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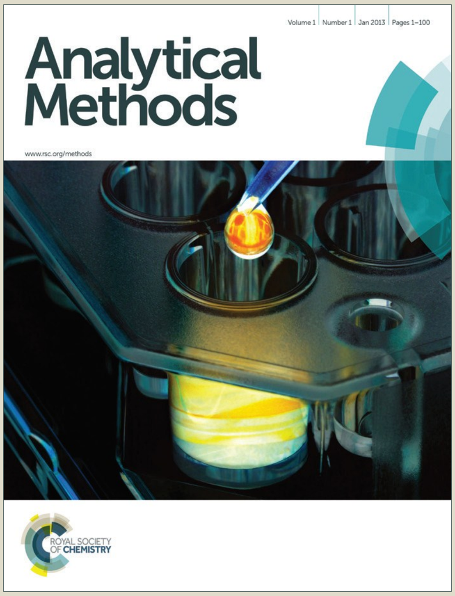

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Switchable dispersive liquid-liquid microextraction for lead enrichment: A green alternative to classical extraction techniques

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Abstract

A new innovative and green switchable dispersive liquid-liquid microextraction (SDLLME) method has been first time introduced as a preconcentration tool for the removal of the toxic metal lead (Pb) in fresh and waste water samples prior to determination with flame atomic absorption spectrometry (FAAS). We developed a switchable polarity solvent (SPS) system based on 1,8-diazabicyclo-[5.4.0]-undec-7-ene and decanol, which was reversibly switched on and off from heterogeneous biphasic nonpolar hydrophobic to homogenous monophasic polar hydrophilic phase in aqueous medium by exposing to anti solvent trigger (CO_2) for specific interval of time (1-10 min). Then SPS of polar microemulsions was switched-on from polar phase through bubbling CO_2 followed by switched-off to non polar phase by heating in the range of 40-70°C in the presence of N_2 gas. The switching phenomenon of SPS from low polarity to high polarity was confirmed by FTIR spectrophotometry and conductivity measurements. The SDLLME was successfully applied as an extracting medium for the preconcentration of hydrophobic chelate of Pb with 1-(2-pyridylazo)-2-naphthol (Pb-PAN) from real water system. Then hydrophobic enriched Pb-PAN-SPS were treated with 1.5 mol L^{-1} HNO_3 and purge CO_2 for different time interval, to switch back to its miscible polar hydrophilic monophasic state. The recovery of SPS solvent was carried out by heating at 55°C and purging of N_2 gas. The SPS solvent easily recycled up to 12 times with >2 % loss of efficiency of the developed method. Under the optimized experimental conditions the limit of detection (LOD) and the enhancement factor (EF) were obtained to be 0.25 µg L^{-1} and 50, respectively.

Keywords: Lead, switchable polarity solvent, preconcentration, 1-(2-pyridylazo)-2-naphthol, flame atomic absorption spectrometry

1. Introduction

The release of large quantities of non-essential toxic metals into the environment is responsible for environmental risk and health problems.[1] Lead (Pb) is comparatively common toxic metal in the environment; create environmental health impacts among adults and children.[2,3] The maximum contaminant levels in drinking water allowed by environmental protection agency (EPA) are 15.0 µg L^{-1} while world health organization (WHO) for drinking water quality containing the guideline value of 10 µg L^{-1} for Pb. When the concentration exceeds the permissible level, it may cause harmful effects on aquatic environment.[4] Since Pb and their compounds are widely used as chemical materials in modern society, which drastically increase the exposure level in natural waters and soils. A great piece of work has been required to trace out the low concentration of Pb in environmental samples to reduce its exposure and risk to the environment.[5,6] Direct determination of Pb in water and soil samples by absorption spectrometry[7-9] and other advance instrumental techniques[10-12] is usually not possible, due to low concentration and complex matrix interferences. Therefore, a separation/pre-concentration step is often required for these metals analysis. The determination of trace levels of toxic metals has become an increasing trend, but due to its low concentration often required more sensitive instrumental techniques or a preconcentration step before analysis.[13] In this regard, a range of preconcentration procedures have been developed for the preconcentration, like liquid-liquid microextraction (LLME),[14] cloud point extraction[15] and solid phase extraction.[16] Despite the great evolution in analytical sciences in the last decade, sample pre-treatment is still an unavoidable step in most analytical procedures due to the complexity or low concentration of the target analytes. In this general context, the development of new techniques (or the improvement of the existing ones) which answer these main requirements have become a key trend in analytical chemistry. Liquid-phase microextraction emerged in the mid late 90s when Jeannot and Cantwell proposed for the first time the use of organic solvents in the low-microliter range as extractant in liquid-liquid extraction.[17-20] Room temperature ionic liquids (RTILs) have aroused increasing interest for their promising role as alternative media in synthesis,[21,22] separation [23,24] and electrochemistry [25,26] as a result of their unique chemical and physical properties.[27,28] RTILs have potential to be alternative reaction media for “Green Chemistry”.[29,30] Applications of RTILs in analytical chemistry have also started to receive attention recently.[31,32] RTILs are very expensive and could not be recycled, which reduced demand in a modern green era. Green analytical chemistry (GAC) mainly pursues the objectives of replacing toxic reagents, and miniaturizing and automating analytical methodologies, to minimize environmental and human hazards by replacing polluting methods with clean ones. As far as sample preparation is concerned, development and improvement of new sustainable analytical procedures are fast growing trend in analytical chemistry. In this context, microextraction techniques have evolved from the more classical sample-pretreatment techniques.[33]

