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Preconcentration of trace amounts of lead in water samples with cetyltrimethylammonium bromide coated magnetite nanoparticles and its determination by flame atomic absorption spectrometry



Mohammad Faraji ^a, Shahab Shariati ^{b,*}, Yadollah Yamini ^c, Mahnaz Adeli ^d

^a Young Researchers Club, Rasht Branch, Islamic Azad University, Rasht, Iran

^b Department of Chemistry, Rasht Branch, Islamic Azad University, Rasht, Iran

^c Department of Chemistry, Tarbiat Modares University, Tehran, Iran

^d Knowledge Development & University Relationship Department, Iran Khodro Company, Tehran, Iran

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Abstract A sensitive and simple magnetic solid phase extraction procedure was presented for the preconcentration of lead ions in environmental water samples. In the present study, lead ions form complexes with 1-(2-pyridilazo)-2-naphthol reagent (PAN) in basic medium, and then are quantitatively extracted to the surface of cetyltrimethylammonium bromide (CTAB)-coated magnetite nanoparticles (Fe₃O₄ NPs). After magnetic separation of adsorbent, the adsorbent was eluted with 0.5% (v/v) HCl in methanol prior to its analysis by flame atomic absorption spectrometry (FAAS). The pH of sample, concentrations of PAN, amounts of CTAB and Fe₃O₄ NPs, sample volume and desorption conditions were optimized. Under optimum conditions, the calibration curve was linear in the range of 0.05–100 ng mL⁻¹ with $R^2 = 0.9996$. Detection and quantification limits of the proposed method were 0.005 and 0.05 ng mL⁻¹, respectively. Enhancement factor of 1050 was achieved using this method to extract 1000 mL of different environmental water samples. Compared with conventional solid phase extraction methods, the advantages of this method still include

* Corresponding author. Tel.: +98 131 4224343; fax: +98 131 4224949.

E-mail address: shariaty@iaurasht.ac.ir (S. Shariati).

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easy preparation of sorbents, short times of sample pre-treatment, high extraction yield, and high breakthrough volume. It shows great analytical potential in preconcentration of lead from large volume water samples.

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1. Introduction

Lead enters food and drinks, contaminating them and therefore, it is a serious health hazard for everybody (Mosquera, 1999). Lead is particularly harmful, but even at high levels it is considered innocuous in the past (Ladron de Guevara, 1995). Water is one of the main sources of lead contamination for the general public. Even though the lead quantity in these samples is low, its introduction in the daily diet may have significant physiological effects (Cabrera, 1994). Determination of lead at trace levels in water samples requires the use of highly sensitive and reliable analytical techniques (Mena et al., 1997). Only few techniques such as electrothermal atomic absorption spectrometry (ET-AAS) (Bruno et al., 1994; Jorhem and Sundström, 1995), or anodic stripping voltammetry with microelectrodes (Baldo et al., 1997) have enough sensitivity to directly determine the low quantities of lead. Flame atomic absorption spectrometry (FAAS) is available in most laboratories and is normally less subjected to interferences, but it requires a preconcentration step in order to increase the lead concentration because of lead concentrations in environmental water samples are typically below the FAAS detection limit. Preconcentration and separation procedures coupled with FAAS offer the possibility of using a relatively simple and cheap detection system (Naghmush et al., 1995; Ferreira et al., 2001).

Several methods have been proposed for separation and preconcentration of trace amounts of lead such as dispersive liquid-liquid microextraction, cloud point extraction, liquid-liquid extraction, and solid-phase extraction (SPE). Such systems improve the sensitivity and the selectivity of FAAS allowing the determination of traces of lead in water samples, and could represent an alternative to ET-AAS (Ferreira et al., 2001). Among these techniques, the SPE procedures, either off- or on-line, are considered superior to the other procedures for their simplicity, consumption of small volumes of organic solvents, capability to eliminate undesirable matrix components, and their ability to achieve a higher enrichment factors (Fang et al., 1991).

More recently, the use of magnetic NPs for sample extraction and preconcentration is gaining researchers interest (Huang and Hu, 2008a,b; Zhao et al., 2008a,b; Suleiman et al., 2009; Zargar et al., 2009; Sun et al., 2009; Faraji et al., 2010a). Compared with micrometer-sized particles used in the SPE, the NPs offer a multitude of benefits that make them a better choice. They have significantly higher ratio of surface area-to-volume and a short diffusion route, resulting in higher extraction capacity; rapid dynamics of extraction and higher extraction efficiencies (Moeller et al., 2007). Moreover, by using superparamagnetic NPs such as Fe_3O_4 a shorter analysis time can be achieved, due to the magnetically assisted separation of these particles from the sample solution. These particles are attracted to a magnetic field but retain no magnetic charge

after the field removal. This property makes them particularly suitable for sample preparation because in comparison with non-magnetic adsorbents no centrifuging or filtration of the sample is needed after extraction.

