

## Preconcentration and Determination of Trace Amounts of Lead and Cadmium in Food Samples with Ionic Liquid Coated Magnetic Nanoparticles as a New Nano Adsorbent

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### Abstract

In the present study, a new, simple and rapid method is developed for pre-concentration and determination of the trace amounts of Pb (II) and Cd (II) ions in food samples through solid phase extraction using (Fe<sub>3</sub>O<sub>4</sub>SiO<sub>2</sub> (DABCO-PDO) Cl) ionic liquid modified magnetic nanoparticles. This adsorbent was used for the first time to extract and pre-concentrate lead and cadmium metals. Herein, Pb (II) and Cd (II) contents were quantified with Flame Atomic Absorption Spectroscopy (FAAS). The effect of different empirical parameters (such as sample pH, adsorbent amount, type and amount of the solvent, extraction and desorption times and the ligand concentration) was evaluated and optimized for Pb (II) and Cd (II) extraction and pre-concentration. The calibration curve was linear under the optimum condition in the concentration range of 0.8-4.5 µg L<sup>-1</sup> with the correlation coefficient of 0.9986. The concentration factor was 100 with the detection limit of 0.25 µg L<sup>-1</sup> and 0.068 for Pb and Cd, respectively. The repeatability of Relative Standard Deviations (RSD%) for the concentration of 1 mg L<sup>-1</sup> was 1.8 for Pb and 1.4 for Cd. The developed method was successfully used to determine lead and cadmium content in food samples (milk, yogurt, rice, fish, olive oil, sunflower oil). The ionic liquid-modified magnetic nanoparticles were further characterized using Fourier Transform Infrared Spectroscopy (FT-IR) analysis, Scanning Electron Microscopy (SEM), X-Ray Powder Diffraction (XRD), Transmission Electron Microscopy (TEM) and Vibrating Sample Magnetometer (VSM) techniques.

**Keywords:** Pb (II); Cd (II); Solid-phase extraction; Ionic liquid; Food samples

### Introduction

Nowadays, the determination of trace heavy metals in environmental and food samples is of crucial importance. These elements can cause unpleasant effects such as damaging the internal organs, the nervous system, kidneys, liver and lungs. Almost all heavy metals have detrimental effects on the body, some of which including lead, cadmium, nickel and mercury are toxic and hazardous to human health even in trace amounts. Lead is a highly poisonous and carcinogenic metal capable of causing chronic diseases, such as headache, irritability, abdominal pain, nerve injuries, kidney injury, hypertension, lung and stomach cancer. Lead can replace calcium in the bones in the long run.

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Regarding the importance of measuring the lead and cadmium content, there is a need for a sensitive, simple, repeatable and accurate analytical method to determine trace amounts of lead and cadmium in different types of samples. Lead and cadmium are among the prevalent toxic elements in the food samples with a long half-life after the absorption in humans and animals [1].

There are various methods to identify this cation in different samples consisting of Graphite Furnace Atomic Absorption (GFAA), Inductively Coupled Plasma Emission Spectrometry (ICP-OES) Inductively Coupled Plasma Mass Spectrometry (ICP-MS), electrothermal atomic absorption spectrometry and FAAS. Among these methods, FAAS has been widely used due to its lower costs and ease of application. FAAS is a simply available analytical instrument in many laboratories. Many people are known to have suffered from Itai-Itai syndrome by consuming rice contaminated with cadmium [2-4].

Solid-Phase Extraction (SPE) is one of the efficient methods for the extraction of heavy metals from real samples involving advantages such as high concentration factors, reduced organic solvent consumption, simplicity and the final phase free of the contamination. The magnetic SPE is an emerging, efficient and simple method in which magnetic particles are considered as the solid phase and in which the magnetic field could serve as the separating force. SPE is widely used for the extraction and pre-concentration of analytes in various environmental and food samples [5-8].

In this study, DABCO-PDO Ionic Liquid (IL) modified Magnetic Nano-Particles (MNPs) were applied as nano-adsorbents for pre-concentration and determination of lead and cadmium ions. Ionic liquids are not simple liquids but they are environmentally-friendly. Their ions are generally asymmetric, with delocalized electrostatic charges. Pb (II) and Cd (II) ions were adsorbed by the synthesized DABCO-PDO IL nano-sorbent, ILs have attracted great attention in analytical chemistry and separation science.

New materials with interesting properties can be generated by immobilizing ILS on the solid substrates. In this work, DABCO-PDO IL modified silica-coated MNPs were synthesized and employed as a new nano-adsorbent for the extraction and pre-concentration of Pb (II) and Cd (II) ions.

After desorption with acidic methanol, Pb (II) and Cd (II) were quantified by FAAS. The effect of experimental factors on the extraction efficiency was also evaluated and optimized. To investigate the applicability of the proposed method, it was utilized for the determination of Pb (II) and Cd (II) ions in different food samples (milk, yogurt, rice, fish, olive oil, sunflower oil) [9-11].

