

Investigation on *Dracaena Sanderiana* Phytoremediation Ability for Hg and Cd using Multivariate Optimized Task Specific Ionic liquid-based Dispersive liquid-liquid Microextraction

Sereshti, H. *, Eskandarpour, N., Samadi, S. and Aliakbarzadeh, Gh.

Department of Chemistry, Faculty of Science, University of Tehran, Tehran, Iran

Received 22 March 2014;

Revised 11 May 2014;

Accepted 21 May 2014

ABSTRACT: The task specific ionic liquid (TSIL), tricaprylmethylammonium thiosalicylate ([A336][TS]), was synthesized, characterized and subsequently used as extraction solvent in dispersive liquid-liquid microextraction (DLLME) technique. The TSIL-DLLME method followed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) was applied to determination of trace mercury (Hg) and cadmium (Cd) in aqueous sample solutions. The significant parameters of the extraction process were optimized using a response surface methodology. Under the optimal conditions (pH, 6.50; concentration of TSIL, 47.50 mg mL⁻¹; and salt concentration, 8.50 % (w/v)), the analytical figures of merit for Hg and Cd were obtained as: LDR, 1-5000 µg/L; determination coefficients (R²), 0.9990 and 0.9991; LODs (limit of detections), 0.28 and 0.22 µg/L; RSD, 1.1% and 1.0%, respectively. In addition, the removal of Hg²⁺ and Cd²⁺ ions by the plant *Dracaena sanderiana* was investigated using the developed method. The Hg and Cd uptake and storage by the plant from contaminated waters was also evaluated to be approximately equal to 10.32 and 30.90 mg/kg, respectively. The relative recoveries of Hg and Cd were 97.50% and 92.37%, respectively.

Key words: *Dracaena sanderianam*, Cadmium, Mercury, ICP-AES

INTRODUCTION

Mercury and cadmium have been respectively ranked as the third and the seventh in the priority list of hazardous substances by the Agency for Toxic Substances and Disease Registry (ATSDR) due to their toxicity, mobility, biopersistent and relatively long residence time in the environment. These heavy metals are released into the environment from both anthropogenic and natural sources, and eventually end up in soils or surface waters. The contaminated natural and drinking waters with Hg and Cd have the potential to negatively affect human health and environmental conditions. Different analytical techniques including flame atomic absorption spectrometry (FAAS) (Rojas, *et al.*, 2011; Stanisiz, *et al.*, 2013), graphite furnace-atomic absorption spectrometry (GF-AAS) (Anthemidis and Ioannou, 2010; Moraes, *et al.*, 2013), inductively coupled plasma-mass spectrometry (ICP-MS) (Djedjibegovic, *et al.*, 2012; Guo, *et al.*, 2012; Chen *et al.*, 2010), and ICP-AES (Bidari, *et al.*, 2011; Sereshti, *et al.*, 2012) have been widely used for determination of Hg and Cd in environmental and biological samples. Between these techniques, ICP-AES is one of the most

versatile and rapid multi-elemental analysis method with a wide linear dynamic range, excellent matrix tolerance, relatively low interference effects, and improved LOD. However, due to inadequate sensitivity and matrix interferences, direct determination of trace metal ions is restricted. Therefore, a sample pretreatment procedure for isolation and/or enrichment of analytes prior to the analysis is necessary (Sereshti, *et al.*, 2012).

A variety of sample preparation methods such as ultrasound-assisted extraction (UAE) (Rezić, 2009), sequential injection extraction (SIE) (Van Staden and Taljaard, 2004), solidified floating organic drop microextraction (SFODME) (Zolfonoun, *et al.*, 2008) solid phase extraction (SPE) (Zolfonoun, *et al.*, 2008; Hassanien, 2010) magnetic solid phase microextraction (MSPME) (Chen, *et al.*, 2010), cloud point extraction (CPE) (Shoaei *et al.*, 2012), and ionic liquid (IL)-based liquid-liquid extraction (LLE) (De los Rios, *et al.*, 2012; Hernández-Fernández, *et al.*, 2010), IL-liquid phase microextraction (LPME) (Fischer, *et al.*, 2011), IL-based solid phase microextraction (SDME) (Wen, *et al.*, 2013), IL-DLLME (Yousefi and Shemirani, 2010; Li, *et al.*,

*Corresponding author E-mail: sereshti@khayam.ut.ac.ir

2011), and TSIL-based DLLME (Mohamadi and Mostafavi, 2011) have been applied for separation and determination of Hg^{2+} and Cd^{2+} ions in various matrices. Among these techniques, IL-based extraction methods such as TSIL-based DLLME are simple, fast, efficient and eco-friendly. ILs are ionic, non-molecular solvents composed of an organic cation paired with an anionic (organic or inorganic) counter ion (Mohamadi and Mostafavi, 2011; Trujillo-Rodríguez, *et al.*, 2013). ILs can be used in place of organic solvents in LLE of metal ions by adding extractants or attaching a metal ion coordinating group directly to them. The ILs bearing coordinating groups can significantly increase the distribution ratios of metal ions in IL phase. TSILs are a special category of ILs that incorporate additional functional groups into one or both of the ions, and designed to impart to them particular properties or reactivities (Mohamadi and Mostafavi, 2011; Davis, 2004). TSILs can be used in the sample pre-treatment to reduce the usage of volatile organic solvents, and to develop “environmentally friendly” green separation technology. The metal ion can be quantitatively back-extracted from IL phase, so that TSIL can be reused in the extraction of metal ions as a cycle solvent. The DLLME method was first introduced by Assadi *et al* in 2006. In this technique, a suitable mixture of extraction and disperser solvents is rapidly injected into aqueous sample solution. Thereby, the extraction solvent is dispersed as very tiny droplets in the aqueous phase, and thus a cloudy solution is generated. Accordingly, a very large contact surface area between two phases is achieved. Then, the extractant is separated from the cloudy solution by centrifugation, and eventually analyzed for determination of analyte(s) by an appropriate instrumental technique (Rezaee, *et al.*, 2006).