Recently, novel classes of solvents called switchable or smart solvents have offered new possibilities for a green process design. Their ability to readily switch to different form due to different polarity can eliminate the need for a solvent separation by different process such as centrifugation. Switchable solvents had therefore received growing attention in the past decade, both in academia and for industrial applications.[34] In this process a nonpolar ionic liquid (alcohol and amine base) converts to polar ionic liquid (a salt in liquid form) upon exposure to an atmosphere of CO_2, and then reverts back to its non-ionic form, when exposed to heat again. Such switchable solvents should facilitate organic syntheses and separations by eliminating the need to remove and replace solvents after each reaction step.[35-37] One of the best advantages that switchable solvents offer, their ability to be recycled many times without loss of extraction efficiency.

In the present work, green reversible and switchable polar solvent extraction (SDLLME) method has been developed as a preconcentration tool for the removal of trace levels of toxic level of Pb in fresh and waste water samples prior to connect with flame atomic absorption spectrometry (FAAS). A switchable polar solvents (SPS), 1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU) and decanol that can reversibly switch on and off from hydrophobic to hydrophilic when an antisolvent trigger (CO_2) was applied. The different variables such as, pH, concentration of complexing agent, pressure and purging time of CO_2 and pressure were optimized. The proposed method was evaluated by analyzing certified reference material and spiked environmental water samples. This work was first time introduced for the removal of Pb from water samples of the canal and industrial wastewater has not been reported elsewhere as per our knowledge.

2. Experimental

2.1 Chemical Reagents and glassware

Ultrapure water obtained from the ELGA lab water system (Bucks, UK), was used throughout the work. Standard solution of Pb (1000 mg L^{-1}), were purchased from Fluka Kamica (Bush, Switzerland). Dilute working standard solutions were prepared by stepwise dilution of the stock standard solution with 0.2 mol L^{-1} HNO_3. A stock buffer solution was prepared by dissolving appropriate amounts of acetic acid and its sodium salt in ultrapure water, and solutions were prepared with 0.1 mol L^{-1} HNO_3/NaOH. Concentrated nitric acid, hydrochloric acid were analytical reagent grade from Merck (Darmstadt, Germany) and were checked for possible trace Pb contamination by preparing blanks for each procedure. 1-(2-Pyridylazo)-2-naphthol (PAN) was obtained from Fluka and its 0.01% solution was prepared by dissolving 0.01 g in 100 mL of ethanol (Merck). 1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU) was purchased from Merck (Darmstadt, Germany). The 0.1 mol L^{-1} acetate and phosphate buffer were used to control the pH of the solutions. The pH of the samples was adjusted to the desired pH by the addition of (0.1 mol L^{-1} HCl/ NaOH) solution in the buffers. For the accuracy of methodology, certified reference material of the water SRM-1643e National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) was used. The glass and plastic wares were soaked in 10% nitric acid overnight and rinsed many times with deionized water to avoid contamination.

2.2 Instrumentation

A pH meter (Ecoscan Ion 6, Malaysia) was employed for pH adjustments. Global positioning system (iFinder GPS, Lowrance, Mexico) was used for sampling locations. A Perkin-Elmer Model A Analyst 700 (Norwalk, CT) flame atomic absorption spectrophotometer was used. The hollow cathode lamp of Pb was run under the conditions suggested by the manufacturer. A single element hollow cathode lamp was operated at 7.5 mA and spectral bandwidth of 0.7 nm. The analytical wavelength was set at 283.3 nm. The acetylene flow rate and the burner height were adjusted in order to obtain the maximum absorbance signal. UV-Vis spectra were recorded on a

(Bichrom Libra S22 Cambridge UK) spectrophotometer in quartz cells with 0.1 cm path lengths. The measurement of electrical conductivity was analyzed by using a conductometer (InoLabconduc. 720, Germany). A Fourier Transform Infrared Spectrometry 'FTIR' (Thermo Electron Corporation, Nicolet Avatar 5700) was used to characterize the switching phenomena of SPS system, at 400-4000 cm^{-1}.

