated the adequate and high ability of the method for determination of Cd(II) ions. A good agreement was achieved between the added and founded amounts. The recovery values were in the range of 98.0-105%, which confirmed the procedure accuracy, and its independence from matrix effects in the real samples.

The proposed method was fruitfully compared with other reported methods as given in Table 4 for the preconcentration and determination of Cd(II) ion with the same detection system [31-42]. The same absorption

Table 4. Determination of Cd(II) in Real, and Saline Samples

Sample	Amount of Cd(II) ($\mu\text{g l}^{-1}$)				Recovery (%)	Amount of Cd(II) ($\mu\text{g l}^{-1}$)		Recovery (%)
	Certified	Added	Founded \pm SD	RSD (Intra-day)		Founded \pm SD	RSD (Inter-day)	
Tap water (Boroujerd city)	-	0	Not detect	-	-	Not detect	-	-
		100	102 \pm 1.2	1.2	102.0	100 \pm 2.4	2.4	100.0
		300	300 \pm 0.5	0.2	100.0	301 \pm 1.7	0.6	100.3
Mineral water (Kohsaran)	-	0	Not detect	-	-	Not detect	-	-
		100	98 \pm 1.1	1.1	98.0	101 \pm 2.2	2.2	100.0
		300	301 \pm 1.5	0.5	100.3	300 \pm 1.9	0.7	100.0
Lake water (Fadak lake)	-	0	50 \pm 0.9	1.8	-	51 \pm 1.5	2.9	-
		100	154 \pm 1.2	0.8	102.6	150 \pm 1.6	1.0	100.0
		300	352 \pm 0.8	0.2	100.5	347 \pm 3.8	1.1	99.1
Saline sample ^a	100 \pm 1.2	0	105 \pm 0.8	0.8	105.0	102 \pm 2.3	2.2	102.0
	300 \pm 1.0	0	305 \pm 1.5	0.5	105.0	300 \pm 3.4	1.1	100.0

^aContaining 30% w/v of Na_2SO_4 .

Table 5. Comparison between the Present Method and other Microextraction Works to Concentration, and Determination of Cd(II) Ion

Preconcentration method	Measurement system	LOD ($\mu\text{g l}^{-1}$)	LOQ ($\mu\text{g l}^{-1}$)	RSD (%)	EF ^j	ER ^k	Ref.
VALLME ^a	FAAS	2.90	-	4.1	35	88.0-106.0	[31]
DLLME-SQT ^b	FAAS	0.50	1.50	8.2	-	85.2-111.7	[32]
BCDLLME ^c	FAAS	1.20	-	2.1	34.5	97.9-99.6	[33]
ISFME	FAAS	0.07	0.21	2.4	78	97.5-104.2	[34]
DLLME	FAAS	0.40	-	1.9	55	94.4-101.5	[35]
SX ^d	FAAS	0.90	-	<4.0	20	90.0-100.0	[36]
DLLME ^e	FAAS	0.20	-	-	250	97.0-100.0	[37]
DLLME	FAAS	0.31	1.03	-	45	99.2-103.6	[38]
SPSLLM ^f	FAAS	0.16	-	5.4	30	94.0-103.0	[39]
SM- μ -SPE ^g	FAAS	0.15	0.50	3.1	25	98.5-99.5	[40]
VADL-SFOD-SQT ^h	FAAS	0.81	2.69	<6.0	-	92.5-104.9	[41]
USAEME ⁱ	FAAS	0.91	-	1.6	95	94.2-101.7	[42]
ISFME	FAAS	0.23	0.76	1.8	75	98.0-105.0	This work

^aVortex-assisted liquid-liquid microextraction. ^bDispersive liquid-liquid microextraction-slotted quartz tube. ^cBackground corrected dispersive liquid-liquid microextraction. ^dSolvent extraction. ^eDispersive liquid-liquid microextraction. Switchable-polarity solvent based liquid-liquid microextraction. ^fSurfactant mediated magnetic solid phase micro-extraction. ^gVortex-assisted dispersive liquid-liquid-solidified floating organic drop microextraction and slotted quartz tube. ^hUltrasound-assisted emulsification-microextraction. ⁱEnrichment factor. ^jExtraction recovery. ^kExtraction recovery.

measurement system was used to compare the actual capabilities of the methods, because the use of different measuring devices usually leads to differences in the ability of methods. As can be seen, the method shows satisfied and comparable characteristics for Cd determination in real water samples by means of high preconcentration factor, elevated sensitivity as well as lower limit of detection and very good precision.

CONCLUSIONS

The present ISFME analytical method is based on a dual use of a functionalized ionic liquid. Firstly, the functionalized ionic liquid is used as an extractant phase to achieve the efficient separation and preconcentration of the cadmium metal ion, and secondly, functionalized ionic liquid acts as a complexing agent to cadmium complexation at certain conditions which can be said the method has a simple system and free of any complexing

agent. 3-(2-(bis(2-(tert-butoxy)-2-oxoethyl)amino)ethyl)-1-methylimidazolium bromide was used as a functionalized ionic liquid to extract the cadmium metal ions. The ISFME method was successfully applied for the preconcentration and determination of a trace amount of Cd(II) ions in saline and real samples. Analytical characteristics are good, comparable, and better rather than most several microextraction methods for concentration and determination of Cd(II) ion in terms of LOD, RSD, and EF. The method was robust against the very high content of salt (up to 30% w/v). Furthermore, due to the use of environmentally friendly functionalized ionic liquids (most of these compounds have degradation temperatures higher than 350 °C) and since only very small amount of ionic liquids is used, so it can be claimed that the ISFME method has the low toxicity and classified as a green extraction or preconcentration technique. Finally, the proposed method opens a new window in the analytical applications due to its low cost, ease in experimental steps and use of non toxic

solvents as an extracting agent

Conflicts of Interest

No potential conflict of interest relevant to this article was reported.

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