In addition to the above mentioned methods, biosorption and phytoremediation have been developed for the removal of heavy metals from water sources. This method uses living plants to eliminate pollutants from environmental media including contaminated soils and waters. Phytoremediation is an eco-friendly and cost-effective strategy which is able to treat polluted waters without using chemicals that may be hazardous or damage the environment (Ali, *et al.*, 2013). Some plants, named hyper-accumulators, are capable to store great amounts of metals, even metals that are not necessary for plant growth and function (Miller, 1996). Phytoextraction is a subcategory of phytoremediation in which metal-accumulating plants are used to clean soils and waters contaminated with toxic metals. This technique is the most rapidly developing component of this technology (Raskin, 1997).

In the present study, TSIL-based DLLME coupled with ICP-AES technique was used for the measurement of Hg and Cd in aqueous solutions. The TSIL, [A336][TS], was synthesized and employed as the extraction solvent. A central composite design is applied to the optimization of the extraction process and modeling the data. In addition, the proposed method was used to evaluate the capability of the plant *Dracaena sanderiana* to extract and accumulate Hg and Cd from contaminated waters. This plant belongs to *Agavaceae* family, and is native to Africa and ordinarily found in tropical and subtropical open lands of Africa and India. It can grow in poor conditions and requiring little direct sun light, so that it can be placed anywhere in a house. The plant cuttings can be grown into bare rooted plants in water or other root promoting media without soil around their root system (Junaid, *et al.*, 2008; Su, *et al.*, 2007).

MATERIALS & METHODS

A Varian Vista-MPX ICP-AES (Melbourne, Australia) equipped with a slurry nebulizer and a charge coupled device detector was employed for determination of trace metal ions. A 500 MHz Bruker Fourier transform-nuclear magnetic resonance (FT-NMR) spectrometer (Karlsruhe, Germany) was used to record ^1H NMR spectra. The infrared (IR) spectra were obtained on a Shimadzu FT-IR spectrophotometer (Kyoto, Japan). The pH values were measured with an inoLab pH-720 calibrated pH-meter (Weilheim, Germany). The centrifuges were performed with a Hermle Z200A centrifuge (Wehingen, Germany). A Eurosonic 4D Euronda (Montecchio Precalcino, Italy) ultrasonic water bath was used for sonication. Methanol (MeOH), ethanol, carbon tetrachloride (CCl_4), dichloromethane, acetic acid glacial, ammonium acetate, sodium chloride (NaCl), sodium hydroxide (NaOH), thiosalicylic acid, cadmium nitrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), mercuric chloride (HgCl_2), nitric acid (HNO_3), and perchloric acid (HClO_4) all analytical grade were purchased from Merck Chemicals (Darmstadt, Germany). Aliquat[®]336 (tricaprylmethylammonium chloride) was purchased from Sigma-Aldrich (St. Louis, MO, USA). Standard stock solutions (1000 mg/L) of Hg and Cd were prepared by direct dissolution of appropriate amount of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and HgCl_2 in 1M HNO_3 solution. Buffer solution (pH=6.50) was prepared by adding appropriate amount of 1M NaOH solution to 1M acetic acid solution. The certified reference materials were NRCC-SLRS-4 (Riverine water) and SRM 1515 (Apple leaves). All of the laboratory glassware were pickled with HNO_3 10% and then rinsed with distilled water twice before applications. The plant *Dracaena sanderiana* was prepared from a local store in Tehran (capital of Iran).

The ionic liquid [A336][TS] with the chemical name of tricaprilmethylammonium thiosalicylate was synthesized according to the procedure described by Stojanovic *et al.* (Stojanovic, *et al.*, 2010) with a little modification. Briefly, proper amount of thiosalicylic acid was dissolved in a mixture of water/ethanol (1:1, v/v) and subsequently deprotonated with equivalent amount of NaOH. The solution was then added dropwise to equimolar amount of Aliquat336 under an inert atmosphere. After 4 h vigorously stirring at 45 °C, the olive-green organic phase (IL) was isolated in a separation funnel. In order to avoid loss of the IL during washing step, it was dissolved in an appropriate amount of dichloromethane, then washed with ice-cold deionized water for several times. Finally, the solvent was evaporated by a rotary evaporator at 40 °C, and then the resulting IL was dried for 24 h under vacuum at 40 °C.

5 mL of a standard solution of Hg and Cd (500 µg/L) at the pH value of 6.5, containing 8.5 % (w/v) NaCl was placed in a 12 mL screw cap glass test tube. Then, 1 mL methanolic solution of TSIL (consisted of 47.5 mg [A336][TS] and 47.5 µL CCl₄) was injected rapidly into the standard solution using a 2.0 mL syringe. Therewith, a cloudy solution, consisting of very tiny droplets of [A336][TS]/CCl₄ entirely dispersed in the aqueous standard solution, was formed. In this step, Hg²⁺ and Cd²⁺ ions linked the ionic liquid and thus were transferred into the droplets. Then, for the separation of the IL droplets coordinated with Hg²⁺ and Cd²⁺ ions, the cloudy solution was centrifuged at 4000 rpm for 5 min. Thereby, the IL phase was collected at the bottom of the test tube. In the next step, the upper aqueous phase was removed and the sedimented ionic liquid phase dried in an oven at 50 °C. Then, the residue was dissolved in 100 µL of concentrated HNO₃/HClO₄ (4:1, v/v) and was sonicated for 30 min at room

temperature. Finally, it was diluted to 1 mL with double distilled water and analyzed by ICP-AES. The statistical optimization consisted of designing the experiments, modeling the data, analysis of variance (ANOVA) and construction of response surface plots were carried out using the Design-Expert 7.1.6 software package. An ICP expert software package version 2.0, was used for ICP-AES data acquisition and analysis.