## Materials and Methods

The standard lead and cadmium solutions of  $1000 \text{ mgL}^{-1}$  were prepared by dissolving a sufficient amount of lead (II) and cadmium (II) nitrate salt in nitric acid 5% purchased from Chem.Lab Company (Belgium). Methanol, ethanol, acetonitrile and toluene solvents, as well as,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  were prepared from Merck Company (Germany). Tetraethyl Ortho-Silicate (TEOS, 98%) and (3-Chloro-Propyl) Tri-Methoxy-Silane (CPTMS, 97%) were obtained from Sigma-Aldrich company. Deionized water was also used for all the investigations [12-15].

A FAAS (PerkinElmer's PinAAcle 900T) with lead (Pb) and cadmium (Cd) hollow-cathode lamps were used to detect the absorbance of Pb and Cd ions. Preparation and acid digestion of food samples were accomplished using a microwave digestion instrument (analyticjena TOP wave). The pH values were measured using a Sartorius pH-meter. The lead and cadmium solution were stirred for the adsorption/desorption steps using a Heidolph shaker.

A magnet with a magnetic field of 1.4 tesla was used for magnetic separation. The as-synthesized compounds were also characterized using FT-IR spectroscopy and FE-SEM analysis for determining the morphology and size of nanoparticles; while XRD was employed to identify the phases and diffraction patterns of the samples. The average particle size was also determined using the Scherrer equation. The FT-IR spectrum was obtained from JACSO-FT-IR-410 using KBr tablets.

The FE-SEM spectrum and XRD were also obtained by KYKY instrument and XPERT instrument, respectively. The BINDER vacuum oven (Germany) and BANDELIN ultrasonic bath were also used during the process [16-20].

### Synthesis of IL-Modified MNPs

The synthesis of IL-modified MNPs ( $\text{Fe}_3\text{O}_4\text{SiO}_2(\text{DABCO-PDO})\text{Cl}$ ) was carried out in five steps. 11.2 g of 1,4-diazabicyclo [2.2.2] octane was dissolved in 50 ml ethanol followed by adding 8.4 ml 3-chloro-1,2-propanediol. The resultant mixture was refluxed for 24 h, the solvent was then removed by a rotary evaporator. 5 g of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  along with 12.5 g of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  were dissolved in deionized water. Then, 2 ml of concentrated hydrochloric acid was added to the mixture.

The solvent was added to 600 ml of 1.5 M NaOH dropwise under intense stirring at  $7^\circ\text{C}$ . Black  $\text{Fe}_3\text{O}_4$  MNPs were fabricated and the precipitate was eluted three times with deionized water and dried in the vacuum oven (FIG. 1) [21-23].

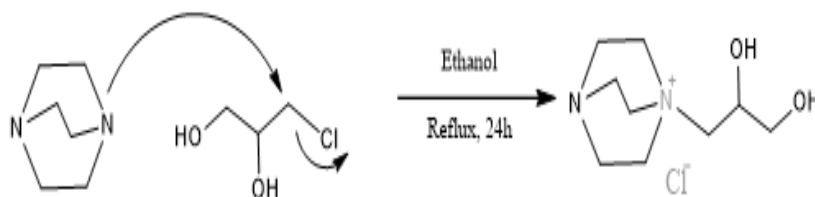


FIG. 1. Preparation of (DABCO-PDO)Cl.

**Synthesis of silica-coated  $\text{Fe}_3\text{O}_4$  NPs ( $\text{Fe}_3\text{O}_4\text{SiO}_2$ ):** A solution containing 2 g  $\text{Fe}_3\text{O}_4$  in 70 ml of deionized water was sonicated for 15 min. Then, 5 ml of ammonia and 5 ml of TEOS were added to the mixture stirring for 24 h. The solution was finally eluted with deionized water reaching pH=7, it was then washed with ethanol for three times (each time with 10 ml) getting dried in a vacuum oven at  $6^\circ\text{C}$  for 12 h [24].

**Synthesis of chloro-functionalization:** In this case, 3 ml of CPTMS along with 3 g of  $\text{Fe}_3\text{O}_4\text{SiO}_2$  was dissolved in 300 ml of dried toluene. The mixture was stirred at the temperature of  $6^\circ\text{C}$  for 22 h. The precipitate was rinsed with 100 ml of dried toluene getting dried in a vacuum oven at  $5^\circ\text{C}$  for 12 h [25].

**Synthesis of DABCO-based IL-functionalized  $\text{Fe}_3\text{O}_4$  NPs:** A mixture of a solution containing 2 g of  $\text{Fe}_3\text{O}_4\text{SiO}_2\text{Cl}$  in 30 ml of ethanol and the other composed of 1 g of (DABCO-PDO) IL in 20 ml of ethanol was sonicated for 1 h. Next, it was refluxed for 24 h, the precipitate was eventually washed with ethanol and dried in a vacuum oven at  $50^\circ\text{C}$  for 12 h (FIG. 2) [26].

