Determination of Trace Amount of Lead (11) and Cadmium (11) Ions in Real Water and Real Samples by Flame Atomic Absorption Spectrometry After Cloud Point Extraction Using Selective Synthesis Ligand2-(3- indolyl) – 4,5 di phynyl imidazole

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ABSTRACT

A simple, sensitive and feasible cloud-point extraction (CPE) methodology has been developed for the separation and preconcentration of cadmium and lead ions in real samples. The metals in the aqueous solution were complexes with 2-(3- indolyl) - 4,5 di phynyl imidazole.(IDPI), at pH = 7.0 and Triton X-114 was added as surfactant. The variables effecting like concentration of Triton X-114 and HNO_3, bath temperature, centrifuge rate and time on the cloud-point extraction were optimized. Under optimum conditions, the response are linear over concentration range of 0.025-1.3(μg mL^{-1}) for Cd^{2+}, 0.064-1.27(μg mL^{-1}) for Pb^{2+} andRSD % (n =5) 1.4 for Cd^{2+}, 1.3 for Pb^{2+}, detection limits (3SDb/m, n =10, m = slope of calibration) of 0.15 (μg.mL^{-1}) for Cd^{2+} and 0.13 (μg.mL^{-1}) Pb^{2+} respectively. The enrichment factors were 31 for Cd^{2+} and 37 for Pb^{2+}. The preconcentration factors were 26 for Cd^{2+} and 31 for Pb^{2+} respectively.

Keywords: cloud-point extraction,2-(3- indolyl) - 4,5 di phynyl imidazole.(IDPI), separation, preconcentration

INTRODUCTION

Lead is a nonessential, heavy metal element, assumed to be toxic and a potential danger to living beings and a pollution source [1, 2]. Its most widespread toxic ions are within industrial wastewater, emissions from traffic, and pesticide residuals [3]. Cadmium is a toxic heavy metal of environmental concern as well and classified as a B1 carcinogen by the US Environmental

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Protection Agency [4]. Cadmium is widely used in various industries, which widely pollutes the environment. In order to remove hazardous pollutants from various environmental sources, e.g. aqueous media, many procedures such as co-precipitation, adsorption, ion-exchange, filtration, electrochemical techniques, and reverse osmosis were proposed. Because of their serious detrimental effects, itis important to determine trace levels of lead and cadmium in almost all matrices as well as to remove these pollutants effectively and cheaply.

Monitoring the presence of toxic trace elements in biological fluids is an extremely important task to evaluate the occupational and environmental exposure [5–7]. The common availability of the instrumentation, simplicity of the procedures, speed, precision and accuracy of the technique still make flame atomic absorption method an attractive alternative [8–10]. Monitoring of trace element concentrations in biological materials, particularly biological fluids, might be considered a difficult analytical task, mostly due to the complexity of the matrix and the low concentration of these elements, which requires sensitive instrumental techniques and often a preconcentration step [11-13].

Several analytical techniques such as flame atomic absorption spectrometry (FAAS) [14], electro thermal atomic absorption spectrometry (ETAAS) [15], and inductively coupled plasma-optical emission spectrometry (ICP-OES) [16], and kinetic- Spectrophotometry [17]. However, the detection limit for measurement of low levels of cadmium and lead ions in samples is not suitable, therefore the preconcentration before measurement with flame atomic absorption spectrometry is necessary. The old methods of separating for example a liquid-liquid extraction are used toxic organic solvents which are dangerous to the environment and humans [18-20].

Cloud point extraction (CPE), employed in analytical chemistry to separate and preconcentrate organic compounds and metal ions, has been well reviewed [21] Cloud point extraction is the process in which the surfactant is added to the aqueous solution which containing the component or components that must be extracted [22].