The aim of the present study was to develop a NP-based method for the preconcentration and determination of trace amounts of lead. The method is based on the extraction of lead as hydrophobic complexes of lead-PAN on cetyltrimethylammonium bromide (CTAB) – coated Fe_3O_4 NPs. The level of lead in extracted phase was then determined by FAAS. To the best of our knowledge, this method has not been employed previously in the extraction and determination of trace amounts of lead from aqueous samples.

2. Experimental

2.1. Instrumentation

A Varian (Mulgrave, Victoria, Australia) flame atomic absorption spectrometer model SpectrAA 110, with an air-acetylene flame was used for lead determinations. Absorbance measurements were carried out at 217.0 nm using lead hollow cathode lamp (from Varian) operated at 4.0 mA with deuterium background correction (at 10 mA). The instrumental parameters were used according to the manufacturer's recommendations. All measurements were based on peak height. The pH of the solutions were measured with a WTW pH meter (Inolab, Germany) which was supplied with a combined pH electrode. TEM images were obtained with an H-800 transmission electron microscope (Hitachi, Japan) and magnetic properties were analyzed using a vibrating sample magnetometer (VSM, LDJ9600).

2.2. Reagents

All chemicals used were of analytical reagent grade. Ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ferrous chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), sodium hydroxide, 1-(2-pyridilazo)-2-naphthol (PAN), lead nitrate ($\text{Pb}(\text{NO}_3)_2$), CTAB, methanol, acetone, and 1-propanol, hydrochloric acid were all purchased from Merck (Darmstadt, Germany). The stock solution of lead ($1000 \mu\text{g mL}^{-1}$) was prepared by dissolving the appropriate amounts of $\text{Pb}(\text{NO}_3)_2$ in doubly distilled water. A solution of $1 \times 10^{-3} \text{ mol L}^{-1}$ PAN was prepared by dissolving the appropriate amount of this reagent in methanol.

2.3. Synthesis of Fe_3O_4 NPs

Fe_3O_4 NPs were prepared by chemical co-precipitation method via a reactor which was designed in our previous work (Faraji et al., 2010b). Briefly, 10.4 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 4.0 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and 1.7 mL of HCl (12 mol L^{-1}) were dissolved in 50 mL of deionized water in order to prepare stock solution

of ferrous and ferric chloride in a beaker which was then degassed with nitrogen gas for 20 min. Simultaneously, 500 mL of 1.5 mol L^{-1} NaOH solution was degassed (for 15 min) and heated to $80 \text{ }^\circ\text{C}$ in a reactor. Then, the stock solution was added dropwise using the dropping funnel during 30 min under nitrogen gas protection and vigorous stirring (1000 rpm) by a glassware stirrer. During the whole process, the solution temperature was maintained at $80 \text{ }^\circ\text{C}$ and nitrogen gas was purged to remove the dissolved oxygen. After completion of the reaction, the obtained Fe_3O_4 NPs were separated from the reaction medium by the magnetic field, and then

washed with 500 mL doubly distilled water four times. Finally, the obtained Fe_3O_4 NPs were resuspended in 500 mL of degassed deionized water.

2.4. Preconcentration procedure

An aliquot of water sample (500 mL, $\text{pH} = 9.0$) was transferred to 2000 mL glassware beakers. Then, 2.0 mL of $1 \times 10^{-3} \text{ mol L}^{-1}$ PAN, 10 mL of the suspension of Fe_3O_4 NPs (10 mg mL^{-1}) and 2.5 mL of the CTAB solution (10 mg mL^{-1}) were sequentially added to the sample solution and then mixed. The mixture was shaken and allowed to complete the extraction process for 2 min. Subsequently, an Nd-Fe-B strong magnet ($10 \times 5 \times 4 \text{ cm}$, 1.4 Tesla) was placed at the bottom of the beaker, and the CTAB-coated Fe_3O_4 NPs were isolated from the solution. After about 10 min, the solutions became limpid and supernatant solutions were decanted. Finally, the preconcentrated lead complex was eluted from the isolated particles with 1.0 mL of 0.5% HCl in methanol and this solution was introduced into FAAS for determination of lead concentration.

