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Ethylenediamine Functionalized Nanoporous Silica Type LUS-1 for Highly Sensitive Analysis of Pb^{2+}, Cd^{2+} and Zn^{2+} in Various Samples

L. Hajiaghababaei[*a], A. Badiei[b], N. Shaabani[a], M.R. Ganjali[c], G. Mohammadi Ziarani[d], M. Javadi Charani[b]

[a]*Department of Chemistry, Islamic Azad University, Shahre rey Branch, Tehran, Iran.*
[b]*School of chemistry, College of Science, University of Tehran, Tehran, Iran.*
[c]*Center of Excellence in Electrochemistry, Faculty of Chemistry, University of Tehran, Tehran, Iran.*
[d]*Department of Chemistry, Faculty of Science, Alzahra University, Tehran, Iran.*

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**Corresponding author:*
E-mail address*:*
lhajiaghababaei@iausr.ac.ir
lhajiaghababaei@yahoo.com
Phone: 98 9125017614
Fax: +98 21 33999022

Abstract

In this work, a novel method is described for the preconcentration of Pb^{2+}, Cd^{2+} and Zn^{2+} ions in environmental samples using uniform silanized mesopor (LUS-1) functionalized by ethylenediamine groups as a new extractant. The determination of ions is done by inductively coupled plasma optical emission spectrometry (ICP-OES). The extraction time and efficiency, pH and amount of adsorbent, minimum amount of stripping acid and break-through volume were investigated. The method's enrichment factor is100 and detection limit is 0.45, 0.05 and 0.03 ng mL^{-1} for Pb^{2+}, Cd^{2+} and Zn^{2+} respectively. The maximum capacity of the one mg of functionalized LUS-1 was found to be 150.0 (±2.0) µg and 93.0 (±1.7) µg and 125.0 (±1.2) µg of Pb^{2+}, Cd^{2+} and Zn^{2+} respectively. The method was applied successfully for the preconcentration and determination of trace amounts of Pb^{2+}, Cd^{2+} and Zn^{2+} in water and food samples.

1. Introduction

In recent years, the pollution of the environment by heavy metals has received considerable attention. Lead is one of the most toxic elements and distributed widely in the environment and produces several diseases. High levels of exposure may result in toxicity in humans which in turn cause problems in the synthesis of hemoglobin, effects on the kidneys, gastrointestinal tract, joints, reproductive system, and acute or chronic damage to the nervous system [1]. Therefore it is important to monitor the levels of lead in environments. Cadmium represents one of the important toxic metals and effect of its acute poisoning is manifested in a variety of symptoms, including high blood pressure, kidney damage, anemia, hypertension, bone marrow disorders, cancer and toxicity to aquatic biota [2]. Zinc is one of the transition metals, which is used in paint, electroplating, pharmaceutical and chemical industries, and thus occurs widely in the environment [3]. Zinc is a toxic element, and it's monitoring in biological, food, and environmental sample is very important.

Determination of these ions in environmental samples can be performed by flame and graphite furnace atomic absorption spectrometry, spectrophotometry, inductively coupled plasma atomic emission, direct current plasma atomic emission spectroscopy, neutron activation analysis, potentiometry and voltammetry [4-12]. But, due to low concentrations and the presence of heavy matrix, a preconcentration or matrix elimination step prior to instrumental measurements usually is required in order to achieve accurate and reliable results. The most widely used techniques for the separation and preconcentration of trace amounts of these ions are liquid-liquid extraction [13] and solid phase extraction. However, the use of classical liquid extraction methods are usually time-consuming labor-intensive and require relatively large volumes of high purity solvents. Additional concern is the disposal of the solvent used, which can create severe environmental problems. Various adsorbents such as green tea leaves [14], silica gel [15], silanized glass beads [16] and resin [17,18] which is used in solid phase extraction have showed several problems like low mechanical and thermal stability and weak chemical union with the metals.

The synthesis of a new form of mesoporous silica molecular sieves using surfactants as organic templates initiated a new field of research in material science. The nanoporous silica materials such as MCM-41 [19], LUS-1 [20] and SBA-15 [21] are suitable for application in catalysis [22], modified carbon paste electrodes [23], and extraction [24-26]. The major advantages of the functionalized mesopore include (1) very short sample processing time due to the warm like of particles which allows the sample processing at very higher flow rates, (2) reduced channelling resulting for the use of uniform diameter sorbent and a greater mechanical stability of the sorbent. For adsorption processes, a variety of functional groups can be grafted or incorporated on the surface of mesopore channels and highly effective adsorbents can be preparated[27,28].