Surfactants are usually organic compounds that are amphiphilic, meaning they contain both hydrophobic groups (their tails) and hydrophilic groups (their heads). Therefore, a surfactant contains either a water insoluble (or oil soluble) component and a water soluble component. The tail of most surfactants is consisting of a hydrocarbon chain which can be linear, branch or aromatic. [23, 24]. Suitable amount of surfactant shall be added to provide the micelles in the solution. It means that the final concentration of the surfactant shall be exceeding from its CMC (Critical Micelle Concentration). Then for micelle or cloud solution formation, conditions (such as increase or decrease in temperature, increase in salt or other surfactants) are changed and with applying the suitable conditions, surfactant molecules form micelles. In order to speed up the separation of two phases, centrifugation can be used. Finally phase separation is done and a surfactant-rich phase and an aqueous phase will observe. [25, 26] The general procedure of cloud point extraction process is shown in **Scheme 1** as following:
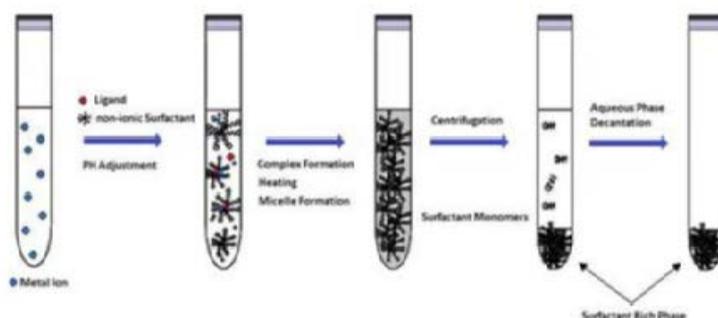
Scheme 1: Cloud point extraction procedure

In this present work a simple , selection and sensitive CPE method for preconcentration and determination of Pb^{2+} and Cd^{2+} ions in various real sample using 2-(3- indolyl)- 4,5 di phynyl imidazole(IDPI)as selective and sensitive complexing agents in basic media was established. Cloud point extraction procedure was presented for preconcentration of lead(II) and cadmium(II) ions in various samples after complexation by 2-(3- indolyl) - 4,5 di phynyl imidazole(IDPI) with lead and cadmium ions are quantitatively extracted in TritonX-114.

EXPERIMENTAL

Reagents

All solutions were prepared with deionized water. Analytical-grade methanol, acids, and other chemicals used in this study were obtained from Merck. A 1.0% (w/v) Triton X-114 from E. Merck (Darmstadt, Germany) was prepared by dissolving 1.0 g of Triton X-114 in a 100 mL volumetric flask with stirring. All chemicals such as nitrate of Cd(II), Pb(II) and other cations were of analytical grade purchased from Merck. The 2-(3- indolyl) – 4,5 di phynyl imidazole.(IDPI) was synthesized, purified and characterized according to the literature[27].

Synthesis of Ligand2-(3- indolyl) – 4,5 di phynyl imidazole (IDPI)

A mixture of benzil (1mmol), ammonium acetate (3mmol) and substituted benzaldehydes (1mmol), was added silica-bonded N-propylsulfamic acid (0.1 g) in solvent free condition at 80 ^{0}Cfor the appropriate time, and heated at 80^{0C} in an oil bath. After completion of the reaction, as indicated by TLC, the reaction mixture was filtered and remaining washed with warm ethanol (2-5 mL). After cooling, the corresponding 2,3-dihydroquinazolinone products were obtained which purified by recrystallization from hot ethanol. The recovered catalyst was dried and reused for subsequent runs. The product was purified by column chromatography on silica gel [eluent: EtOAc/n-hexane (1:3)] to give pure2-(3- indolyl) – 4,5 di phynyl imidazole.(IDPI)in 90% yield. (Scheme2) was synthesized according to literature [27].
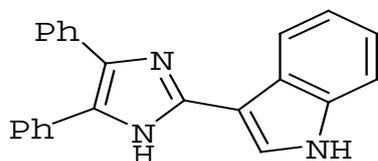
Scheme 2: 2-(3- indolyl) – 4,5 di phynyl imidazole (IDPI)

Mp: 302-305 °C

^{1}H-NMR (DMSO-d_6,400 Hz) δ: 7.05-7.16 (m, 3H), 7.23-7.28 (m, 3H), 7.37 (d, 3H, J=7.8 Hz), 7.44 (d, 2H, J=7.3 Hz), 7.56 (d, 2H, J=7.1 Hz), 7.93 (d, 1H, J=2.5 Hz), 8.40 (d, 1H, J=8.6 Hz), 11.29 (s, 1h), 12.20 (brs, 1H).

^{13}C-NMR (DMSO-d_6, 100 MHz) δ: 106.8, 111.6, 119.7, 121.5, 121.8, 123.7, 125.1, 126.8, 128.1, 128.7, 136.2, 143.7, 145.3, 171.7.