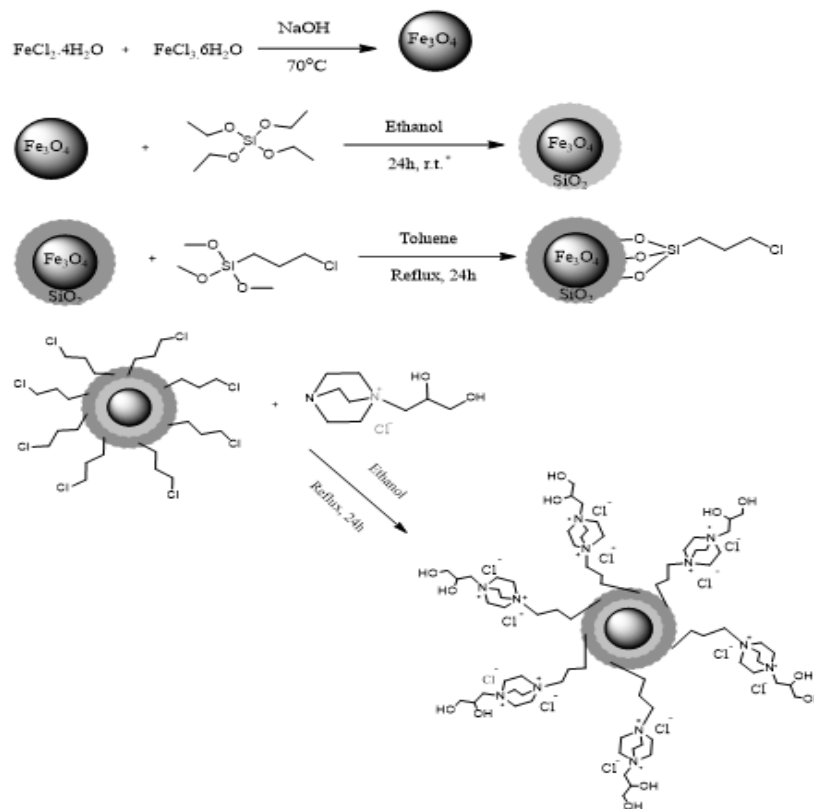


FIG. 2. Synthesis of  $(\text{Fe}_3\text{O}_4\text{SiO}_2(\text{DABCO-PDO})\text{Cl})$  ionic liquid-modified magnetic nanoparticles.

### Preparation of real sample

**Food sample:** Food samples were digested with  $\text{HNO}_3$  and  $\text{H}_2\text{O}_2$  at a specific temperature and pressure in a microwave digestion instrument (analyticjena TOP wave). After that, the sample was cooled, to room temperature followed by dilution with 100 ml of deionized water. Finally, the concentration of lead and cadmium was determined by the procedure described as follows.

**General extraction procedure for lead:** For Pb extraction with IL-modified MNPs,  $0.001 \text{ molL}^{-1}$  of 8-hydroxyquinoline ligand was added to 25 ml of the lead sample with a concentration of  $1 \text{ mgL}^{-1}$ . At first, the solution pH was adjusted at 5, then 50 mg of the adsorbent was added and the mixture was stirred by a shaker for 13 min. The nano-sorbent was maintained with a strong magnet and the liquid phase was removed. Then for desorption of Pb (II) ions 2 ml of  $0.5 \text{ molL}^{-1}$   $\text{HNO}_3$  in methanol was added to the nano-sorbent which was again stirred for 13 min. Eventually, the nano-sorbent was separated from the acidic methanol by the magnet. The clear solution of the eluent containing Pb (II) ions was used for the subsequent FAAS analysis [27].

**General extraction procedure for cadmium:** For cadmium extraction with IL-modified MNPs,  $0.001 \text{ molL}^{-1}$  of diethyldithiocarbamate ligand was added to 25 ml of cadmium sample with the concentration of  $1 \text{ mgL}^{-1}$ . At first, solution pH was adjusted at 11, then 40 mg of adsorbent was added and the mixture was stirred by a shaker for 5 min. The nano-sorbent was maintained with a strong magnet and the liquid phase was removed. Then for desorption of Cd (II) ions 3 ml of  $0.5 \text{ molL}^{-1}$   $\text{HNO}_3$  in methanol was added to the nano-sorbent which was again stirred for 5 min. Eventually, the nano-sorbent was

separated from the acidic methanol with the magnet, the clear solution of the eluent containing Cd (II) ions was used for the subsequent FAAS analysis [28].