RESULTS & DISCUSSION

The synthesized TSIL, was characterized using FTIR and ¹HNMR spectroscopy. Fig. 1a represents the FTIR spectra of thiosalicylic acid, Aliquat®336 and the synthesized [A336][TS] with the main absorption bands marked with the related functional groups. The ¹HNMR spectra of [A336][TS] were displayed in Fig. 1b. The ¹HNMR spectrum of the cation consisted of 0.83-0.86, 1.21-1.26, 1.54-1.62 (m, 45H, -CH₂-CH₃), 2.95 (s, 3H, N-CH₃), 3.09-3.12 (m, 6H, N-CH₂-); and the ¹HNMR spectrum of the anion included 6.74-6.77 (t, 1H_{arom}, -C₅-H), 6.96-6.99 (t, 1H_{arom}, -C₄-H), 7.46-7.48 (d, 1H_{arom}, -C₃-H), 8.01-8.07 (d, 1H_{arom}, -C₆-H-) and 7.26 (CDCl₃, solvent).

In order to obtain the best experimental conditions, the main parameters affecting the efficiency of the proposed method including pH, concentration of TSIL and salt concentration were optimized statistically using a rotatable and orthogonal central composite design (CCD) (Bezerra, *et al.*, 2008). A CCD is composed of a two-level factorial design ($N_f=2^f$), a star design ($N_a=2f$), and center points (N_c), where f is the number of parameters (factors). Center points are commonly repeated to get a good estimate of experimental error (Sereshi, *et al.*, 2009). The star points are located at $+\alpha$ and $-\alpha$ from the center of the experimental domain. Therefore, a CCD has five levels for each factor ($\pm\alpha$, ± 1 , 0). In a rotatable design, the variance of the

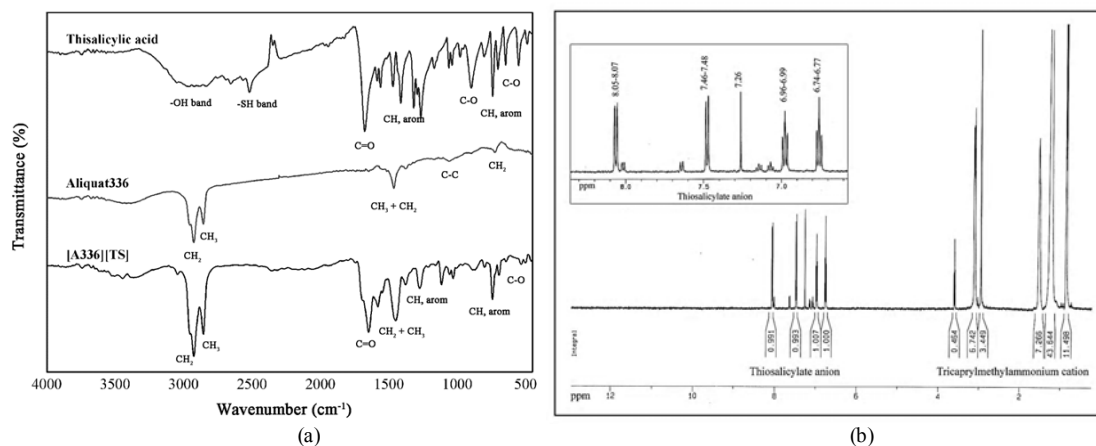


Fig. 1. a) The FT-IR; and b) The ¹HNMR spectra of thiosalicylic acid, Aliquat®336, and [A336][TS] ionic liquid

calculated response for all points, with the same distance from the center of the design, is constant. An experimental design is orthogonal if each parameter is evaluated independently of all the other factors. The values of α and N_0 required to provide the rotatability and orthogonality of the design were calculated equal to ± 1.682 and 9 by using Eqs. (1) and (2), respectively.

$$\alpha = \sqrt[4]{N_f} \quad (1)$$

$$\alpha = \sqrt{\frac{\sqrt{(N_f + N_a + N_0)N_f} - N_f}{2}} \quad (2)$$

The total number of experiments (N) was obtained equals to 23 with the following equation.

$$N = N_f + N_a + N_0 \quad (3)$$

The experiments were performed in a randomized order to minimize the effect of unpredicted factors on the response. Based on the experimental results of the design, a second-order polynomial model with the most sensible statistics, in terms of the coded values of the significant factors, was obtained (Eq. (4)). The model consists of three main effects (P , C and S), three two-factor interaction effects (PC , PS and CS), and three curvature effects (P^2 , C^2 , and S^2), where ER (extraction recovery) is the response, b_0 is the intercept and the b terms (b_0 to b_9) are the regression coefficients.

$$ER = b_0 + b_1P + b_2C + b_3S + b_4PC + b_5PS + b_6CS + b_7P^2 + b_8C^2 + b_9S^2 \quad (4)$$

$$b_0 = 93.09; b_1 = 0.84; b_2 = 2.61; b_3 = 1.09; b_4 = 4.40; b_5 = 0.84; b_6 = 4.14; b_7 = 4.16; b_8 = 8.38; b_9 = 9.13.$$

The positive sign of a coefficient demonstrate that as the value of one effect changes, the value of the response moves in the same direction too, while for the negative sign the response it operates in the opposite direction. The absolute value of the coefficients measures the weight of the relationship factors and response.

In order to evaluate the precision, fitness and significance, and the effect of individual factors and their interactions on the response, analysis of variance (ANOVA) was performed. The F-value which is the test for comparing the variance associated with a term with the residual variance, implies that the model is significant. The *lack of fit* that is the weighted sum of squared deviations between the mean response at each factor level and the corresponding fitted value, with the F-value of 0.12 and *p-value* (probability of error value) of 0.9836 is not significant for the model. The model terms with *p-values* less than 0.05 are significant for 95% confidence intervals and values greater than 0.1000 indicate the model terms are not significant. Therefore, P , C , S , PC , PS , CS , P^2 , C^2 , and S^2 are the significant model terms (Eq. (4)).