IR(KBr) (cm^{-1}): 3412, 3055, 1621, 1598, 1491, 1451, 1336, 1208, 1182, 1049, 940, 854, 761, 749, 696.

Elemental analysis: C, 82.36; H, 5.11; N, 12.53.

Found: C, 82.17; H, 5.17; N, 12.29.

Instrumentation

A SensAA GBC double beam atomic absorption spectrometer (AAS) with hollow cathode lamp operating at 7, 5 and 4 mA was used to determine cadmium and lead in the surfactant-rich phase. The selected wavelengths were 228.8 and 217.0 nm, for Cd and Pb, respectively. An adjustable-capillary nebulizer and supplies of acetylene and air were used for the generation of aerosols and atomization. Deuterium lamp background correction was employed to correct for the non-specific absorbance. Operation in a double beam-background correction mode was essential due to the complexity of the aspirated sample, which apart from the target metal and excessive chelating agent, causing a suppression of the signal. Measurements were performed in the integration mode.

Shimadzu double beam UV-Vis spectrophotometer UV-1700 (Japan) , shimadzu single beam UV-Vis spectrophotometer UV-1000-02 (Japan) , shimadzu Testscan FTIR 8400 series, shimadzu AA6300 (Italy),

A centrifuge (Shimifan) was used to accelerate the phase separation process. A Jenway model 3510 pH-meter was used for pH measurements. An electronic analytical balance (220LA) was used for weighting the solid materials. A thermostated water bath (Fater Ltd.) model W610B was employed to maintain the experimental temperature.

Spectrophotometric Titrations

Standard stock solutions of IDPI (3.5×10^{-6}mol/L) and the metal ions ($5.o \times 10^{-5}$mol/L) were prepared by dissolving appropriate and exactly weighed (accuracy of $\pm$ 0.0001 g) amounts of pure solid compounds in pre-calibrated 25.0 mL volumetric flasks, and diluting to the mark with MeOH. Working solutions were prepared by appropriate dilution of the stock solutions. Titration 1mL of the IDPI (3.5×10^{-6}mol/L) and solution was carried out by the addition of micro-liter amounts of a concentrated standard solution 1mL of the metal ion ($5.o \times 10^{-5}$mol/L) using a pre-calibrated micro-syringe, at 25°C, with the spectrum subsequently recorded.

Procedure

For CPE, an aliquot of 15 ml of a solution containing cadmium and lead ions, 0.1 % Triton X-114 and 0.26 mM of IDPI was adjusted to pH 7.0 with HCl. The mixture was kept for 20 min in the thermostatic bath maintained at 50° C. The phase separation is accelerated by centrifuging at 4000 rpm for 15 min. The whole system was cooled in an ice-bath so for 15 min that the surfactant rich phase would regain its viscosity. In this way, the bulk aqueous phase was easily decanted. The remaining micellar phase was dissolved in 500 μl of 2.0 M HNO_3 in methanol and then the cadmium and lead ions content were readily evaluated by FAAS.

Preparation of Real Samples

Water samples

Tap, well, natural mineral and sea water samples were collected in acid-leached polyethylene bottles. Bushehr tap water sample was collected from our Lab (Bushehr, Iran). The natural mineral water, well water samples and sea water sample was prepared from Persian Gulf (Iran) were selected from Bushehr and Persian Gulf, respectively in Iran. Al water samples were collected (if needed), filtered through 0.45 μm Millipore cellulose acetate membrane filters to remove particles and diluted with distilled water to the ratio of 1:1. The samples were then adjusted to pH7.0 and immediately analyzed [28].

Soil samples

Accurately weighed 1.0 g of soil samples from near Bushehr petrochemical center (less than 200 meshes), dried at 110 °C were poured into a 250-mL beaker and 10 ml concentrated nitric acid was added to it. The mixture was gently heated under a hood until drying. After complete dry and the mixture was cooled to room temperature, A second 10-mLportion of concentrated nitric acid was added and the procedure. Then 10 mL concentrated hydrochloric acid was added to the beaker and the mixture was gently heated until complete drying. After cooling, the residue was dissolved in 10 mL of 1 M HCl and the solution was then filtered into a 100-mL calibrated flask, using a syringe filter (0.45 μ m pore sized). The sample was neutralized by proper amounts of a 1 M NaOH solution and finally diluted to the mark with water [29].