2.3 Design of SDLLME procedure

The switchable polarity solvent (SPS) was prepared in a three-necked flask using a stirring apparatus. Added equimolar mixture of DBU/decanol (1:1 mL) in aqueous media, the resulted mixture termed as SPS which is nonpolar in nature and not dissolved in water made a bypass system as shown in **(Fig. 1a)**. Then added 25 mL replicate six samples of standard (20 µg L^{-1}), certified reference material and triplicate sample solution of real fresh and waste water samples. The pH of the solution was adjusted in the range of 2 to 8, and then added 200-500 µL of 0.01% (m/v) PAN solution. The three-necked flask was also equipped with gas diffuser and exposed to a steady stream of CO_2, bubbled slowly into the [DBUH]/[decanol]:water system for 2-10 min, while being stirred with a magnetic stirring bar in the range of 200-600 rpm. The resulting product is a clear monophasic homogenous solution (**Fig. 1b**). The[DBUH]/[decanol]: aqueous system, function as a hydrophobic ionic liquid, significantly improve the extractive recoveries of chelate of Pb-PAN from aqueous medium to polar enriched SPS microemulsion due to its tunable properties. The polar SPS/aqueous monophasic system was separated into its respective SPS and aqueous layers by bubbling with N_2 and heating at 55°C until the two layers of biphasic system formed (**Fig. 1c**). After this, switching process was complete, a low-polar part of the SPS separated from the aqueous solution carefully by a syringe, for detail see graphical scheme. The enriched Pb-PAN complex in SPS was again treated with 0.5 mL of 1.5 molar of HNO_3 solution. The biphasic system of acidic aqueous SPS medium were again exposed to stream of carbon dioxide CO_2 with a pressure of 1 to 10 MPa with continued stirred, until the homogenous mass of the product achieved. In highly acidic medium mostly metal complex is unstable, which can leach from enriched SPS to aqueous medium. For recovery of SPS for the next experiment, from polar SPS/water monophasic system into its respective SPS and aqueous layers by bubbling with N_2 and heating at 55°C until the two layers of biphasic system formed, a low-polarity portion of SPS (1.9 ml) was separated from the aqueous acidic solution. The SPS was again used for the next experiment and acidic aqueous solution were directly couple with FAAS for analysis of Pb.

(Fig. 1a, 1b and 1c)

2.4 Distribution Ratios and Percentage Extraction of SPS system

The Extraction efficiency of SDLLME method depends on metal complex partitions between two immiscible biphasic phases. The following equation is used for distribution ratio (D):

$$D = \frac{[M]_{org}}{[M]_{aq}}$$

Where, $[M]_{org}$ (μg L^{-1}) and $[M]_{aq}$ (μg L^{-1}) are the metal concentration in the organic phase (SPS) and the aqueous phase, respectively.

The percentage extraction (*% E*) of the metal could be found from the following equation:

$$\%\,E = \frac{Amount\ of\ metal\ extracted\ to\ SPS}{Total\ amount\ of\ metal\ in\ aqueous\ medium} \times\ 100$$

The concentration of metal ions extracted to SPS and total concentration of Pb in aqueous medium before treatment of SDLLME procedure.

3. Results and discussion

3.1 Characterization of SPS

Infrared (IR) spectroscopic technique was used to characterize the switching phenomena of the SPS system from [DBUH] [decanol] to [DBUH][decanol-CO_2] after CO_2 bubbling. The IR spectra were obtained in the range of 4000 - 500 cm^{-1} at room temperature. The cut-off region between 2250 cm^{-1} and 1950 cm^{-1} could not be used for spectral analysis because of the absorbance of CO_2. A new peaks at 1639 cm^{-1} was assigned to the stretching vibrations of ν(C=O), due to the $DBUH^+$ free cation **(Fig. 2)**. The absorbance of the ν(C=N) band at 1623 cm^{-1} decreased with increasing absorbance of the bands at 1639 after the reaction of [DBUH][decanol] with CO_2. These changes indicate that CO_2 reacts with [DBUH][decanol] to generate [DBUH][decanol-CO_2] and to promote the formation of free ions. After the reaction of [DBUH][decanol] with CO_2, new peaks appeared at 1639 cm^{-1}, which are attributed to the carbonate ν(C=O) stretching.[38] A broad peak appeared at 3344 cm^{-1} of [DBUH] [decanol-CO_2] is due to (O-H) stretching of H_2O, indicated that system is developed in aqueous medium **(Fig. 2)**.