In this work, we introduce a novel method for simple, fast and simultaneous preconcentration and ICP-OES determination of ultra trace amounts of Pb^{2+}, Cd^{2+} and Zn^{2+} in various samples. For this purpose, ethylenediamine functionalized LUS-1 was synthesized and used as a new extractant. To the best our knowledge, this is the first application of ethylenediamine functionalized LUS-1 for simultaneous preconcentration of ultra trace amounts of Pb^{2+}, Cd^{2+} and Zn^{2+} ions.

2. Experimental

2.1. Reagents

Hexadecyltrimethylammonium-*p*-toluene-sulfonate (CTATos), N-(2-Aminoethyl)-3-aminopropyltrimethoxysilane from Merck and Ludox HS-40 (40% SiO_2) from Aldrich were purchased. Toluene and NaOH were from Merck chemical company. All acids used were of the highest purity available from Merck. Analytical grade nitrate salts of elements (all from Merck) were of the highest purity available and used without any further purification. Doubly distilled deionized water was used throughout. The stock metal ion solutions (1000 mg L^{-1}) of Pb^{2+}, Cu^{2+}, Zn^{2+} and other cations were prepared by dissolving the appropriate amounts of nitrate salts of elements in double-distilled water. Working standard solutions were prepared by appropriate dilution of the stock standard solutions with doubly distilled water.

2.2. Synthesis of LUS-1

LUS-1 was prepared according to a synthetic procedure previously established [29]. Typically, Ludox (15.5 g, 0.26 mol) was added to sodium hydroxide (2 g, 5×10^{-2} mol) in distilled water (50 mL), and then stirred at 313 K until clear (about 24 h). A second solution of CTATos (2.5 g, 5.5×10^{-3} mol) in distilled water (90 mL) was stirred during 1 h at 333K. The first solution was added drop wise to second one and then stirred at 333K during 2 h. The resulting sol-gel was heated in an autoclave at 403 K during 20 h. After filtration and washing with distilled water, the as-made solid was dried at 353 K. The extraction of surfactant was performed with 0.1 N HCl / ethanol solution [27].

2.3. Preparation of en- LUS-1

To a mixture containing dry LUS-1 (5 g) and dry toluene (100 mL), N-(2-Aminoethyl)-3-aminopropyltrimethoxysilane (1.67×10^{-2} mol, 4 mL) was added. The mixture was refluxed for 24 h under inert atmosphere. Finally, the solid was filtered and soxhleted under inert atmosphere with toluene for 48 h. The schematic representation of reaction is shown in Fig.1.

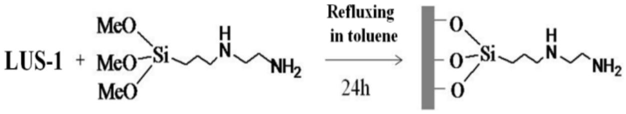

Fig. 1. Preparation of en-LUS-1

2.4. Apparatus

Mesoporous structures were characterized by means of N_2 adsorption–desorption isotherm measurements at 77 K with a BELSORP-mini, BEL Japan, Inc. The TGA measurement was performed on TA Q50 instrument in the temperature range from ambient to 1000 °C. The FT-IR spectra of materials were obtained using Bruker EQINOX 50. The XRD (X-ray Diffraction) was obtained from Siemens D500 diffractometer employing nickel filtrated CuKα (λ = 1.5418 ºA).

The Pb^{2+}, Cd^{2+} and Zn^{2+} and other cations determination were carried out on an ICP-OES Varian, model LIDERTY 150 AX Turbo. The operation conditions and the analytical line of Pb^{2+}, Cd^{2+} and Zn^{2+} are presented in following:

Wavelength (nm)	Pb^{2+} (220.3), Cd^{2+} (226.5), Zn^{2+} (213.9)
Forward rf power	1.2 (KW)
Plasma flow	15.0 (L/min)
Auxiliary flow	1.50 (L/min)
View height	8 (mm)
Detector	PMT

2.5. Metal adsorption experiments

The general procedure for Pb^{2+}, Cd^{2+} and Zn^{2+} ions extraction by the functionalized LUS-1 was as follows. To a suitable volume of the sample solution containing 5 µg Pb^{2+}, Cd^{2+} and Zn^{2+}, 20 mg of functionalized LUS-1 was added and the mixture was stirred for at least 5 minutes. Then, the resulting mixture was filtrated on a paper filter. The extracted ions by the functionalized LUS-1 were then stripped using 20 mL of 3.0 mol L^{-1} solution of nitric acid into 20 mL volumetric flask. Finally the Pb^{2+}, Cd^{2+} and Zn^{2+} ions content in extracted and stripping solution were determined by ICP-OES.