The coefficient of determination (R^2), indicates how well the data points fit the model. Using the following equation, R^2 was calculated equal to 0.9997.

$$R^2 = 1 - \left[\frac{SS_{residual}}{SS_{residual} + SS_{model}} \right] \quad (5)$$

where $SS_{residual}$ is the residual sum of square, and SS_{model} is the model sum of square. Adjusted- R^2 ($adj-R^2$) is a modification of R^2 that adjusts for the number of explanatory terms in a model. Unlike R^2 , the $adj-R^2$ increases only if the new term improves the model more than would be expected by chance. The $adj-R^2$ can be negative, and will always be less than or equal to R^2 . In this case, $adj-R^2$ was equal to 0.9995.

$$adj - R^2 = \left[\left(\frac{SS_{residual}}{df_{residual}} \right) / \left(\frac{SS_{residual} + SS_{model}}{df_{residual} + df_{model}} \right) \right] \quad (6)$$

Predicted- R^2 ($pred-R^2$) is a measure of the amount of variation in new data explained by the model. Predicted R-squared can prevent over-fitting the model and can be more useful than adjusted R-squared for comparing models because it is calculated using observations not included in model estimation. The $pred-R^2$ and the $adj-R^2$ should be within 0.20 of each other. Otherwise there may be a problem with either the data or the model. Here, $pred-R^2$ was equal to 0.9995 and in reasonable agreement with $adj-R^2$.

$$pred - R^2 = 1 - \left[\frac{PRESS}{SS_{residual} + SS_{model}} \right] \quad (7)$$

$$PRESS = \sum_{i=1}^n (e_{i_0-i})^2 = \sum_{i=1}^n \left(\frac{e_i}{1 - h_{ii}} \right)^2$$

where $PRESS$ is (*predicted residual error sum of squares*) is a measure of how the model fits each point in the design. The $PRESS$ is computed by first predicting where each point should be from a model that contains all other points except the one in question. The squared residuals (difference between actual and predicted values) are then summed.

Adequate precision that is a signal to noise ratio, compares the range of the predicted values at the design points to the average prediction error. Ratios greater than 4 indicate adequate model discrimination. In the present work the adequate precision is equal 176.24. Therefore, this model can be used to navigate the design space.

$$\left[\frac{\max(\hat{Y}) - \min(\hat{Y})}{\sqrt{\hat{\sigma}(\hat{Y})}} \right] > 4 \quad \hat{\sigma}(\hat{Y}) = \frac{1}{n} \sum_{i=1}^n V(\hat{Y}) = \frac{p\sigma^2}{n} \quad (8)$$

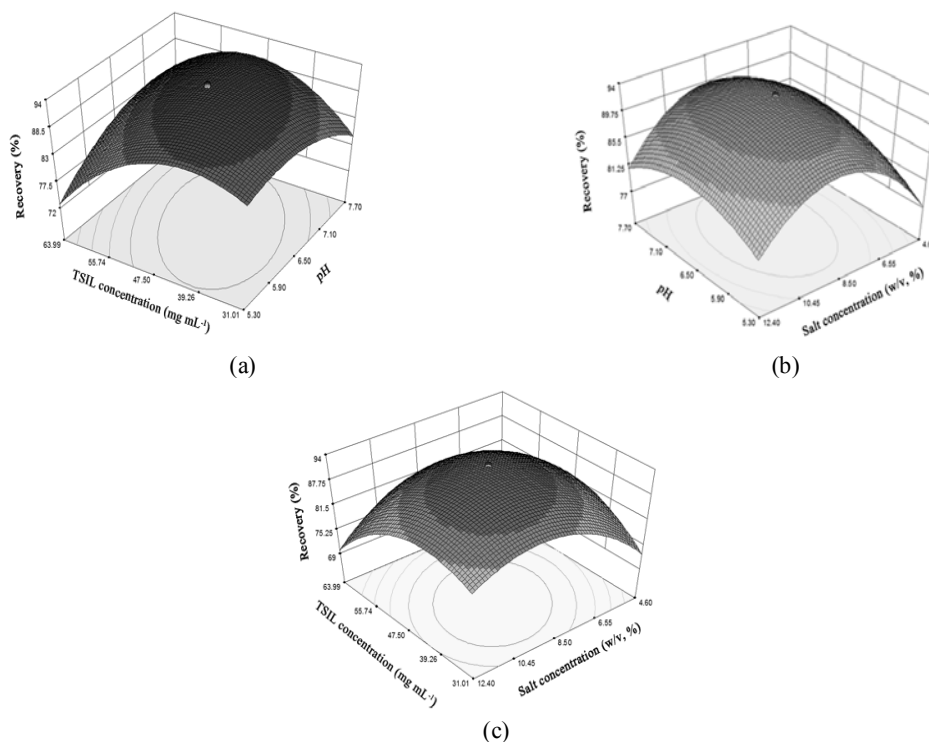


Fig. 2. The 3D response surface plots for the effect of: a) pH-TSIL concentration, b) pH-salt concentration, and c) TSIL concentration-salt concentration on the average ER (%)

where p is number of model parameters (including intercept (b_0) and any block coefficients), σ^2 is residual MS from ANOVA table, and n is number of experiments.