3.2 Conductivity measurement

A platinum conductivity probe was placed in a vial containing 5 mL of the equimolar SPS solution to measure the initial conductivity. Then CO_2 was bubbled into the sample and conductivity was measured at the interval of 1 min until a constant value was obtained. It was observed that the SPS has a low conductance (8 µS cm^{-1}), before treated with CO_2 (400 µS cm^{-1}). So it was confirmed that SPS changed from low to high polar solvent.

3.3 Optimization of extraction parameters of SDLLME

A number of factors have a crucial role in the ability and viability of the developed method to achieve satisfactory extraction recovery of Pb from aqueous medium to SPS system. The pH is not only important for the complex stability of Pb-PAN but also have a vital role on interface transfer from hydrophilic polar to hydrophobic nonpolar medium in SPS-aqueous medium. The effects of pH range 2-8 on the extraction efficiency of SDLLME as shown in **Fig. 3**. It was observed that the extraction was almost quantitative at pH range of 6.0-7.0 and decreased slightly after pH 7. From this result, it could be inferred that hydrophobic interaction between Pb-PAN complex and SPS solvent was quantitative at a neutral pH range. So, pH 7.0 was selected for subsequent experimental work. The effect of concentration of PAN on recovery was examined in the range of 100 µL to 600 µL of 0.01% (m/v). In this case, the extraction efficiency increases up to 300 µL PAN, reaching a plateau, which is considered as the complete complexation of study analyte. Thus volume of 350 µL was chosen as the optimal for selective extraction of the target analyte from aqueous solution into SPS to prevent any interference. Purging time and pressure of CO_2 also have key role on switching of SPS from nonpolar to polar which drastically improved extraction of metals from aqueous medium. CO_2 have vital role on switching polarity of SPS-aqueous system. We used pressure as an anti solvent trigger for switching on and off from nonpolar to the polar of SPS system in aqueous medium in the range of 1 to 10 MPa. As we increased CO_2 pressure at an optimum level although the biphasic medium of SPS-aqueous system changed to monophasic but the content of the flask was spelled out due to high pressure. Time is also has an important role in aspect of method efficiency and performance and it can be seen that it takes only 5 min to change from nonpolar to polar SPS as shown in **Fig 4**. So, 5MPa and 5 min for CO_2 purging were selected as a desired condition to achieve the best result.

(Fig. 3 and 4)

3.4 Interference studies

Many coexisting ions in sample solution might be reacting with PAN along with the target analyte at desire SDLLME procedure; this would lead to effects the extraction efficiency of the analyte. To assess the selectivity of the developed method, the potential interference of foreign ions in terms of the tolerance limit was explored. An ion was considered as an interfering, when at cause a variation of greater than 5% in the recovery of the analyte. A series of experiments have been carried out by subject different ratio of coexisting ions to 10 µg L^{-1} of Pb and analyzed at desire procedures. The observed Pb recoveries in the presence of the coexisting ions were above 95%. Commonly encountered matrix components in real samples such as alkali and alkaline earth elements generally do not form stable complexes under the experimental conditions. The results are shown in Table 1.

(Table 1)

3.5 Effect of HNO_3 on metal stripping to aqueous medium from SPS

Other critical factors which affect the extraction efficiency are the concentration of striping acidic solution used for the removal of analyte from SPS to aqueous medium. The influence of acid concentration on the stripping efficiency of analyte from Pb-PAN enriched SPS phase at optimum values. For this purpose 2 ml of HCl at the concentrations range of 0.5 to 4 mol L^{-1} were used. The need of higher concentration of HCl for Pb stripping in the presence of PAN can be attributed to the strength of hydrophobic Pb-PAN complex in SPS system. It seems that concentrated of >1.0 mol L^{-1} cannot completely striped the retained metal ions in the form of complexes due to stability of Pb-PAN complex and it could be taken into to the liquid phase at acid concentration >2.0 mol L^{-1}. It was observed that 99% stripping of analyte could be obtained at HNO_3 concentrations of 1.5 mol L^{-1}. The percentage stripping (% S) of Pb from SPS to acidic aqueous medium could be calculated from the following equation:

$$\% S = \frac{Amount\ of\ metal\ stripped\ to\ acidic\ medium}{Total\ amount\ of\ metal\ in\ SPS} \times 100$$

3.6 Recovery and Recycling of SPS

One of the advantages of a liquid-liquid extraction system based on SPS is its insolubility in water phase. To investigate the recovery of the SPS from aqueous phases, after stripping the analyte by acid solution as described in experimental section and shown in **(Fig. 1)**. The SPS organic phase recoverable volume was ~1.90 ml slightly less than the initial volume of SPS. The results indicated that SPS could be successfully recycled more than 12 times with lose of <2% extraction efficiency of desire SDLLME method.