3. Results and discussion

3.1. Characterization of Fe_3O_4 nanoparticles

Characterization of synthesized Fe_3O_4 NPs was done using IR, VSM and TEM instruments (Fig. 1). IR spectra of pure Fe_3O_4 NPs (i) and CTAB-coated Fe_3O_4 NPs (ii) are shown in Fig. 1a. The peak at $\sim 3455 \text{ cm}^{-1}$ is attributed to the stretching vibrations of $-\text{OH}$, which is assigned to surface OH groups of Fe_3O_4 NPs. The peak at $\sim 571 \text{ cm}^{-1}$ is attributed to the Fe–O band vibration of Fe_3O_4 . Also, the peak at $\sim 1380 \text{ cm}^{-1}$ is attributed to C–N band and the peaks at 2885 and 2925 cm^{-1} are attributed to two different C–H bands vibration of CTAB. The IR spectra show that the surface of Fe_3O_4 NPs was well modified by CTAB. Also, the TEM image of the prepared NPs is shown in Fig. 1b. Based on the TEM image, the Fe_3O_4 surface morphology analysis demonstrated the agglomeration of many ultrafine particles with a diameter of about 20 nm. On the other hand, it is important that Fe_3O_4 NPs should possess sufficient magnetic and superparamagnetic property for magnetic carrier technology (MCT) practical application. Fig. 1c shows VSM magnetization curves of Fe_3O_4 NPs at room temperature. Fe_3O_4 NPs exhibited typical superparamagnetic behavior due to not exhibiting hysteresis, remanence and coercivity. The large saturation magnetization of Fe_3O_4 NPs was 76 emu/g , which is sufficient for magnetic separation with a conventional magnet.

3.2. Effect of solution's pH

The charge density of mineral oxide surface is a main factor affecting the adsorption of analytes and it varies strongly with pH. Thus, pH is a very important parameter for the adsorption of target compounds. On the other hand, pH plays an important role in the complexation of lead with PAN. To examine the effect of pH on extraction efficiency of lead ions, pH of the solution varied in the range of 6.0–12.0 (Fig. 2). As can be seen from Fig. 2, the Fe_3O_4 NPs do not exhibit obvious

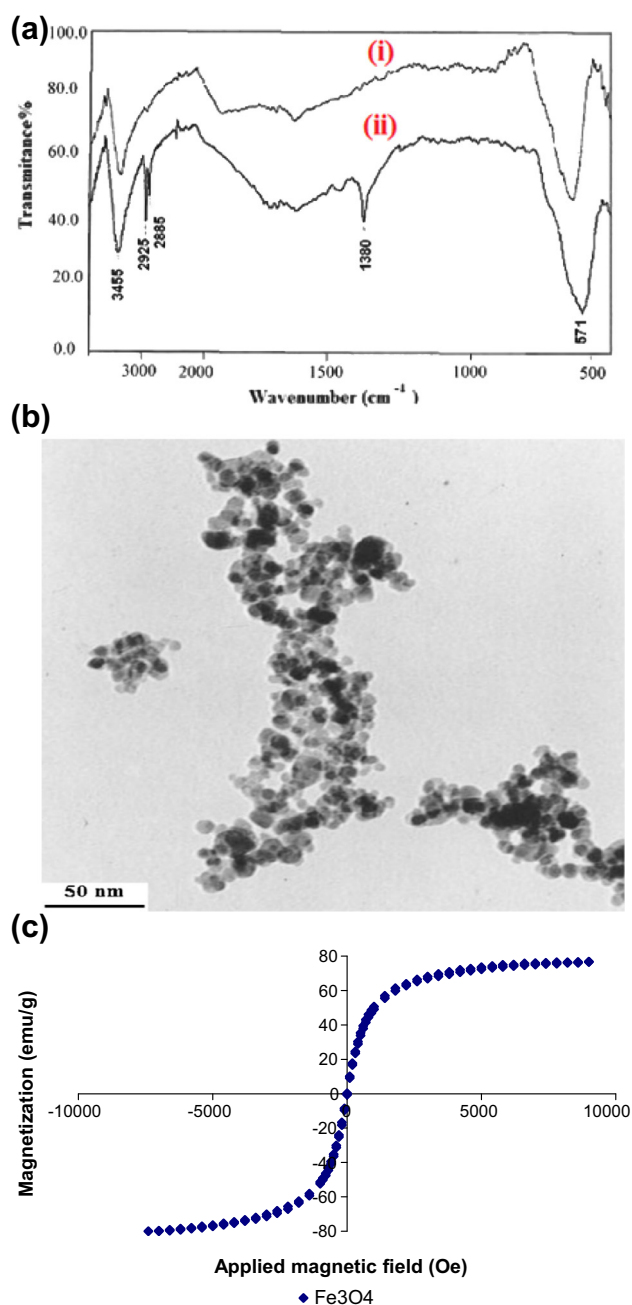


Figure 1 Characterization of the CTAB-coated Fe_3O_4 NPs. (a) The IR spectra before (i) and after the modification with CTAB (ii). (b) The TEM image of the Fe_3O_4 NPs. (c) VSM magnetization curves of Fe_3O_4 NPs.