To see the effect of significant interactions on the response, three-dimensional (3D) response surface plots were constructed. These plots represent the relationship between the response (ER) and levels of two factors simultaneously, while the other factors are fixed at their center points. Fig. 2a depicts the effect of TSIL concentration and pH on the extraction recovery of Hg^{2+} and Cd^{2+} . The TSIL concentration demonstrated quadratic effect on the response; hence ER increased up to about 47.5 mg m/L of TSIL/MeOH followed by a decline with its further increase. The pH value that is one of the most important parameters controlling the complexation process, displayed a quadratic effect on the response yielding maximum at 6.5. At pH values less than 6.5, the complexes of Hg^{2+} and Cd^{2+} with TSIL dissociate due to protonation of thiosalicylate, and thus ER is decreased. While at pH values higher than 6.5, the $-\text{SH}$ functional group of thiosalicylate is deprotonated and hence dissolves in aqueous phase. Moreover, at the pH values greater than 8.50, Hg^{2+} and Cd^{2+} ions begin to precipitate as metal hydroxides and oxides. Both phenomena at pH values higher than 6.5, result in reduction of ER.

The effect of salt concentration and pH on ER is shown in Fig. 2b. Salt concentration displayed a quadratic effect on the response yielding maximum 8.5% (w/v). By increasing the salt concentration from 4.6 up to about 8.5% the response increases due to the salting-out effect, but decreases with further increase of salt concentration. The later may be attributed to the increased viscosity of aqueous solution overcame the salting-out effect, resulted in difficult mass transfer and low extraction efficiency (Ge and Lee, 2012). The effect of pH on the response is also quadratic with the maximum response at 6.5. Fig. 2c indicates response surface of the effect of TSIL concentration and salt concentration on the ER. Both factors influenced the response in a quadratic manner. ER improves with increasing TSIL concentration up to 47.5 mg m/L, but decreases with increasing TSIL concentration due to the dilution effect.

Eventually, the optimum value of the effective factors (pH, concentration of TSIL and salt) was estimated using numerical optimization of the Design Expert software package. In this strategy, the criteria for each factor are combined into an overall desirability function. The program seeks to maximize this function. The goal seeking begins at a random starting point and proceeds up the steepest slope to a maximum. By

starting from several points in the design space chances improve for finding the “best” local maximum. Therewith, the optimal conditions were obtained as: pH, 6.50; concentration of IL, 47.50 mg mL⁻¹; and NaCl concentration, 8.50 % (w/v).

To evaluate the performance of the method, the main analytical characteristics of the method were established under the optimal conditions. The calibration curves were prepared with ten concentration levels of each metal ions. The method was linear within the range of 1-5000 µg/L for Cd²⁺ and

Hg²⁺ and characterized by the determination coefficients (R^2) of 0.9991 and 0.9990 for Cd²⁺ and Hg²⁺, respectively. The LODs were calculated according to $3S_d/m$ (S_d is standard deviation of the blank signal (n=5)), and m is slope of the calibration graph) equal to 0.22 µg/L for Cd and 0.28 µg/L for Hg. The precision based on RSD (n=3) was equal to 1.0% for Cd²⁺ and 1.1% for Hg²⁺. Reproducibility of the method was studied with examination of four sample solutions in three times on four successive days in accordance with the proposed procedure. The RSDs were equal to 3.05% and 5.67% for Cd²⁺ and Hg²⁺, respectively. The

Table 1. Effect of coexisting ions on the extraction recovery of Cd²⁺ and Hg²⁺ ions

Interference	Interference to analyte ratio (w/w) ^a	Recovery (%)	
		Cd ²⁺	Hg ²⁺
K ⁺	4000	103.53	100.83
Ca ²⁺	2000	98.97	97.58
Ni ²⁺	25	95.61	93.05
Cu ²⁺	10	93.09	90.26
CO ₃ ²⁻	400	97.54	96.38
PO ₄ ³⁻	400	102.21	91.77
SO ₄ ²⁻	200	92.55	90.86

^aConcentration of analyte is 500 µg/L.

Table 2. Analysis of the certified reference materials (CRM) for the determination of Cd²⁺ and Hg²⁺ with IL-based DLLME-ICP-AES method

	SRM 1515 Apple leaves		NRCC-SLRS-4 Riverine water	
	Cd (µg/g)	Hg (µg/g)	Cd (µg/L)	Hg (µg/L)
Certified value	0.013 ± 0.002	0.044 ± 0.004	0.012 ± 0.002	n.r. ^b
Added	5.00	10.00	5.00	10.00
Amount found ^a	5.02 ± 0.02	9.62 ± 0.04	4.96 ± 0.03	9.73 ± 0.06
Recovery (%)	100.14	95.78	98.96	97.3

^aAverage ± standard deviation (n=3). ^bNot reported.

Table 3. Determination of Cd²⁺ and Hg²⁺ in real samples (the plant *Dracaena sanderiana* and drinking water)

Sample	Cd ²⁺	Hg ²⁺
<i>Dracaena sanderiana</i> ^a (mg/kg)	10.32 ^b ± 0.03	30.90 ^c ± 0.08
Added (mg/kg)	10	35
Found ^a (mg/kg)	20.07 ± 0.06	63.23 ± 0.18
Relative recovery (%)	97.5	92.37
Drinking (tap) water (µg/L)	n.d. ^d	n.d.
Added (µg/L)	500	500
Found ^a (µg/L)	491.05 ± 5.19	467.30 ± 5.23
Relative recovery (%)	98.21	93.46

^aAverage ± standard deviation (n=3). ^{b,c}The amount of cadmium^a and mercury^b accumulated in the growing sprouts of the plant placed in the water containing 1 mg L⁻¹ of Cd²⁺ and Hg²⁺ ions (pH, 3-4) for 16 days. ^dNot detected.

selectivity of the proposed method for determination of trace levels of Hg^{2+} and Cd^{2+} , was evaluated by the recovery of the analytes in the presence of potential interference from coexisting ions. For this purpose, 5.0 mL of the standard solution of Hg^{2+} and Cd^{2+} (500 $\mu g/L$) with different interference to analyte ratios of common coexisting ions was tested according to the proposed procedure and the results are given in Table 1. The possible interferences were evaluated as a $\pm 10\%$ error in the recovery of the analytes. It was indicated that the method has a good tolerance to matrix interference and no considerable adverse effect on determination of the analytes was observed.