3.7 Method validation

The analytical performance and capability of desire SDLLME including linearity, precision, accuracy, repeatability, and limits of detection were investigated under optimum condition. A

Calibration graph of Pb was linear with a correlation coefficient (R^2) of 0.9987 in the concentration range of (5-25 µg L^{-1}). Accuracy and precision of the method were evaluated by the relative standard deviation (RSD) after six replicates analysis containing 10 µg L^{-1} of Pb, was found to be 3.5%, indicating good reproducibility of the method. Limit of detection of Pb was 0.25 µg L^{-1} calculated according to three times the standard deviation (n= 10) of the blank signals. Enhancement factor was calculated as the ratio of the slopes of calibration graphs with and without preconcentration by SDLLME procedure and was found to be 50 (Table 2). Validity and accuracy of the desired method was checked by analysis of real water samples while using standard addition method. The relative recoveries of Pb from tap and waste water at a spiking level of 1.50 and 2.50 µg L^{-1} and it was found that the recovery was >96%, respectively (Table 2). Furthermore, the comparison of the SDLLME method with other reported methods for determination of Pb in water samples are shown in Table 3.

(Table 2 and 3)

3.8 Application to real samples

Water samples were collected in late summer of 2013 from fresh water canal receiving waste water of industrial area. Water samples were collected in plastic containers previously cleaned by washing with non-ionic detergent, rinsed with tap water and later soaked in 10% HNO_3 for 24 hours and finally rinsed with deionized water prior to use. The waste water samples were also collected simultaneously before entering into the canal. The samples were labeled and transported to the laboratory, stored in the refrigerator at about 4°C prior to analysis. The desire SDLLME method was successfully applied to quantify the trace level of Pb and checked their accuracy by the standard addition method (Table 3). A reasonable recovery, 97% to 98% of spiked samples was obtained which confirmed, that despite the presence of diverse coexisting ions with different concentrations, Pb ions can be separated and determined with good recoveries, which indicated the potential and probability of the developed method. The results of Pb obtained by proposing method was compared with literature values (Table 4).

(Table 4)

4. Conclusion

Innovative green, switchable polarity solvent extraction method have been first time introduced as a separation tool for the removal of trace levels of toxic metal Pb in real surface water samples prior to connect with FAAS. The basic theme of this work is to introduce a green process that utilizes switchable solvents to allow solvent recycle and reuse. In this method, 1, 8-diazabicyclo-[5.4.0]-undec-7-ene and decanol were reversibly switched on and off from nonpolar hydrophobic to polar hydrophilic, when an antisolvent trigger (CO_2) was applied. The CO_2 is superior to other triggers; it has many advantages such as inexpensive, non hazardous, non-accumulating in the system and easily removed. The method was shown to be a good alternative to the determination of trace amount of Pb and other heavy metals in relatively complicated matrices and further research is expected to attempt research in the trace elemental analysis. We believe that this method will provide a useful tool for the screening and quantitative determination of other metal ions in and expect that it will become more popular as a pretreatment of method for different environmental samples.

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Figure Captions

Fig. 1. Visual representation of of SPS of [DBU][decanol] in aqueous medium (a) before adding the upper immiscible SPS and lower aqueous aqueous layers (b) converted to a clear homogenous monophasic solution of SPS in aqueous medium by exposing to 5 MPa of CO_2 while stirrer for 5 min at 500 rpm (C) The polar SPS/water monophasic system was separated into its biphasic respective SPS and aqueous layers by bubbling with N_2 and heating at 55°C.

Fig. 2. In-situ IR spectra of the SPS system of (a) before adding sample [DBU][decanol] (b) After homogenization of [DBU][decanol-CO_2] by CO_2 bubbling into the mixture and (c) and after the final separation of phases [DBU][decanol] by CO_2 removal from the mixture by bubbling with N_2 and heating at 55°C.

Fig. 3. Effect of pH on the recovery (%) of (SDLLME): 20 μg L^{-1} Pb, PAN 0.015 %, 250 μL, 5 MPa of CO_2 while stirrer for 5 min at 500 rpm, N_2 and heating at 55°C, HCl concentrations of 2.5 mol L^{-1}.

Fig. 4. Time percent concentration profiles of conversion of DBU/decanol to DBU/decanol-CO_2 by exposing to 5 MPa of CO_2 while stirrer at 500 rpm.

Table 1. Influence of interfering ions in the determination of Pb.