Blood samples

Homogenized blood sample 20 mL was weighed accurately and in a 200 mL beaker was digested in the presence of an oxidizing agent with addition of 10 mL concentrated HNO_3 and 2 mL 70 % $HClO_4$ was added and heated for 1 hour. The content of beaker was filtered through a Whatman No. 40 filter paper into a 250 mL calibrated flask and its pH was adjusted to 7.0 and diluted to mark with deionized water [30].

Vegetable sample

Spinach sample was bought from Bushehr, Iran. Afterwards, they were taken in small mesh. A 40 g sample was heated in silica crucible for 3 hours on a hot plate and the charred material was transferred to furnace for overnight heating at 650°C. The residue was cooled, treated with 10 mL concentrated nitric acid and 3 mL 30% H_2O_2 and again kept in furnace for 2 hours at the same temperature so that no organic compound traces are left. The final residue was treated with 3 mL hydrochloric acid and 2–4 mL 70% perchloric acid and evaporated to fumes, so all the metals change to respective ions. The solid residue was dissolved in water, filtered and by keeping the pH at7.0 made up to 15 mL by addition of KOH [31].

RESULTS AND DISCUSSION

Spectrophotometric Investigation

A typical kinetic Spectrophotometric method experiment required the following steps: In order to investigate the complexation process between Ligand2-(3- indolyl) – 4,5 di phynyl imidazole.(IDPI) and the Cd^{2+} and Pb^{2+} cations, the spectrophotometric titration was utilized and the complexation procedures were analyzed in acetonitrile at 25°C due to the absorbance alteration which occurs with the cation to ligand ([M]/[L]) ratio conversion. The electronic absorption spectra of ligand (3.5×10^{-6}mol/L) without and in the presence of the metals (5.0×10^{-5} mol L^{-1}) ions to the volumetric flask, the time of the reaction beginning is recorded, The spectra of IDPI with the addition of Cd^{2+} and Pb^{2+} ions, corresponding mole ratio plot and curve fitting at wavelengths of 498 or 495 nm, are depicted in **Figures 1** and **2**, respectively. complexation occurs through binding of Cd^{2+} and Pb^{2+} ions to nitrogen atoms, leading to the ML, or ML, ML_2 models. Formation constants and stoichiometries of complexes were calculated using the Kinfit program [32, 33] and results are shown in **Table 1**.