The accuracy and applicability of the method was assessed with the measurement of Hg^{2+} and Cd^{2+} in certified reference materials including SRM 1515 Apple leaves and NRCC-SLRS-4 Riverine water. The reference materials were treated according to the proposed procedure. The results given in Table 2 indicate a good agreement between the analyzed and certified values.

In order to demonstrate the efficiency of the method for extraction and determination of Cd and Hg in different type of matrices, it was applied to analysis of the plant *Dracaena sanderiana* and water samples.

First, a solution containing 1 mg/L of Hg^{2+} and Cd^{2+} ions with the pH value of 3-4 was prepared. Then, several sprouts of the plant were placed in the solution so that the roots and major portions of the stem were completely immersed. After appropriate time they were dried in an oven at 60-70 °C for 24 h, and finally ground into a homogenized powder. In the next step, 1.0 g of the ground plant was placed in a 50 mL beaker. Thereupon, 5 mL HNO_3 and 2 mL $HClO_4$ were added to it and heated to 100 °C on a heater in a fume hood to reach a final volume of approximately 3 mL. Afterward,

15 mL double distilled water was added to it and the solution was filtered through an acid-washed filter paper into a 50 mL volumetric flask and eventually made up to the mark with double distilled water. Finally, the solution was analyzed by ICP-AES for Hg and Cd contents.

The tap water sample was taken from our laboratory and analyzed (spiked and non-spiked).

The relative recovery (RR) was obtained using Eq. (9).

$$RR = \frac{C_{found} - C_{real}}{C_{added}} \times 100 \quad (9)$$

where C_{found} is concentration of analyte in the final solution after addition of a known amount of a standard into the real sample, C_{real} is the concentration of analyte in the real sample, and C_{added} is concentration of a known amount of the standard which was spiked into the real sample. The results given in Table 3, show that the high relative recoveries for the spiked samples (92.37-93.46% for Hg^{2+} and 97.50-98.21% for Cd^{2+}) are acceptable and the sample matrices had no significant interference of matrix with the analytes.

In order to evaluate the plant capability to accumulate Hg^{2+} and Cd^{2+} ions, the influence of concentration and time were studied and the results were presented in Fig. 3. The results displayed in Fig. 3a demonstrate that by increasing concentration of the metal ions in water, more Hg^{2+} and Cd^{2+} were accumulated in the plant. On the other hand, the results represented in Fig. 3b show that with increasing the time, the plant uptake increased with a jump within 10th to 16th days and then remained constant. Therefore, it can be concluded that the plant is capable to absorb and accumulate considerable amounts of Cd (1900 mg/L) and Hg (12500 mg/L).

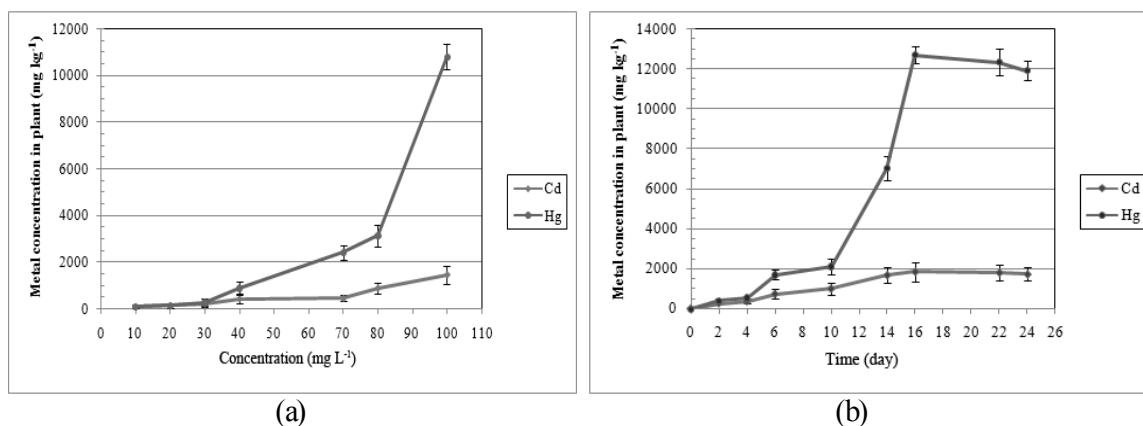


Fig. 3. a) The influence of concentration; and b) the effect of exposure time on the accumulation of Hg^{2+} and Cd^{2+} in *Dracaena sanderiana*

Table 4. Comparison of the proposed method with other methods for determination Cd²⁺ and Hg²⁺

Method	Detection	Analyte	LDR (µg/L)	LOD (µg/L)	RSD %	Ref.
SFODME	ETV-ICP-MS	Cd, Hg	0.01-20, 0.02-20	0.0020, 0.0041	2.8, 4.5	[10]
SPE	FAAS ^a , CV ^b -AAS	Cd, Hg	-	0.013, 0.002	2	[16]
MSPME	ETV-ICP-MS	Cd, Hg	0.01-10, 0.01-10	0.00072, 0.00082	5.5, 10.2	[11]
DLLME	CZE ^c -UV	Hg	1-1000	0.62	4.1	[26]
DLLME	FAAS	Cd	1-400	0.4	1.7	[6]
CPE	ICP-OES	Hg	10-100	1.1	3.2	[18]
CPE	ICP-OES	Cd	20-500 ^d & 15-500 ^e	4.0 ^d & 5.3 ^e	1.6 ^d & 3.3 ^e	[19]
USAEME ^f	ICP-OES	Cd	1-1000	0.19	4.27	[13]
IL-based SDME	W-coil ET-AAS	Cd	0.2-2	0.015	5.2	[24]
IL-based DLLME	UV-Vis.	Hg	12-140	3.9	1.7	[27]
IL-based DLLME	FAAS	Cd	0.1-15	0.03	2.3	[25]
TSIL-DLLME	FAAS	Cd	-	1.16	1.8	[28]
TSIL-USA DLLME	CV-AAS	Hg	0.5-100	0.03	4	[5]
TSIL-DLLME	ICP-OES	Cd, Hg	1-5000, 2-5000	0.22, 0.28	1.0, 1.1	This work

^aFlame atomic absorption spectrometry. ^bCold vapor. ^cCapillary zone electrophoresis. ^d[1-(2-Pyridylazo)-2-naphthol](PAN) as chelating agent. ^e[2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol] (5-Br-PADAP) as chelating agent. ^fUltrasound-assisted emulsification microextraction.