Interfering ions	Tolerance Limit (mgL^{-1})
Na^+, K^+	10000
Ca^{2+}, Mg^{2+}	6500
Fe^{3+}, Cu^{2+}, Zn^{2+}, Cd^{2+}	35
Ni^{2+}, Co^{2+}	40
Cl^-	5000
CO_3^{2-}, SO_4^{2-}	1000
PO_4^{3-}	550

Table 2. Performance and validaty of the proposed SDLLME method.

SDLLME	Concentration range (µg L^{-1})	5–25
Limit of detection	LOD[a] (µg L^{-1})	0.25
Correlation coefficient	R^2	0.9986
Precession	(RSD %)[b] (n=10)	3.5 (10 µg L^{-1})
Sample volume (mL)		25
Enhancment factor[c]	EF	50

[a] Pb concentration was 10 µg L^{-1} for which the R.S.D. was obtained.

[b] Limit of detection. Calculated as three times the S.D (3σ) of the blank signal.

[c] Calculated as the ratio of slope of preconcentrated samples to that obtained without preconcentration.

Table 3. Determination of Pb in certified reference material and real water samples by Standard addition method using SDLLME method.

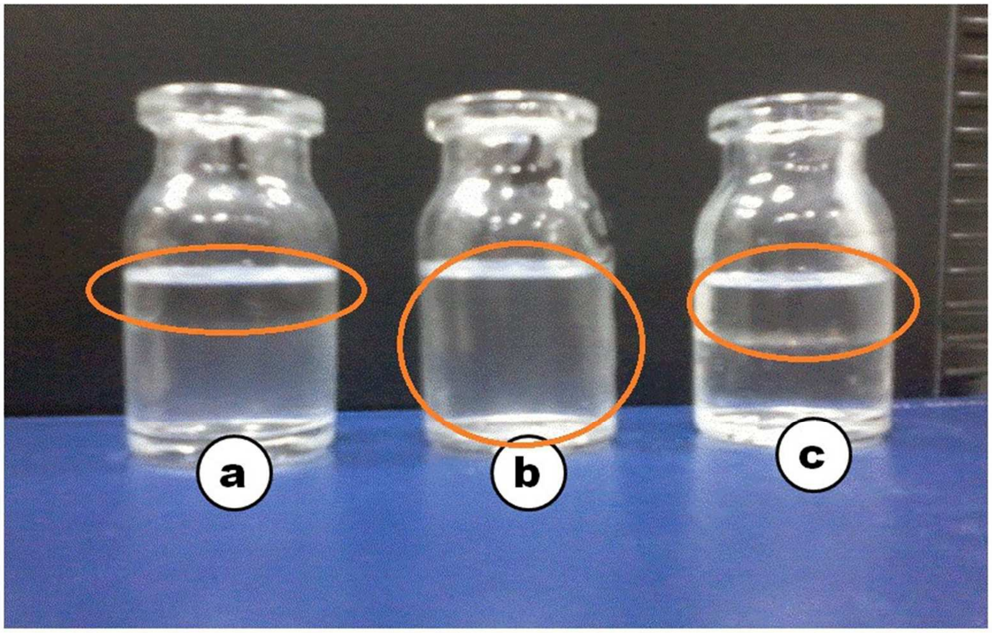
Certified reference material	Certified values (µg L^{-1})	Measured values (µg L^{-1})	Recovery (%)
SRM 1643e	19.63 ± 0.2	19.24 ± 0.5	98.0
		Water samples	
Samples	Added (µg L^{-1})	Measured (µg L^{-1})	Recovery (%)
Waste water	0	18.5 ± 0.18*	---
	1.50	20.0 ± 0.19	100
	2.50	20.98 ± 0.22	99.2
Canal water	0	7.22 ± 0.13*	---
	1.50	8.72 ± 0.14	100
	2.50	10.33 ± 0.16	124.4

Key: *Mean ± S.D. (n = 3)

Table 4. Comparison of proposed SDLLME with previously reported microextraction techniques for Pb in water samples.