## Results

### Characterization of the nano-sorbent

The FT-IR spectra of  $\text{Fe}_3\text{O}_4\text{SiO}_2$ ,  $\text{Fe}_3\text{O}_4\text{SiO}_2\text{Cl}$  and  $(\text{Fe}_3\text{O}_4\text{SiO}_2(\text{DABCO-PDO})\text{Cl})$  IL. According to this figure, the peak at  $3455\text{ cm}^{-1}$  represents -OH stretching vibrations and a peak at  $571\text{ cm}^{-1}$  is attributed to vibration of Fe-O bond in the iron oxide nanoparticle. Peaks emerged at  $980\text{ cm}^{-1}$ ,  $2800\text{ cm}^{-1}$  and  $1000\text{ cm}^{-1}$  are related to Si-OH, aliphatic carbons and Fe-O-Si, respectively. The Si-O-Si vibrations are also attributed by peaks at  $800\text{ cm}^{-1}$  and  $1091\text{ cm}^{-1}$ . The FT-IR spectra confirm that the silica-coated  $\text{Fe}_3\text{O}_4$  NPs were functionalized to the Dabco-based IL (FIG. 3).

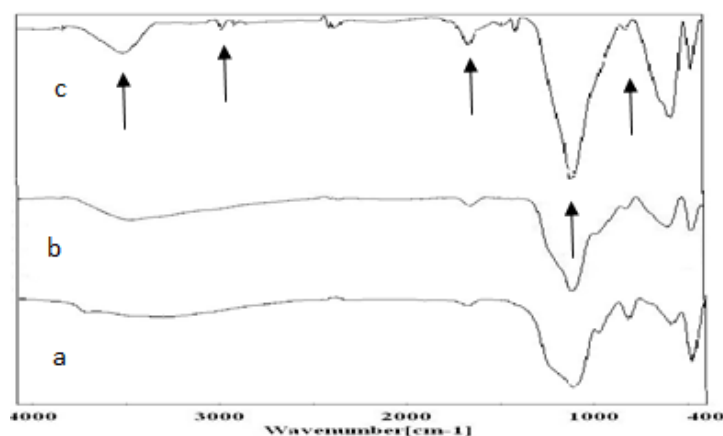


FIG. 3. FTIR spectra; a)  $\text{Fe}_3\text{O}_4\text{SiO}_2$ ; b)  $\text{Fe}_3\text{O}_4\text{SiO}_2\text{Cl}$ ; c)  $\text{Fe}_3\text{O}_4\text{SiO}_2(\text{DABCO-PDO})\text{Cl}$  IL.

The XRD for the synthesized adsorbent, having the cubic crystal structure. The as-synthesized adsorbent was completely pure since there were no additional peaks related to possible impurities. As can be seen, the diffraction peaks of prepared  $\text{Fe}_3\text{O}_4$  nanoparticles were in accordance with those of standard magnetic  $\text{Fe}_3\text{O}_4$ , which are ascribed to the crystal plane of (220), (311), (222), (400), (511), (440), respectively (FIG. 4) [29].

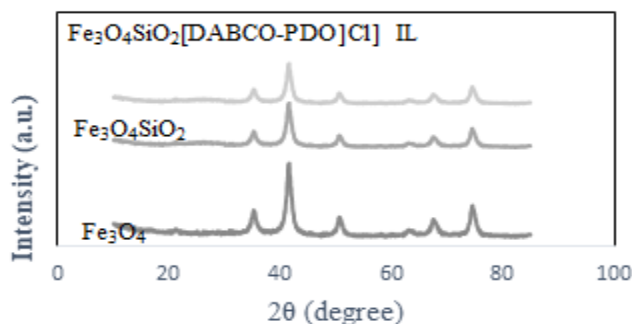


FIG. 4. XRD pattern.

SEM analysis was employed to investigate the surface morphology and shape of IL-modified MNPs as well as the estimation of particle size. Nanoparticles are spherical with a relatively appropriate distribution range reflecting the efficiency of the method. The FE-SEM micrograph of  $(\text{Fe}_3\text{O}_4\text{SiO}_2(\text{DABCO-PDO})\text{Cl})$  IL. The particles modified with the ionic liquid had an average size of  $\sim 25.69$  nm (FIG. 5).

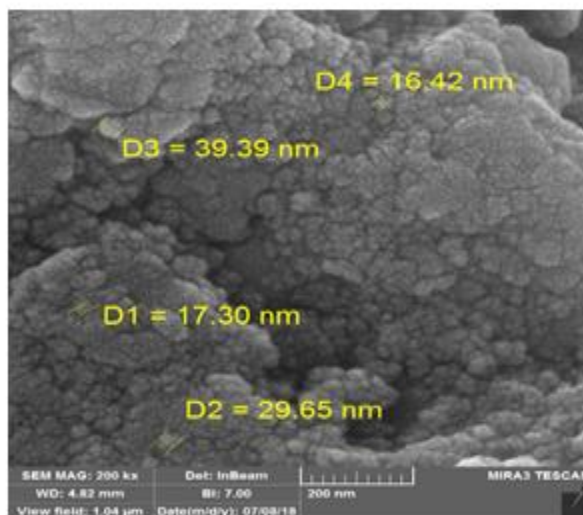


FIG. 5. FE-SEM of  $\text{Fe}_3\text{O}_4\text{SiO}_2(\text{DABCO-PDO})\text{Cl}$  IL.