Effect of pH

A complex with sufficient hydrophobicity is required for separation of metal ions. The mentioned complex can be extracted in a small volume of surfactant-rich phase. The extraction efficiency is dependent on the pH at which complex formation occurs. Therefore, pH is the most important parameter affecting the extraction efficiency and it is necessary to choose the optimum pH at first [34-36]. The effects of pH on to extract metal complexes are given in **Figure 3**. In the pH range of 6.5-7.0, extraction was quantitative. The decrease in recoveries at pH >7.0 is probably due to the precipitation of metal ions in the form of hydroxide, and at pH < 6.5
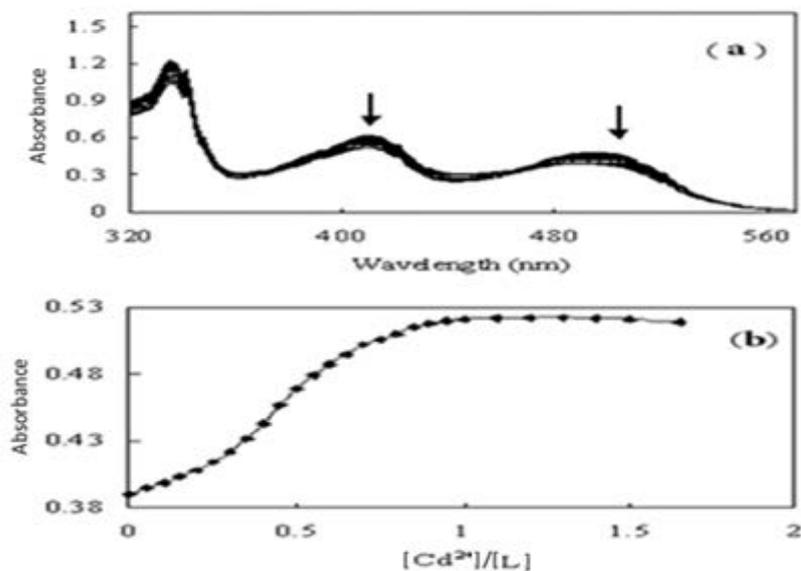
Figure 1. U.V- Visible spectra for titration of IDPI (3.5 × 10⁻⁶mol/L) with Cd²⁺ (5.o × 10⁻⁵mol/L) in MeOH (T = 25⁰ᶜ) and I = 0.05 M) (a) molar ratio plot at 495 nm (b)
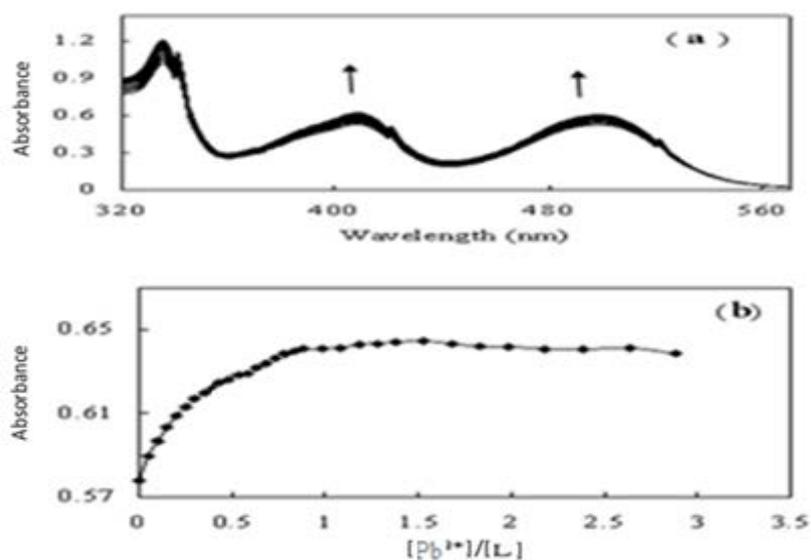
Figure 2. U.V- Visible spectra for titration of IDPI (3.5 × 10⁻⁶mol/L) with Pb²⁺ (5.o × 10⁻⁵mol/L) in MeOH (T = 25⁰ᶜ) and I = 0.05 M) (a) molar ratio plot at 495 nm (b)

may be due to competition from hydronium ion toward ions for complexation with IDPI or decomposition of complex at pH <7.0, which led to the decrease in recoveries. In later experiments a pH of 7.0 was selected.

Table 1. Stepwise stability constsnts of complexation between metal ions and IDPI in Me

Metal ion	Log K_1	Log K_2	M/L
Cd^{2+}	5.70 + 0.23	1.24 + 0.39	1:1 , 1:2
Pb^{2+}	4.46 + 0.33	1.06 + 0.27	1:1 , 1:2
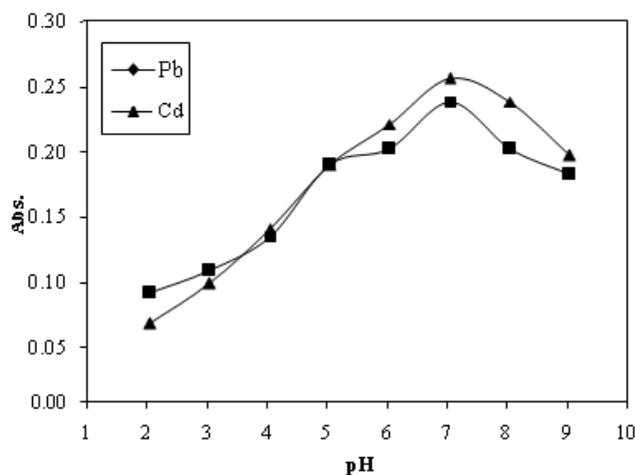
Figure 3. Effect of pH on the extraction recovery of cadmium and lead ions. Conditions: 0.01 mg mL^{-1}, 0.26 mM IDPI, 0.1% (w/v) Triton X-114. Other experimental conditions are described in Procedures

Effect of IDPI Concentration

The absorbance of extracted metal ions as a function of the concentration of IDPI is shown in **Figure 4**. As can be seen, increasing IDPI concentration up to a 0.26 mM causes increasing absorbance. Thus, a IDPI concentration of 0.26 mM was chosen to optimize other variables. At lower than 0.26 mM of IDPI, insufficient concentration leads to incomplete complexation. A possible explanation for the decrease in absorption with higher concentrations may be attributed to the formation of charged complexes with excess IDPI in the medium or with remaining excess IDPI in aqueous solution, competing with surfactant-rich phase for formation of complex with metal ions in aqueous phase.