3. Results and Discussion

3.1. Mesoporous adsorbent

The low angle XRD powder patterns of LUS-1 and en-LUS-1 (Fig.2) were showed typical of a hexagonal mesophase with the *P6mm* symmetry characteristic of MCM-41 [19]. No lattice change was observed between en-LUS-1 and LUS-1. According to the BJH model, the pore size distribution of en-LUS-1 and LUS-1 solid is still typical a MCM-41 and centered at 2.0 and 3.1 nm, respectively. The BET specific surface area (S_{BET}) for en-LUS-1 and LUS-1 were 560 m^2g^{-1} and 800 m^2g^{-1}, respectively. The decrease in S_{BET} and average BJH pore diameter after functionalization can be interpreted due to the presence of organic ligand on the surface.

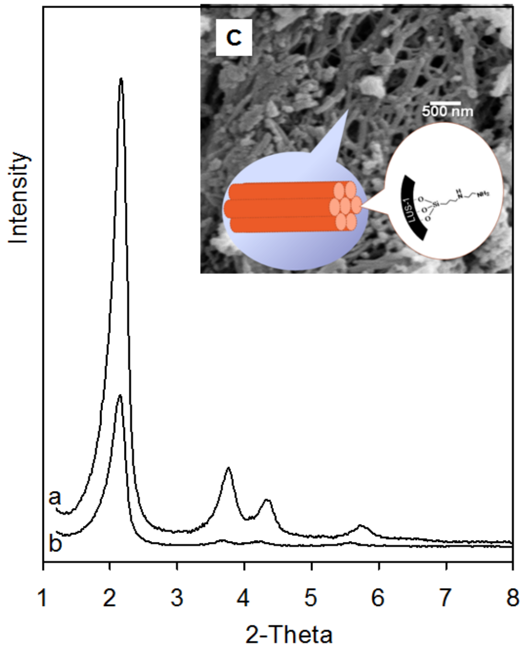

Fig. 2. XRD pattern of a) LUS-1 and b) en-LUS-1 and, c) SEM image of en-LUS-1

The SEM image of en-LUS-1 shows a texture form (Fig.2c). It can be concluded that the morphology of LUS-1 remain during the functionalized of surface. Also, TEM image of LUS-1 (Fig.3) reveals the parallel channels, which resemble the pores configuration of MCM-41.

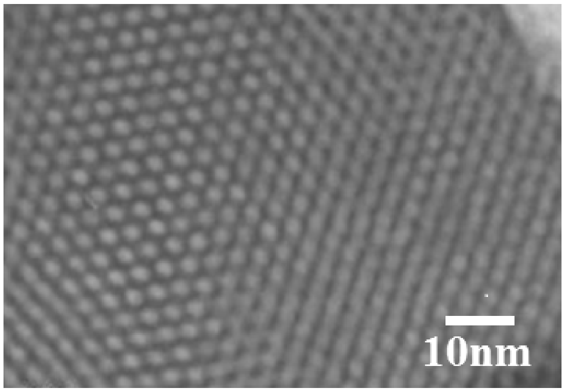

Fig. 3. TEM image of LUS-1

The FTIR spectrum of en-LUS-1 is shown in Fig.4. The strong peak observed at about 1550 cm^{-1} was assigned to N-H vibration.