Extraction Technique	EF	LOD (µg L^{-1})	Reference
SPE	36	0.5	39
IL-DLME	40	1.5	40
Grinded eucalyptus stem	50	4.5	41
Amberlite XAD-2 loaded with 1-(2-pyridylazo)-2-naphthol	50	23.2	42
Functionalized resin	10	3.5	43
Amberlite XAD-2 functionalized with o-aminophenol	40	25	44
Sodium dodecyl sulfate (SDS)-coated alumina	63	2.8	45
Chromosorb 108/bathocuproinedisulfonic acid	80	0.6	46
MWNTs	20	8.9	47
SDLLME	50	0.25	Present work

Solid phase extraction (SPE), Ionic liquid-dispersive liquid phase microextraction (IL-DLME), Multi walled carbon nanotubes (MWNTs),



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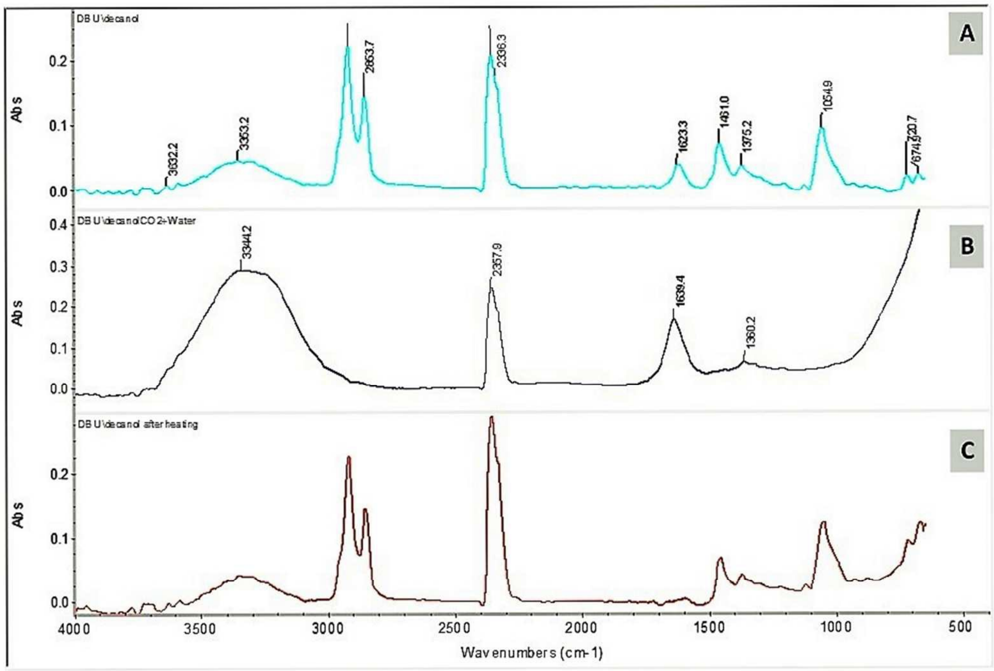

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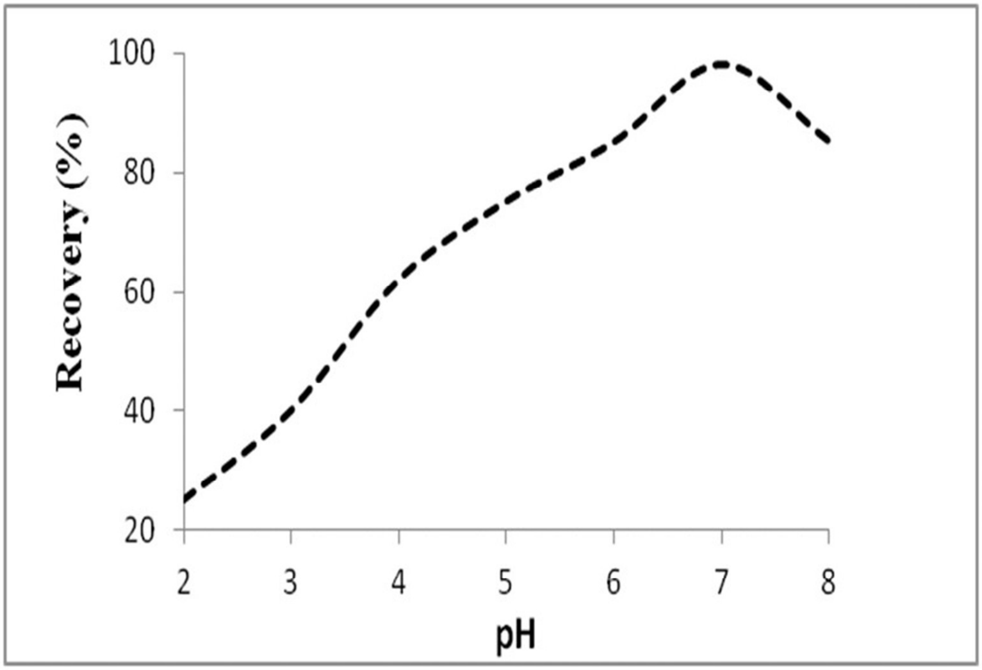