TEM imaging was also used for further assessment of the shape of the magnetic NPs functionalized with IL. The TEM image of the  $(\text{Fe}_3\text{O}_4\text{SiO}_2(\text{DABCO-PDO})\text{Cl})$  IL. As shown in the TEM micrograph, it is evident that a magnetic/IL core-shell structure was formed. The spherical-shaped NPs can be seen. A light shell clearly surrounded the dark core of  $\text{Fe}_3\text{O}_4$ . In fact, the TEM image allows confirmation of the core-shell encapsulation of  $\text{Fe}_3\text{O}_4$  NPs within a layer of  $(\text{DABCO-PDO})\text{Cl}$ . The TEM and SEM images provide visual evidence for the successful synthesis of NPs (FIG. 6) [30].

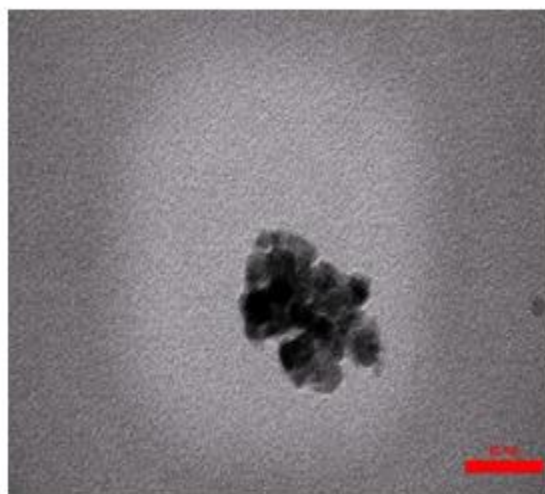


FIG. 6. TEM of  $\text{Fe}_3\text{O}_4\text{SiO}_2(\text{DABCO-PDO})\text{Cl}$  IL.

The magnetic properties of the iron oxide nanoparticles synthesized and modified with ionic liquid, which decreased some of their magnetic properties as the ionic liquid covered the surface of the iron oxide (FIG. 7).

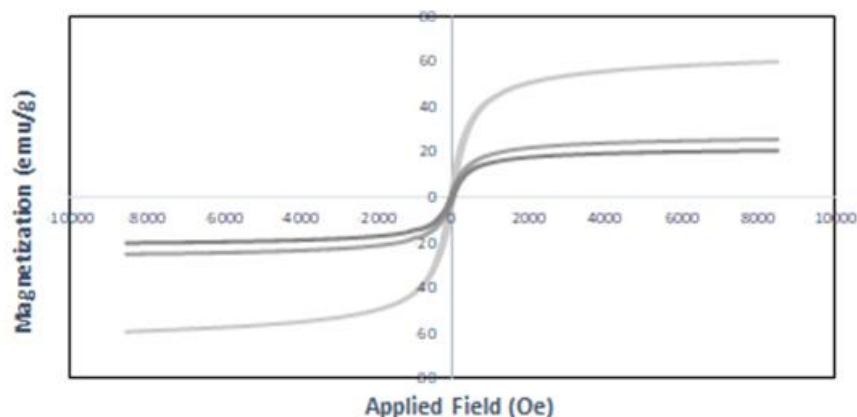


FIG. 7. VSM of  $\text{Fe}_3\text{O}_4\text{SiO}_2[\text{DABCO-PDO}]\text{Cl}$  IL. Note:  $\blacksquare$  :  $\text{Fe}_3\text{O}_4\text{SiO}_2$ ;  $\blacksquare$  :  $\text{Fe}_3\text{O}_4\text{NP}$

**Optimization of conditions for magnetic solid-phase extraction:** To determine the most effective conditions for the extraction and pre-concentration of Pb (II) and Cd (II) ions, several experimental factors were optimized. The optimization of the method was performed by a single-factor method.  $1\text{mgL}^{-1}$  solutions of Pb (II) and Cd (II) were used for all the measurements and three replicates were tested in all cases.

**The effect of pH:** The pH value has a prominent role in the adsorption procedure, especially the adsorption capacity. Studies have proposed that the surface of magnetic nanoparticles has a positive and negative charge in acidic and alkaline pH values, while it is neutral in pH values near 7. Hence, it is essential to accurately optimize this parameter to achieve the quantitative recovery of these heavy metals. The pH values varied in the range of 2-12. The proper pH value for the extraction was 5 and 11 for Pb (II) and Cd (II), respectively due to forming stable bases. So they were considered as the optimal pH (FIG. 8) [31].