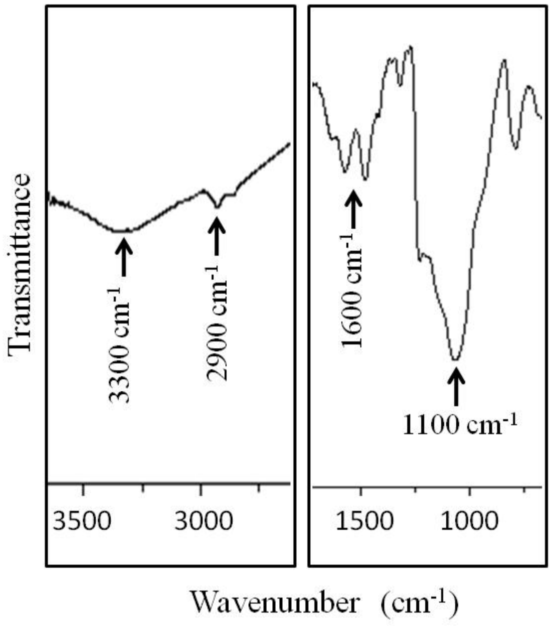

Fig. 4. FTIR spectrum of en-LUS-1

In the region between1000-1200 cm^{-1}, C-N stretching vibrational band cannot generally be resolved due to its overlap with Si-O-Si stretching bands in this range and Si-CH_2-R stretching in the range 1200-1250 cm^{-1}. Weak bands located at 2950 to 2830 cm^{-1} correspond to C-H asymmetric and symmetric stretching vibration modes, respectively. Furthermore a broad band containing a double peak in the range 3200-3400 cm^{-1} is assigned to the asymmetric and symmetric stretching vibration of NH_2 groups and O-H stretching.

Fig.5 shows the thermal gravimetric analysis of en-LUS-1 sample. The mass loss up to 150°C is related to the physisorbed water which is 4% of this compound. Moreover this analysis shows the mass loss between 150 °C and 600 °C (12% weight loss) which was associated with decomposition of the organic groups anchored onto LUS-1. The amount of organic groups immobilized on LUS-1 was determined by TGA (1.1×10^{-3} mol en /g of sample).

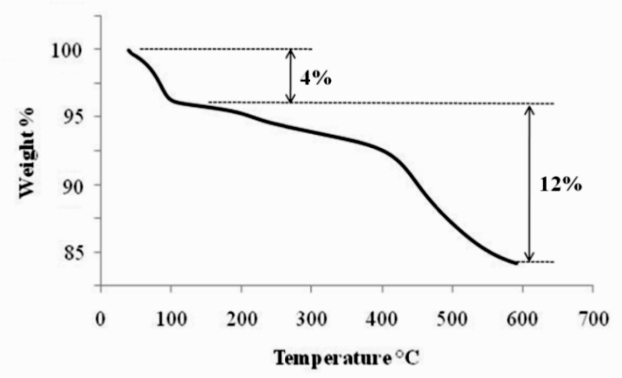

Fig. 5. Thermogravimetric analysis of en-LUS-1

3.2. Optimization of amount of the functionalized LUS-1

The optimum amount of the sorbent for maximum take up was determined by increasing the amount of functionalized LUS-1 added into 25 mL of 0.2 mg L^{-1} solution of Pb^{2+}, Cd^{2+} and Zn^{2+}.

Results are given in Fig.6. As it is obvious, initially, percentage of adsorption on functionalized LUS-1 is increased with increasing sorbent amount and finally the extraction of ions is done quantitatively by using 20 mg of functionalized LUS-1. Hence, subsequent extraction experiments were carried out with 20 mg of functionalized LUS-1.

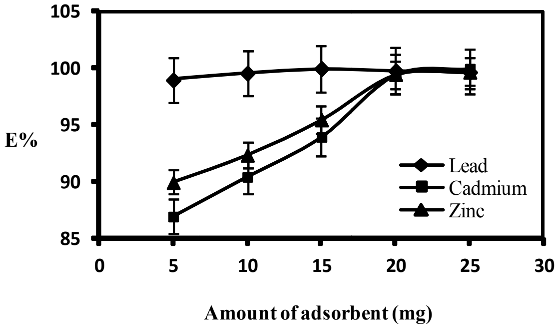

Fig. 6. Effect of amount of adsorbent on the percent of extraction of Pb^{2+}, Cd^{2+} and Zn^{2+}ions

3.3. The effect of the extraction time on extraction yield

The effect of the stirring time (from 2 to 20 min) on the efficiency of the extraction for a series of solutions containing 5 µg of Pb^{2+}, Cd^{2+} and Zn^{2+} was investigated and the results are depicted in Fig.7.