Effect of Triton X-114 Concentration

Triton X-114 was used as extractant and the concentration of this surfactant affects both the extraction efficiencyand the volume of the surfactant-rich phase. In order to obtain easy phase separation and maximum extractionefficiency the optimum amount of Triton X-114 should be determined [37]. The variation in absorbance of extracted Cd^{2+} and Pb^{2+} ions within the Triton X-114 concentration range of 0.01 - 0.15% (w/v) was examined and results shown in **Figure 5**. The results show that quantitative extraction was obtained with an optimum Triton X-114 concentration of 0.1% (w/v), at which the highest absorbance for extracted Cd^{2+} and Pb^{2+} ions were obtained. For concentrations lower than 0.1% (w/v), the preconcentration efficiency of the formed complexes was very low, since the assemblies at low concentration
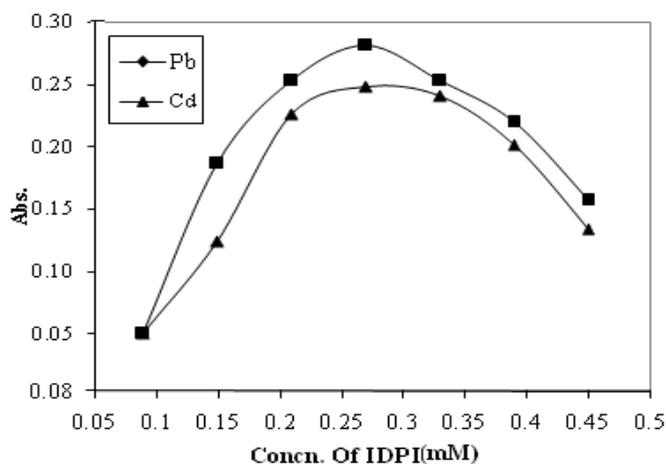
Figure 4. Effect of IDPI concentration on the extraction recovery of cadmium and lead ions. 0.01 mg mL^{-1}, 0.1% Triton X-114, pH 7.0. Other experimental conditions are described in Procedures
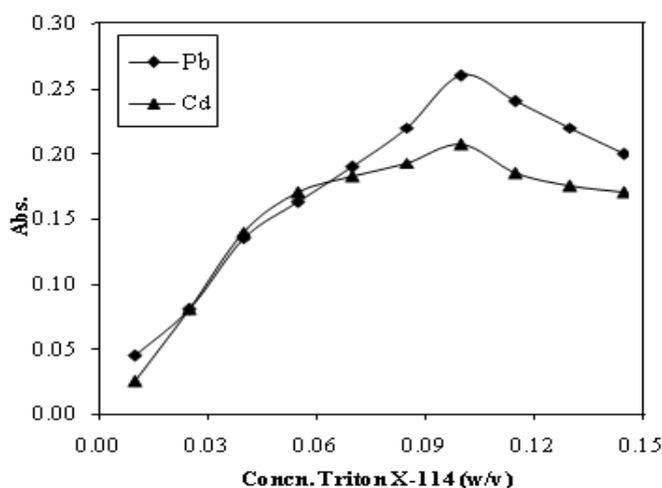
Figure 5. Effect of Triton X-114 on cadmium and lead ions Recovery, Condition: 15 mL 1.0 µg mL^{-1} cadmium ion at various Triton X-114, 0.26 mM IDPI, pH=7.0, 0.2 % (w/v) KCl, eluting solution 0.5ml of 2.0 M HNO$_3$ in methanol

were probably inadequate to preconcentrate trace amounts of Cd^{2+} and Pb^{2+} ions [38]. The decreasing of absorbance at a concentration higher than 0.1% (w/v) is due to the remaining of some part of Triton X-114 and IDPI in aqueous solution as this phase can compete with surfactant-rich phase to draw analyte ions.