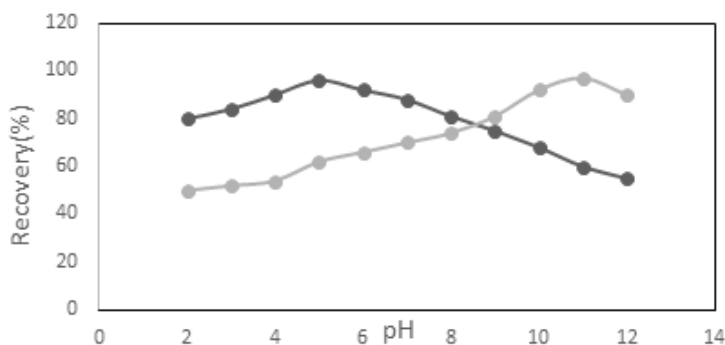


FIG. 8. Effect of pH on the adsorption of Pb (II) and Cd (II)  $\text{Fe}_3\text{O}_4\text{SiO}_2(\text{DABCO-PDO})\text{Cl}$  JIL nanosorbent. Note:  $\bullet$  : Pb (II);  $\bullet$  : Cd (II)

**The effect of ligand concentration:** The extraction efficiencies of lead and cadmium depend on the concentration of ligand. The effect of ligand concentration was thus examined. The concentration of the ligand reagent was increased until the complete complexation of all the lead and cadmium contents. Concentrations higher than  $0.001\text{ molL}^{-1}$  represented no changes in efficiency.

**The effect of type and concentration of the elution:** An appropriate elution should be capable of fully eluting the adsorbed analyte. For this purpose, different solvents including  $0.5\text{ molL}^{-1}\text{ HNO}_3$  in ethanol,  $0.5\text{ molL}^{-1}\text{ HNO}_3$  in methanol and  $0.5\text{ molL}^{-1}\text{ HNO}_3$  in acetonitrile were investigated, among which,  $0.5\text{ molL}^{-1}\text{ HNO}_3$  in methanol with a maximum extraction was chosen as the optimal solvent (FIG. 9).

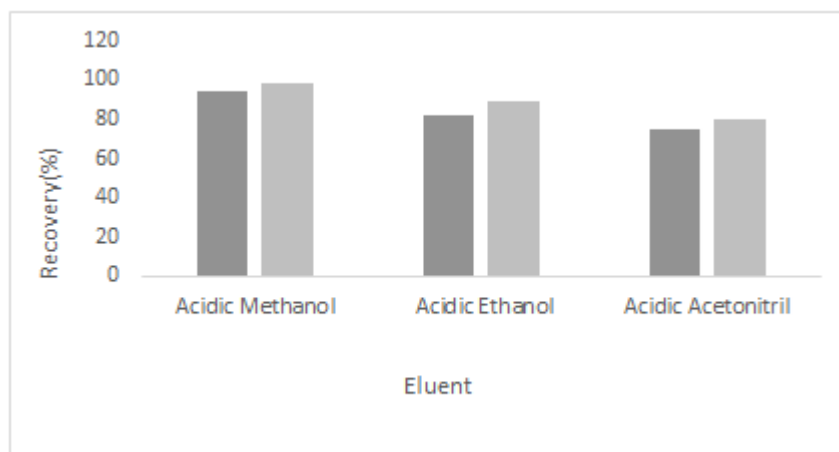


FIG. 9. Effect of eluent adsorption of Pb (II) and Cd (II)  $\text{Fe}_3\text{O}_4\text{SiO}_2(\text{DABCO-PDO})\text{Cl}$  IL nanosorbent. Note: ■: Pb (I); □: Cd (II)

It is also essential to find the minimum amount of solvent for Pb (II) and Cd (II) desorption from nanoparticles to achieve a high concentration factor. In this regard, methanol volume was varied in the range of 2 ml-5 ml. Based on the results, 2 ml and 3 ml of  $\text{HNO}_3$  in methanol exhibited maximum extraction efficiency for Pb (II) and Cd (II), respectively (FIG. 10).

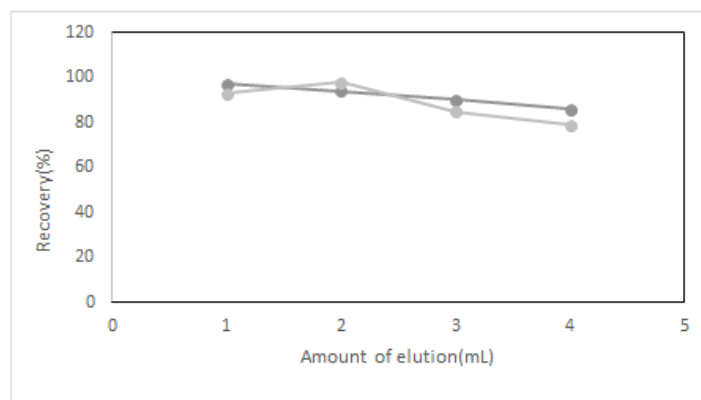


FIG. 10. Effect of amount of elution (ml) adsorption of Pb (II) and Cd (II)  $\text{Fe}_3\text{O}_4\text{SiO}_2(\text{DABCO-PDO})\text{Cl}$  IL nanosorbent. Note: ●: Pb (II); ●: Cd (II)