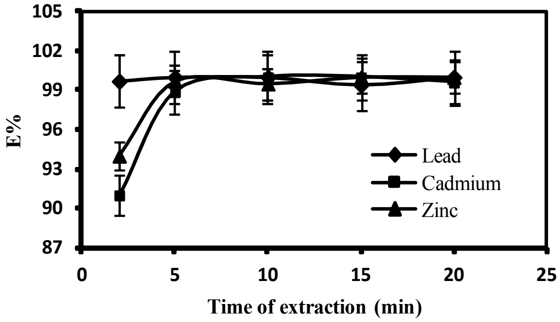

Fig. 7. Effect of stirring time on the percent of extraction of Pb^{2+}, Cd^{2+} and Zn^{2+} ions

As it is seen, Pb^{2+}, $Cd^{2+}$and Zn^{2+}can be extracted quantitatively by the functionalized LUS-1 in the stirring time of 5 minutes and more than it. Thus, the mixtures were stirred for 5 min in all of the experiments.

3.4. The influence of the pH on the Extraction yield

The effect of the pH of aqueous samples on the extraction of 5 µg Pb^{2+}, Cd^{2+} and Zn^{2+} ions from 25 mL solution was investigated in the pH range 2-8.0 (pH was adjusted using 1 mol L^{-1} of either nitric acid or sodium hydroxide solution). As can be seen from Fig.8, ions can be extracted quantitatively by the functionalized LUS-1 in the pH≥3. At higher acidic media, the nitrogen atoms of the ethylenediamine groups could be protonated and reduces the stability of the complex formation between amine groups and Pb^{2+}, Cd^{2+} and Zn^{2+} ions. It was decided to use a pH value of about 5 as a compromise for the simultaneous extraction of all target species.

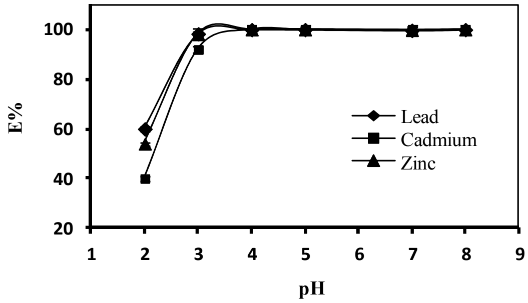

Fig. 8. Effect of pH on the percent of extraction of Pb^{2+}, Cd^{2+} and Zn^{2+} ions

3.5. The effect of the volume of acid on the stripping of Pb^{2+}, Cd^{2+} and Zn^{2+}

Some experiments were carried out in order to choose a proper volume of nitric acid for the retained Pb^{2+}, Cd^{2+} and Zn^{2+} ions after extraction by the functionalized LUS-1. The ions were stripped with varying volumes of acid from 5 to 25 mL. Results showed (Fig.9) that, 20 mL of 3.0 mol L^{-1} nitric acid can accomplish the quantitative elution of Pb^{2+}, Cd^{2+} and Zn^{2+} from the functionalized LUS-1.

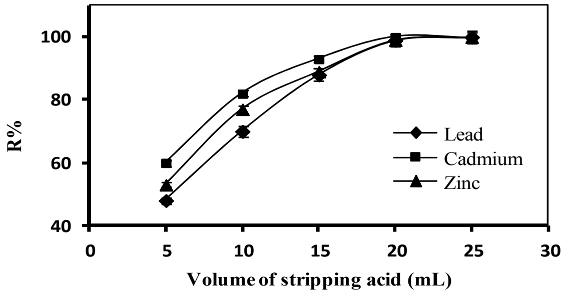

Fig. 9. Effect of the volume of stripping acid on the recovery of Pb^{2+}, Cd^{2+} and Zn^{2+}ions

3.6. Break-through volume determination

The break-through volume of the sample solution was studied by dissolving 5 µg of Pb^{2+}, Cd^{2+} and Zn^{2+} in 100, 250, 500, 1000, 2000 and 2500 mL of water, and the recommended procedure was followed. Up to 2000 mL, the extraction by the functionalized LUS-1was found to be quantitative. Thus the break through volume for the method should be greater than 2000 mL. As recovery of ions was done with 20 mL nitric acid, thus, preconcentration factor is 100.