Comparison with other analytical methods

A literature review was conducted searching for the articles related to the methods for determination of Hg and Cd for a comparative study. The results summarized in Table 4, indicate that the LDR of the proposed method for Hg²⁺ and Cd²⁺ is considerably wider than that of the other methods. The precision based on the relative standard deviation is better than that obtained by other methods. And the LOD in this study for Hg²⁺ is better than the most of other methods and for Cd²⁺ is comparable with the precision of other methods.

CONCLUSIONS

Task specific ionic liquids (TSILs) made a generation of state-of-the-art solvents which can be designed to play the dual role of extraction solvent and liganding agent for selective extraction and determination of metal ions or molecules with special functional groups. The TSIL ([A336][TS]) was synthesized and employed in DLLME in tandem with ICP-AES for the extraction and determination of Hg²⁺ and Cd²⁺ in water solutions. The main factors of the extraction process were optimized using a central composite design methodology with the least number of experiments. The data was modeled with a second order polynomial equation. The proposed analytical method has a relatively wide LDR (1-5000 ppb), a LOD better than 0.3 ppb, and low solvent consumption (1 mL). The optimized method was

used to evaluate capability of the plant *Dracaena sanderiana* to extract and accumulate Hg and Cd. The results indicated that the plant can be considered as an effective biosorbent for the removal of Hg and Cd from contaminated waters. The uptake and accumulation of the analytes in the plant were affected by the exposure time and the metals concentration. In addition, the *Dracaena sanderiana* was able to accumulate Hg about six times higher than Cd.

ACKNOWLEDGEMENTS

The authors would like to thank University of Tehran for the financial support of this project

REFERENCES

- Ali, H., Khan, E., Sajad, M. A. (2013). Phytoremediation of heavy metals—Concepts and applications. *Chemosphere*, **91**, 869-881.
- Anthemidis, A. N. and Ioannou, K. I. G. (2010). Development of a sequential injection dispersive liquid-liquid microextraction system for electrothermal atomic absorption spectrometry by using a hydrophobic sorbent material: Determination of lead and cadmium in natural waters. *Anal. Chim. Acta*, **668**, 35-40.
- Bezerra, M. A., Santelli, R. E., Oliveira, E. P., Villar, L. S. and Escalera, L. A. (2008). Response surface methodology (RSM) as a tool for optimization in analytical chemistry. *Talanta*, **76**, 965-977.
- Bidari, A., Ganjali, M. R., Assadi, Y., Kiani, A. and Norouzi, P. (2011). Assay of total mercury in commercial food