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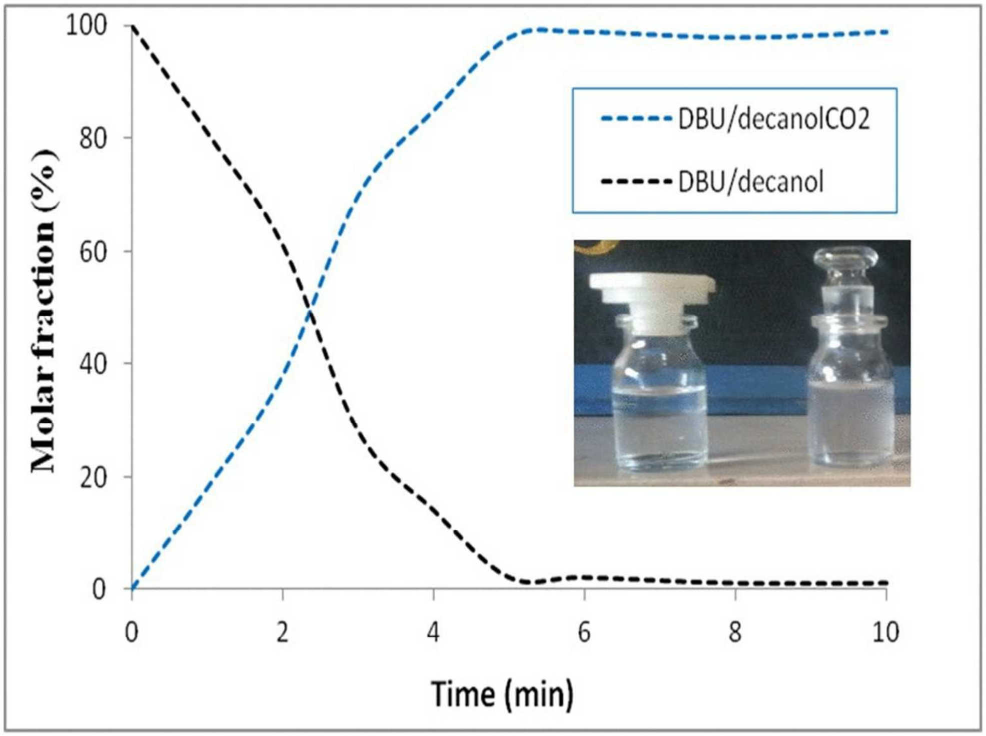

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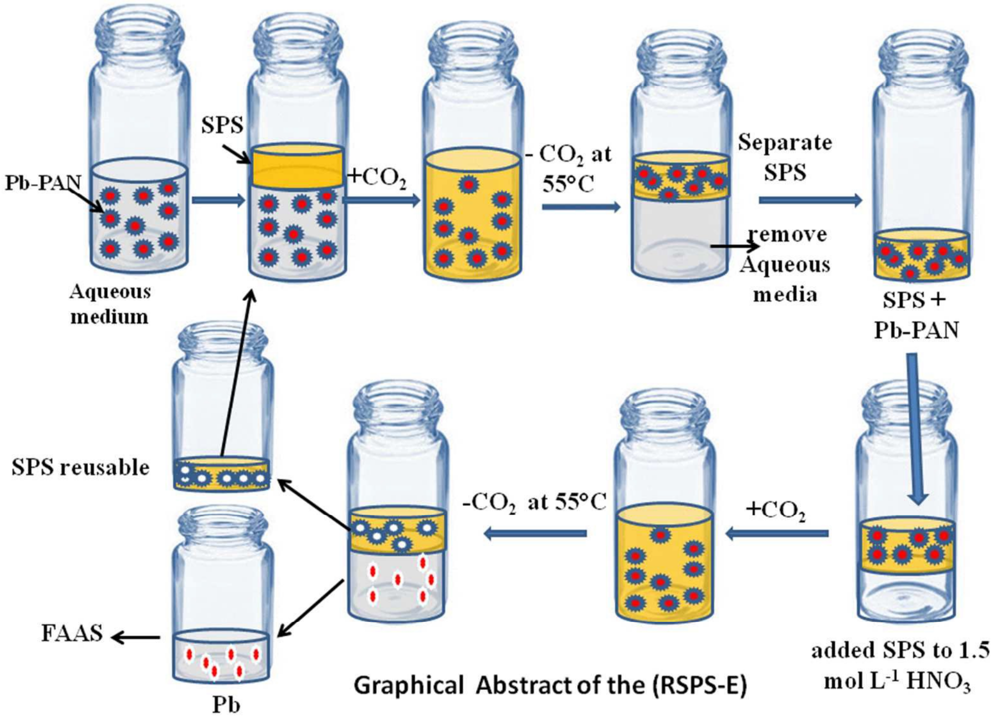

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