3.7. Capacity of the functionalized LUS-1

The maximum capacity of the functionalized LUS-1was determined by adding adsorbent to 25 mL portions of an aqueous solution containing 12.5 mg Pb^{2+}, Cd^{2+} and Zn^{2+}, and stirring it for 5 minutes and passing the resulting mixture through a paper filter, followed by determination of the retained metal ions using ICP-OES. The maximum capacity was found to be 150.0 (±2.0) µg and 93.0 (±1.7) µg and 125.0 (±1.2) µg of Pb^{2+}, Cd^{2+} and Zn^{2+}/mg functionalized LUS-1, respectively.

Table 1. Recovery percent of Pb^{2+}, Cd^{2+} and Zn^{2+} ions from mixture solutions[a]

Diverse ions	Amount taken (μg)	%Recovery of Pb^{2+}	% Recovery of Cd^{2+}	% Recovery of Zn^{2+}
Na^+	10000	99.4 (0.6)[b]	99.4 (0.9)	99.7 (1.2)
Ca^{2+}	10000	100.0 (0.9)	99.0 (0.6)	99.8 (0.5)
Fe^{2+}	5000	100.2 (0.8)	99.5 (1.3)	100.0 (0.7)
Mn^{2+}	5000	100.1 (1.4)	100.0 (0.8)	99.8 (0.6)
Mg^{2+}	5000	99.4 (0.7)	99.7 (0.9)	100.2 (1.0)
Cu^{2+}	500	99.0 (0.9)	99.3 (0.5)	99.9 (0.8)
Cr^{3+}	500	99.8 (0.9)	99.4 (1.2)	99.7 (1.1)
Ni^{2+}	500	99.9 (1.4)	100.0 (0.9)	99.4 (1.1)
Co^{2+}	500	100.0 (0.8)	99.2 (0.7)	100.0 (0.6)

[a] Initial samples contained 5 μg Pb^{2+}, Zn^{2+} and Cd^{2+} ions in 25 mL water

[b] Values in parentheses are RSDs based on three replicate analysis

Table 2. Extraction of Pb^{2+}, Zn^{2+} and Cd^{2+} ions from synthetic samples[a]

Sample	% Extraction of Pb^{2+}	% Extraction of Zn^{2+}	% Extraction of Cd^{2+}
synthetic sample 1(Mn^{2+}, Mg^{2+}, Ni^{2+} and Co^{2+}, 500 μg of each cation)	99.31 (0.92)[b]	100.00 (0.84)	99.68(0.92)
synthetic sample 2(Fe^{2+}, Cr^{2+}, Na^+ and Ca^{2+}, 500 μg of each cation)	100.11 (1.44)[b]	99.07 (0.92)	98.65(0.72)

[a] Initial samples contained 5 μg Pb^{2+}, Zn^{2+} and Cd^{2+} ions in 2000 mL water

[b] Values in parentheses are RSDs based on three replicate analysis

3.8. Extraction and determination of Pb^{2+}, Cd^{2+} and Zn^{2+} ions in mixtures

In order to investigate the selective separation and preconcentration of Pb^{2+}, Cd^{2+} and Zn^{2+} ions from water containing diverse metal ions, an aliquot of aqueous solution (25 mL) containing 5 μg Pb^{2+}, Cd^{2+} and Zn^{2+} and various amounts of other cations was taken and the recommended procedure was followed, and the results are shown in Table1. As is obvious from Table 1, the Pb^{2+}, Cd^{2+} and Zn^{2+} ions in the mixtures were retained completely by the ethylenediamine functionalized LUS-1.

3.9. Analytical characteristics of the method

The limit of detection, limit of quantitation, precision, enrichment factor and regression equations were the parameters which were used for the method validation. The limit of detection (LOD) for Pb^{2+}, Cd^{2+} and Zn^{2+} were determined by passing a blank solution trough the functionalized LUS-1 under the optimal experimental conditions. The LOD obtained from $C_{LOD}=K_bS_bm^{-1}$ for a numerical factor $K_b=3$, are 0.45, 0.05 and 0.03 ng mL^{-1} for Pb^{2+}, Cd^{2+} and Zn^{2+} respectively. "S_b" is standard deviation of blank solution and "m" is the slope of calibration curve. The limit of quantitation, defined as ten times of the S values of blanks, was calculated as 1.5, 0.2 and 0.1 ng mL^{-1} for Pb^{2+}, Cd^{2+} and Zn^{2+} respectively. The method precision was evaluated using six solutions containing 2 ng mL^{-1} Pb^{2+}, Cd^{2+} and Zn^{2+}. The relative standard deviations (%R.S.D.) for six preconcentration experiments were found to be 2.7, 2.3 and 1.8 % for Pb^{2+}, Cd^{2+} and Zn^{2+} respectively. The method enrichment factor which was calculated as the ratio of the sample volume and the consumed acid volume to recovery was 100. The regression equations for Pb^{2+}, Cd^{2+} and Zn^{2+} determination were $A=406.6C–245.57$, $A=3793.2C-297.87$ and $A=5081.8C+174.28$ respectively, where A is the absorbance and C is the metal concentration in solution (ng mL^{-1}).