- supplements of marine origin by means of DLLME/ICP-AES. *Food. Anal. Methods*, **5**, 695–701.
- Chen, B., Heng, S., Peng, H., Hu, B., Yu, X., Zhang, Z., Pang, D., Yue, X. and Zhu, Y. (2010). Magnetic solid phase microextraction on a microchip combined with electrothermal vaporization-inductively coupled plasma mass spectrometry for determination of Cd, Hg and Pb in cells. *J. Anal. Atom. Spectrom.*, **25**, 1931-1938.
- Davis, J. H. Jr. (2004). Task-Specific Ionic Liquids. *Chem. Lett.*, **33**, 1072-1077.
- De los Ríos, A. P., Hernández-Fernández, F. J., Alguacil, F. J., Lozano, L. J., Ginestá, A., García-Díaz, I., Sánchez-Segado, S., López, F. A. and Godínez, C. (2012). On the use of imidazolium and ammonium-based ionic liquids as green solvents for the selective recovery of Zn (II), Cd (II), Cu (II) and Fe (III) from hydrochloride aqueous solutions. *Sep. Purif. Technol.*, **97**, 150-157.
- Djedjibegovic, J., Larssen, T., Skrbo, A., Marjanović, A. and Sober, M. (2012). Contents of cadmium, copper, mercury and lead in fish from the Neretva river (Bosnia and Herzegovina) determined by inductively coupled plasma mass spectrometry (ICP-MS). *Food Chem.*, **131**, 469-476.
- Fischer, L., Falta, T., Koellensperger, G., Stojanovic, A., Kogelnig, D., Galanski, M., Krachler, R., Keppler, B. K. and Hann, S. (2011). Ionic liquids for extraction of metals and metal containing compounds from communal and industrial waste water. *Water Res.*, **45**, 4601-4614.
- Ge, D. and Lee, H. K. (2012). Sonication-assisted emulsification microextraction combined with vortex-assisted porous membrane-protected micro-solid-phase extraction using mixed zeolitic imidazolate frameworks 8 as sorbent. *J. Chromatogr. A*, **1263**, 1-6.
- Guo, X., He, M., Chen, B. and Hu, B. (2012). Solidified floating organic drop microextraction combined with ETV-ICP-MS for the determination of trace heavy metals in environmental water samples. *Talanta*, **94**, 70-76.
- Hassanien, M. (2010). Silica glass modified with flavonoid derivatives for preconcentration of some toxic metal ions in water samples and their determination with ICP-MS. *Environ. Monit. Assess*, **167**, 587-598.
- Hernández-Fernández, F. J., Ríos, A. P., Ginestá, A., Sánchez-Segado, S., Lozano, L. J., Moreno, J. I. and Godínez, C. (2010). Use of ionic liquids as green solvents for extraction of Zn²⁺, Cd²⁺, Fe³⁺ and Cu²⁺ from aqueous solutions. *Chemical Engineering Transactions*, **21**, 631-636.
- Junaid, A., Mujib, A., Sharma, M. P. (2008). Effect of growth regulators and ethyl methane sulphonate on growth, and chlorophyll, sugar and proline contents in *Dracaenasanderiana* cultured *in vitro*. *Biol. Plantarum*, **52**, 569-572.
- Li, J., Lu, W., Ma, J. and Chen, L. (2011). Determination of mercury (II) in water samples using dispersive liquid-liquid microextraction and back extraction along with capillary zone electrophoresis. *Microchim. Acta*, **175**, 301-308.
- Miller, R. R. (1996). Phytoremediation: technology overview report. Ground-Water Remediation Technologies Analysis Center, 615 William Pitt Way, Pittsburgh, PA, USA. 15238.
- Mohamadi, M. and Mostafavi, A., (2011). Flame atomic absorption determination of trace amounts of cadmium after preconcentration using a thiol-containing task-specific ionic liquid. *J. AOAC. Int.*, **94**, 959-967.
- Moraes, P. M., Santos, F. A., Cavecci, B., Padilha, C. C. F., Vieira, J. C. S., Roldan, P. S. and Padilha, P. D. M. (2013). GFAAS determination of mercury in muscle samples of fish from Amazon, Brazil. *Food Chem.*, **141**, 2614-2617.
- Raskin, I., Smith, R. D. and Salt, D. E. (1997). Phytoremediation of metals: using plants to remove pollutants from the environment. *Plant Biotechnol.*, **8**, 221–226.
- Rezaee, M., Assadi, Y., Milani Hosseini, M. R., Aghaee, E., Ahmadi, F. and Berjani, S. (2006). Determination of organic compounds in water using dispersive liquid–liquid microextraction. *J. Chromatogr. A*, **1116**, 1-9.
- Rezić, I. (2009). Optimization of ultrasonic extraction of 23 elements from cotton. *Ultrason. Sonochem.*, **16**, 63-69.
- Rojas, F. S., Ojeda, C. B. and Pavón, J. M. C. (2011). Dispersive liquid–liquid microextraction combined with flame atomic absorption spectrometry for determination of cadmium in environmental, water and food samples. *Anal. Methods*, **3**, 1652-1655.
- Sereshti, H., Entezari Heravi, Y., Samadi, S. (2012). Optimized ultrasound-assisted emulsification microextraction for simultaneous trace multielement determination of heavy metals in real water samples by ICP-OES. *Talanta*, **97**, 235-241.
- Sereshti, H., Karimi, M., Samadi, S. (2009). Application of response surface method for optimization of dispersive liquid–liquid microextraction of water-soluble components of *Rosa damascena Mill.* essential oil. *J. Chromatogr. A*, **1216**, 198-204.
- Shoae, H., Roshdi, M., Khanlarzadeh, N. and Beiraghi, A. (2012). Simultaneous preconcentration of copper and mercury in water samples by cloud point extraction and their determination by inductively coupled plasma atomic emission spectrometry. *Spectrochim. Acta Part A*, **98**, 70-75.
- Stanisz, E., Werner, J. and Matusiewicz, H. (2013). Mercury species determination by task specific ionic liquid-based ultrasound-assisted dispersive liquid–liquid microextraction combined with cold vapor generation atomic absorption spectrometry. *Microchem. J.*, **110**, 28-35.
- Stojanovic, A., Kogelnig, D., Fischer, L., Hann, S., Galanski, M., Groessl, M., Krachler, R. and Keppler, B. K. (2010). Phosphonium and Ammonium Ionic Liquids with Aromatic Anions: Synthesis, Properties, and Platinum Extraction. *Aust. J. Chem.*, **63**, 511-524.
- Su, L., Gao, S., Huang, Y., Ji, C., Wang, D., Ma, Y., Fang, R. and Chen, X. (2007). Complete genomic sequence of

Dracaena mottle virus, a distinct badnavirus. *Virus Genes*, **35**, 423-429.

Trujillo-Rodríguez, M. J., Rocio-Bautista, P., Pino, V. and Afonso, A. M. (2013). Ionic liquids in dispersive liquid-liquid microextraction. *TrAC, Trend Anal. Chem.*, **51**, 87-106.

Van Staden, J. F. and Taljaard, R. E. (2004). Determination of Lead (II), Copper (II), Zinc (II), Cobalt (II), Cadmium (II), Iron (III), Mercury (II) using sequential injection extractions. *Talanta*, **64**, 1203-1212.

Wen, X., Deng, Q., Wang, J., Yang, S. and Zhao, X. (2013). A new coupling of ionic liquid based-single drop microextraction with tungsten coil electrothermal atomic absorption spectrometry. *Spectrochim. Acta A*, **105**, 320-325.

Yousefi, S. R. and Shemirani, F. (2010). Development of a robust ionic liquid-based dispersive liquid-liquid microextraction against high concentration of salt for preconcentration of trace metals in saline aqueous samples: Application to the determination of Pb and Cd. *Anal. Chim. Acta*, **669**, 25-31.

Zolfonoun, E., Rouhollahi, A. and Semnani, A. (2008). Solid-phase extraction and determination of ultra trace amounts of lead, mercury and cadmium in water samples using octadecyl silica membrane disks modified with 5,50-dithiobis (2-nitrobenzoic acid) and atomic absorption spectrometry. *Int. J. Environ. Anal. Chem.*, **88**, 327-336.