Effect of Temperature and Equilibrium Time on CPE

It was desirable to employ the shortest equilibration time and the lowest possible equilibration temperature as a compromise between completion of extraction and separation of phases. The dependence of extraction efficiency upon equilibration temperature and time above the cloud point in the range 30-70°C and 5-30 min were thoroughly optimized,
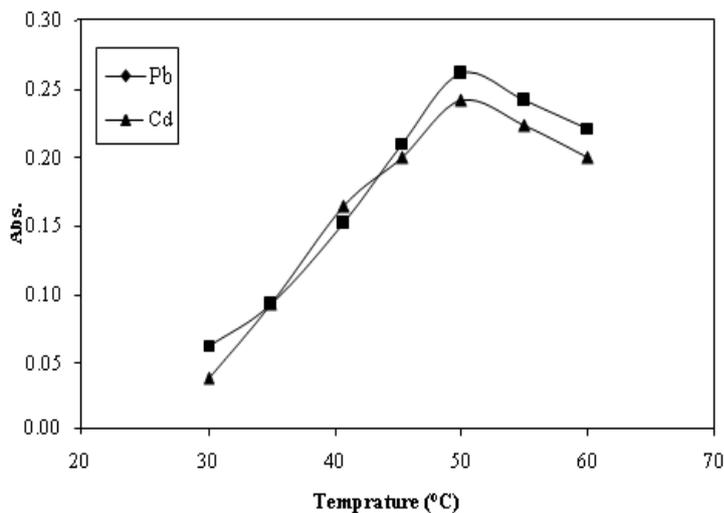
Figure 6. Effect of temperature on cadmium and lead ions recovery, Condition: 15 mL 1.0 µg mL^{-1} cadmium and lead ions at various temperature, 0.1% (w/v) Triton X-114, 0.26 mM IDPI, pH=7.0, 0.2% (w/v) KCl, eluting solution 0.5ml of 2.0 M HNO$_3$ in methanol

respectively [39]. Holding the sample solutions for 25 min at 50$^{\circ C}$ was found to be satisfactory to achieve a small volume of the surfactant-rich phase, quantitative extraction and experimental convenience.

Effects of Added Electrolyte

The cloud point of micellar solutions can be controlled by addition of salts, alcohols, non-ionic surfactants and some organic compounds (salting-out effects) [40]. To date, most of the studies conducted have shown that ionic strength has no appreciable effect on the extraction efficiency. An increase in the ionic strength in the CPE does not seriously alter the efficiency of extraction of the chemical forms. Moreover, the addition of a salt can markedly facilitate the phase-separation process, as demonstrated with some non-ionic surfactant systems, since it alters the density of the bulk aqueous phase [41, 42]. In this way, 2.0 M KCl concentration was used in all further experiments.

Effect of Methanol

Since the surfactant-rich phase obtained after the cloud point pre-concentration contains a high concentration of Triton X-114 and, at the same time, the volume obtained is rather small (500µl), methanol containing 2.0 mol L^{-1} HNO$_3$ was added to the surfactant-rich phase after phase separation. Moreover, it was necessary to decrease the viscosity of the rich phase without excessive dilution of the micelle to facilitate the introduction of the sample into the atomizer of the spectrometer. There is an optimum volume (500µl) with respect to the cadmium ion recovery. Smaller volumes of methanol were not tested because in this case it was not possible to quantitatively transfer the rich phase from test tubes to the graduated tubes

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Table 2. Optimum Conditions for the Presented CPE Method

Parameter	Optimum Value for ions
pH	7.0
IDPI concentration (mM)	0.26 mM
Triton X-114(w/v)	0.1 % (w/v)
Eluting agent	0.5 mL 2.0 mol L^{-1} HNO$_3$ in methanol
Bath temperature	50^{0C}
Temperature time	20 min
Centrifuge time	15 min
Centrifuge rates	4000 rpm

Table 3. Specification of Method at Optimum Conditions for Each Element

Parameters	Element	
	Pb	Cd
Linear Range (µg mL^{-1})	0.064-1.27	0.025-1.3
Correlation Coefficient	0.9985	0.9993
Detection Limit (µg.mL^{-1}) (n =10)	0.13	0.15
Enrichment factor	37	31
Preconcentration factor	31	26
RSD % (n =5)	1.3	1.4
Recovery %	99	99

and measuring the absorbance. Larger volumes of acidified methanol dilution are clearly predominated resulting in a gradual absorbance reduction. A 500µl volume of methanol was therefore used throughout the remaining experiments.