3.10. Determination of Pb^{2+}, Cd^{2+} and Zn^{2+} in synthetic sample

In order to assess the applicability of the method to samples with different matrices containing varying amounts of other ions, it was applied to the extraction and recovery of Pb^{2+}, Cd^{2+} and Zn^{2+} ions from two synthetic samples. 2000 mL aqueous solution containing 5 µg Pb^{2+}, Cd^{2+} and Zn^{2+} and much more amounts of other cations was taken and the recommended procedure was followed, the results are summarized in Table2. As is immediately obvious, the recovery of the proposed method was found to be quantitative in synthetic samples.

3.11. Determination of Pb^{2+}, Cd^{2+} and Zn^{2+} in water samples

To assess the applicability of proposed method in real samples an attempt was made to determine Pb^{2+}, Cd^{2+} and Zn^{2+} ions in water samples. At first, the proposed method was applied to the extraction and determination of Pb^{2+}, Cd^{2+} and Zn^{2+} in various water types including distilled water and Karaj river water. Water samples were filtered using a 0.45-µm pore size membrane filter to remove suspended particulate matter. To 2000 mL of the some sample solutions 20 µg of the Pb^{2+}, Cd^{2+} and Zn^{2+} ions were added and to some of the solutions were added nothing and the recommended procedure was followed for all of solutions.

Table 3. Determination of Pb^{2+}, Zn^{2+} and Cd^{2+} ions in water samples

Sample	Metal	Added Amount of each ion (ng mL^{-1})	Found, ng mL^{-1} (RSD)[a]	
			SPE-ICP_OES	Ev-ICP_OES[b]
Distilled water	Pb^{2+}	20	19.66(1.84)	18.70(2.17)
	Zn^{2+}	20	20.27(1.45)	19.34(1.09)
	Cd^{2+}	20	18.99(1. 96)	19.53(2.01)
Karaj river	Pb^{2+}	0.0	<LOD	<LOD
	Zn^{2+}	0.0	18.94(1.95)	19.01(1.73)
	Cd^{2+}	0.0	<LOD	<LOD
Karaj River	Pb^{2+}	20	21.02(1.78)	20.45(1.96)
	Zn^{2+}	20	39.51(1.44)	40.00(1.60)
	Cd^{2+}	20	20.43(1.27)	19.86(1.40)

[a] %RSD based on three replicate analysis

[b] Measurements were done after ten times concentration by evaporated

As shown in Table 3, the proposed method could be applied successfully for the preconcentration and determination of trace amounts of Pb^{2+}, Cd^{2+} and Zn^{2+} in various water types. On the other hand, validation of the method was performed using a comparison of the results obtained by the proposed method and determination by ICP-OES after concentration by evaporation. As can be seen in Table3, they are in satisfactory agreement.

3.12. Determination of Pb^{2+}, Cd^{2+} and Zn^{2+} in wastewater samples

The proposed method was also applied to the determination of Pb^{2+}, Cd^{2+} and Zn^{2+} in two different wastewater samples (Calcimine and Dandy, Zanjan, Iran), (Table4). The results obtained by the proposed method and inductively coupled plasma atomic emission spectrometry (ICP-OES) after a four-fold preconcentration (by evaporating the solution) are in satisfactory agreement. Concentration of the sample solution before detection by ICP-OES is necessary because the concentration of lead is lower than the detection limit of this technique.