**The effect of extraction time and desorption time:** The contact time between the solution and adsorbent is another effective feature for the extraction process. The times 2, 5, 8, 10, 13, 15, 20 and 30 min were considered to study the effect of extraction time as well as desorption time. Results represented that both processes were high-yielded at 13 and 5 min for Pb (II) and Cd (II), respectively.

**The effect of the adsorbent amount:** The adsorbent amount is one of the important parameters affecting the cationic metal retention and its pre-concentration. At a fixed concentration of metal ions, more amounts of adsorbent provide adsorbed cations with greater surface and more adsorption sites. The parameter of adsorbent content was evaluated in the range of 10-80 mg. According to the results, 50 mg for Pb (II) and 40 mg for Cd (II) led to maximum extraction (FIG. 11) [32].



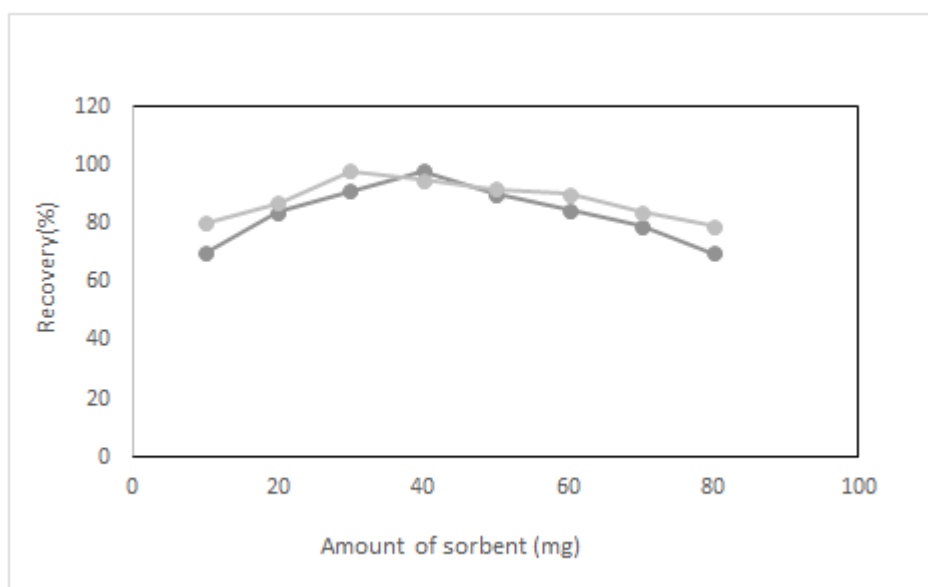


FIG. 11. Effect of amount of sorbent on the extraction efficiency of Pb (II) and Cd (II) ( $\text{Fe}_3\text{O}_4\text{SiO}_2(\text{DABCO-PDO}) \text{Cl}$ ) IL nanosorbent. Note: ● : Pb (II); ○ : Cd (II)

## Discussion

### The effect of the NaCl salt

Considering fixed values for other parameters, the effect of ionic strength on the solid-phase extraction efficiency was evaluated by adding different amounts of NaCl in the range of 0%-30% (w/v). Results revealed that the extraction efficiency remained almost constant in the studied concentration range, thus salt addition had no effect on the adsorption, indicating high resistance of this technique toward higher salt concentrations (TABLE 1).

TABLE 1. The optimal chemical conditions for pre-concentration of Pb (II) and Cd (II).

Optimal parameters	Amount	
	Pb	Cd
pH	5	11
Ligand concentration	0.001 mol	0.001 mol
Adsorbent amount	50 mg	50 mg
solvent	Methanol	Methanol
Solvent volume	2 ml	2 ml
Extraction and desorption times	13 min	13 min

Enrichment Factor (EF) is an important parameter in the SPE performance. The EF can be calculated by:  $EF = c_r/c_s$ . Where  $c_r$  and  $c_s$  are the concentration of the analyte in the eluent phase and the initial concentration of the analyte in the sample solution, respectively. The accuracy of this method was evaluated by determining the mentioned elements in and food samples. Since the quantitative analysis of this element is difficult in the real samples due to their very low concentrations, the accuracy of this method was tested by adding a specified amount of the desired element to real samples. The analysis results with regard to relative efficiencies, the proposed method has the proper efficiency to determine Pb content in the real samples (TABLE 2).