Characteristics of the Method

Calibration graphs were obtained by preconcentrating 2.0 mL of standard solution in the presence of pH 7.0, 0.1% (w/v) Triton X-114, 0.26 mM IDPI with 0.2% (w/v) KCl, under the experimental conditions specified in the optimized procedure section. The solutions were introduced into the flame by conventional aspiration. The characteristics of the proposed method are shown in **Table 2**.

Table 3, gives the characteristic performance of the proposed method of standard solutions subjected to the entire procedure. Limits of detection and quantification according to IUPAC are also included. The limit of detection and the linear range of the proposed method are comparable to other methods that also employed FAAS.

Interferences

In view of the high selectivity provided by flame atomic absorption spectrometry, the only interferences studied were those related to the preconcentration step. Cations that may react with IDPI, and anions that may form complexes with the metal ions were studied [43-46]. The results were shown in **Table 4**. It was proved that cadmium and lead ions recoveries were almost quantitative in the presence of foreign cations.

Table 4. Effects of the matrix ions on the recoveries of the examined metal ions (N=3)

Ions	Added As	Tolerance Limit, mg L^{-1}
Cl^-, K^+, Na^+,	KCl, NaCl, $MgCl_2$,	800
Zn^{2+}, Ba^{2+}	Nitrate salts	300
PO_4^{3-}	Na_3PO_4	800
Cu^{2+}, Ni^{2+}, Cr^{3+}, Hg^{2+}	Nitrate salts	200
Ca^{2+}, Mg^{2+}	Nitrate salts	50
Ti^+, Al^{3+},	Nitrate salts	150
HCO_3^-	$NaHCO_3$	800

Table 5. Determination of analyte ions in soil, blood and vegetable

Ion	lood				Soil			Vegetable		
	Added ($\mu g.mL^{-1}$)	Found ($\mu g\ mL^{-1}$)	RSD %	Recovery %	Found ($\mu g\ mL^{-1}$)	RSD %	Recovery %	Found ($\mu g\ mL^{-1}$)	RSD %	Recovery %
Cd	0	0.09	1.4	-	1.23	0.9	-	0.14	1.2	-
	0.15	0.20	1.1	96	2.51	1.0	94	0. 30	1.3	101
Pb	0	0.03	1.3	-	0.23	1.1	-	0.13	1.3	-
	0.15	0.07	1.5	103	0.39	1.1	99	0.19	1.3	99

Determination of Metal Ions in Real Samples

To validate the proposed method, the developed procedure was applied to the determination of metal ions in real samples. For this purpose, 15 mL of each of the samples were pre-concentrated with 0.1% (w/v) Triton X-114 and IDPI concentration of 0.26mM in pH 7.0, following the proposed procedure. The results are shown in **Table 5** and **6**.

CONCLUSIONS

The proposed cloud point extraction method, using ligand 2-(3- indolyl) - 4,5 di phynyl imidazole.(IDPI), as a stable and fairly selective complexing agent offers a simple, rapid, inexpensive and environmentally benign methodology for preconcentration and separation of Cd^{2+} and Pb^{2+} ions in aqueous solutions. This method gives very low LOD, good RSD and was applied to the determination of trace amounts of Cd^{2+} and Pb^{2+} ions in various real samples. In a full comparison of presented results in this paper with those previously reported, it is found that this method is superior in terms of linear range, detection limits and selectivity. For comparison, the analytical performance data of similar method reported in literature have been listed in **Table 5** and **6**. As it can be seen, the figures of merit of the developed method are comprisable or better than the reported methods.

Table 6. Determination of analyte ions in water samples

Water Samples	Ion	Added (µg mL⁻¹)	Found (µg mL⁻¹)	RSD % (n=5)	Recovery %
Tap	Cd	0	0.13	1.2	-
		0.15	0.28	1.3	98
	Pb	0.0	0.20	1.3	-
		0.15	0.32	1.1	102
Mineral	Cd	0	0.10	1.3	-
		0.15	0.25	1.4	98
	Pb	0	0.12	1.2	-
		0.15	0.33	0. 9	99
Sea	Cd	0	0.12	1.4	-
		0.15	0.26	1.5	96
	Pb	0	0.45	1.3	-
		0.15	1.12	1.2	99

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