Table 4. Determination of Pb^{2+}, Zn^{2+} and Cd^{2+}ions in wastewater samples

[a] %RSD based on three replicate analysis

Metal	Sample	Found, ng mL^{-1}(RSD)^{a}	
		(SPE- ICP-OES)	(ICP-OES)
Pb^{2+}	1	35.77(2.19)	35.90(1.78)
	2	36.47(1. 90)	35.63(2.27)
Zn^{2+}	1	3894.27(1.69)	3902.49(1.75)
	2	3871.13(1.15)	3880.09(1.49)
Cd^{2+}	1	11.70(1.71)	12.44(1.82)
	2	12.03(1.54)	12.51(1.38)

[b] Measurements were done after four- fold concentration by evaporate

3.13. Determination of Pb^{2+}, Cd^{2+} and Zn^{2+} in tea and pepper samples

Finally, the proposed method was applied to the determination of Pb^{2+}, Cd^{2+} and Zn^{2+} and Cd^{2+} in black tea and pepper samples. The procedures used for the extraction of these metals from these samples were similar to that reported in the literature [30]. One gram of the dry tea sample (dried at 110 ºC) was placed in a 50-mL beaker, followed by the addition of 7mL of concentrated nitric acid, and the beaker was covered with a watch glass. The beaker was allowed to stand overnight, than the contents were heated on a hotplate (150 ºC), for 15 min. The sample was cooled, 8mL of perchloric acid was added, and the mixture was heated again at 200 ºC until the solution became clear (about 1 h). The watch glass was removed and the acid evaporated to dryness at 150 ºC. The residue was completely dissolved in 5mL of 1M nitric acid and the solution was transferred to a 100-mL calibrated flask. The solution was neutralized with NaOH solution and diluted to the mark, and the recommended procedure was followed. The results obtained by the proposed method and by evaporating the solution are shown in Table5.

Also, a 100 mg pepper was taken in a beaker and dissolved in concentrated nitric acid (5 mL) with heating. The solution was cooled, neutralized with NaOH solution, diluted and filtered. The filtrate was made to 100 ml with water in a calibrated flask and the recommended procedure was followed. The results obtained by the proposed method and by evaporating the solution are given in Table5. As can be seen, the amounts of Pb^{2+}, Cd^{2+} and Zn^{2+} in black tea, and hot and black pepper samples can be accurately determined with the proposed method.

Table 5. Determination of Pb^{2+}, Zn^{2+} and Cd^{2+}ions in tea and pepper samples

Sample	Metal	Found, μgg^{-1} (RSD)^{a}	
		(SPE-AAS)	(ICP-AES)^{b}
Iranian black tea (Lahijan)	Pb^{2+}	37.10(1.96)	36.84(1.80)
	Zn^{2+}	74.09(0.87)	73.88(0.92)
	Cd^{2+}	0.49(1. 56)	0.53(1.60)
Indian black tea (Ceylon)	Pb^{2+}	20.56(2.05)	21.17(1.84)
	Zn^{2+}	80.61(1.21)	79.44(1.05)
	Cd^{2+}	0.58(1.64)	0.60(1.34)
Black pepper	Pb^{2+}	401.93(1.56)	402.51(1.79)
	Zn^{2+}	277.44(1.15)	276.90(1.18)
	Cd^{2+}	0.97(1.80)	0.92(1.92)
Hot pepper	Pb^{2+}	22.05(1.99)	22.48(2.32)
	Zn^{2+}	237.29(0.95)	238.00(1.29)
	Cd^{2+}	0.85(1.58)	0.80(1.96)

[a] %RSD based on three replicate analysis

[b] Measurements were done after ten times concentration by evaporate

4. Conclusion

Although there are very sensitive techniques to determination of heavy metal ions, it may still be necessary to apply a preconcentration step due to low ion concentration in environmental water samples. Therefore, in this study, ethylenediamine functionalized LUS-1 has been introduced as a new adsorbent to preconcentration of Pb^{2+}, Cd^{2+} and Zn^{2+} ions. The ng mL^{-1} level of concentration of Pb^{2+}, Cd^{2+} and Zn^{2+} ions can be determined in water and food samples including distilled water, river water, black tea, black and hot pepper. The method's enrichment factor is100 and detection limits are 0.45, 0.05 and 0.03 ng mL^{-1} for Pb^{2+}, Cd^{2+} and Zn^{2+} respectively. The proposed method has the following advantages: The method is very fast (extraction time is 5 min), sensitive, efficient, inexpensive and very simple. The method doesn't need to consume of harmful organic solvents and can apply in variety of samples. In addition, it is important to point out that Pb^{2+}, Cd^{2+} and Zn^{2+} ions can simultaneously preconcentrate by ethylenediamine functionalized LUS-1

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