**TABLE 2. Validation results of Pb, Cd analysis in food and aqueous samples by the proposed method under the optimum condition (n=3).**

Sample	Element	added	Found ( $\mu\text{g L}^{-1}$ )	Recovery (%)
Milk	Pb	0.00 20 40	$1.2 \pm 1.3$	-
			$20.21 \pm 1.6$	95
			$38.25 \pm 0.8$	92.6
	Cd	0.00 20 40	$0.8 \pm 1.1$	-
			$19.15 \pm 1.3$	91.75
			$37.46 \pm 1.6$	91.65
Yogurt	Pb	0.00 20 40	$2.12 \pm 1.9$	-
			$20.54 \pm 1.4$	91.7
			$37.25 \pm 2.1$	87.6
	Cd	0.00 20 40	$3.25 \pm 1.3$	-
			$21.52 \pm 1.7$	91.35
			$40.85 \pm 1.6$	94
Rice	Pb	0.00 20 40	$5.28 \pm 1.7$	-
			$24.15 \pm 1.3$	94.3
			$42.78 \pm 1.1$	93.75
	Cd	0.00 20 40	$7.85 \pm 0.7$	-
			$25.65 \pm 1.4$	89
			$43.24 \pm 1.8$	88.47
Fish	Pb	0.00 20 40	N.D	-
			$19.54 \pm 1.5$	97
			$37.74 \pm 1.4$	94.3
	Cd	00.00 20 40	$19.85 \pm 0.6$	99.25
			$38.51 \pm 0.9$	96.27
Olive Oil	Pb	0.00 20 40	N.D	-
			$17.75 \pm 1.5$	88.75
			$34.74 \pm 1.4$	86.85

Sunflower	Cd	0.00 20 40	$0.8 \pm 1.1$	-
			$19.63 \pm 1.8$	94.15
			$38.27 \pm 1.5$	93.67
	Pb	0.00 20 40	$5.56 \pm 1.71$	-
			$22.45 \pm 2.1$	84.45
			$36.52 \pm 1.7$	77.4
Cd	0.00 20 40	$1.8 \pm 21$	86.1	
		$1.2 \pm 39.32$	88.85	

**Comparison with other methods:** The proposed method was compared with other reported methods used for the determination and pre-concentration of lead and cadmium. The comparison results indicated that the proposed method possesses comparatively higher sensitivity. This methodology is simple, economical and reproducible, requiring no further instrumentation and compatible with regular FAAS equipment (TABLE 3).

**TABLE 3. Comparison of the developed method with other reported methods used for determination of Pb and Cd.**

10	Analyte	Detection	LOD ( $\mu\text{gL}^{-1}$ )	EF	RSD (%)
SPE/MWCNT	Pb	FAAS	0.3	100	2.8
SPE/IL-based MNPs	Pb	FAAS	1.66	200	1.34
SPE/2-mercaptobenzothiazole impregnated Amberlite XAD-1180 resin	Pb	FAAS	5	20	2.4
Batch SPE-coated	Pb	FAAS	0.5	1050	2.1
SPE/ $\text{Fe}_3\text{O}_4\text{SiO}_2$ core shell	Cd	FAAS	0.05	-	6.4
SPE/Amberlite XAD-16 resin functionalized	Cd	ICP-AES	0.22	50	2.3
Indium hydroxide	Cd	FAAS	0.42	-	0.75-4.2
SPE/Amberlite XAD-16 modified with $\alpha$ -benzoin oxime chelating resin	Cd	FAAS	5.31	36	3.81
SPE/ $(\text{Fe}_3\text{O}_4\text{SiO}_2(\text{DABCO-PDO})\text{Cl})$ IL	Cd	FAAS	0.068	100	1.44

## Conclusion

In this study,  $\text{Fe}_3\text{O}_4\text{SiO}_2(\text{DABCO-PDO})\text{Cl}$  IL was covalently immobilized on the surface of magnetic nanoparticles and employed as an adsorbent for the magnetic solid-phase extraction and pre-concentration of Pb (II) and Cd (II) before their

determination by FAAS. Covalent immobilization endowed the ionic liquid coating with high stability preventing its loss during the extraction and elution processes. Since the entrance of heavy metals to the food chain of living organisms through environmental waters could have disastrous effects on health, the present study was sought to determine the lead and cadmium contents by solid-phase extraction based on magnetic nanoparticles adsorbent. Taking the results into account, the proposed method requires shorter separation and pre-concentration times as it does not require column chromatography. Yet, this method has good precision and accuracy as well as an expanded linear concentration range. Other advantages of this method are its acceptable speed, low cost, sensitivity and selectivity and facile synthesis processes. The developed method was successfully employed to measure the low concentration of Pb and Cd in food samples with high precision and accuracy.

## Acknowledgment

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## Conflict of Interest

Sara Khodadadi declares that she has no conflict of interest. Elaheh Konozi declares that she has no conflict of interest. Ali Ezabadi declares that he has no conflict of interest. Ali Niazi declares that he has no conflict of interest.

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