adsorption of lead as Pb-PAN complex when the pH value was lower than 8.0. With increasing pH, the adsorption efficiency increased dramatically and reached maximum when the pH was between 9.0 and 10.0. This is mainly due to the fact that negative charges were favorable for the adsorption of cationic surfactants. When pH value was around NPs isoelectric point (about 7.0) the charge density of Fe_3O_4 NPs surface was very low (Zhao et al., 2008b). When the pH value was above their isoelectric point, the Fe_3O_4 NPs surface became negatively charged which gave rise to the strong electrostatic attraction between the CTAB molecules and the charged Fe_3O_4 NPs surface. Under this circumstance, hydrophobic complexes of Pb-PAN can be interacted with CTAB-coated Fe_3O_4 NPs surface. But, at pH higher than 10.0, lead can precipitate as hydroxide form. On the other hand, pH between 9.0 and 10.0 is favorable for complexation of lead and PAN (Marczenko, 1986). Therefore, pH of 9.0 was selected for further studies.

3.3. Effect of PAN concentration

PAN acts as a tridentate ligand and can form very stable complexes with metal ions (as ML or ML_2) through hydroxyl oxygen atom, nitrogen atom of pyridine and one of the azo group nitrogen atoms (Marczenko, 1986). PAN complexes of lead can be easily interacted with CTAB-coated Fe_3O_4 NPs, which increases extraction efficiency of lead. At 50 ng mL^{-1} of lead, the effect of PAN concentration on extraction efficiency was studied by changing the molar ratio of PAN to lead in the range of 0–20 (Fig. 3). Results showed that by increasing the PAN to lead ratio up to 16 will cause an increase in the extraction recovery; after that, it remained constant. Therefore, PAN to lead ratio of 16 was used for the subsequent studies.

3.4. Effect of the amount of surfactant

The adsorption of surfactant on the surface of mineral oxides can be divided into three regions (hemimicelles, mixed hemimicelles, and admicelles). In the first region, the zeta potential of mineral oxides changed from negative to zero due to the fact that hemimicelles were gradually formed on the mineral oxide surfaces. Upon increasing the cationic surfactant concentra-

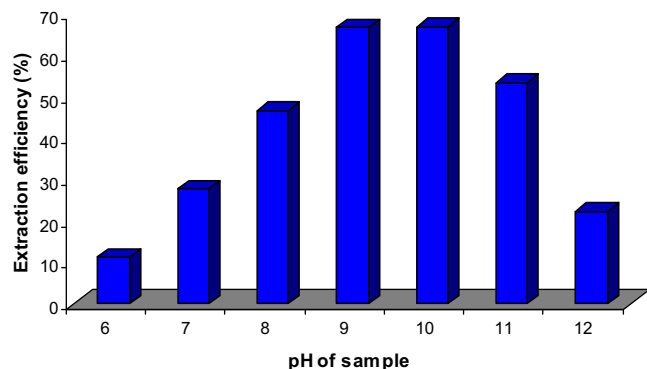


Figure 2 Effect of sample pH on extraction efficiency. Conditions: 500 mL of 50 ng mL^{-1} of lead; 1.0 mL of 0.001 mol L^{-1} 351 PAN solution ($L/M = 8$); 100 mg Fe_3O_4 NPs; 50 mg CTAB; 5 min stirring, elution with 1.0 mL methanol.

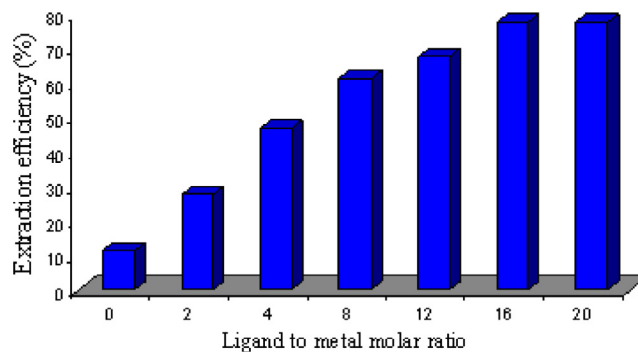


Figure 3 Effect of PAN concentration on extraction efficiency. Conditions: 500 mL of 50 ng mL^{-1} 355 of lead; sample's pH = 9.0, 100 mg Fe_3O_4 NPs; 50 mg CTAB; 5 min stirring, elution with 1.0 mL methanol.

tion, admicelles were formed dominantly on the surface and the zeta-potential increases from zero to positive (Zhao et al., 2008a). Therefore, the outer surface of hemimicelles is hydrophobic whereas that of admicelles is ionic, which provides different mechanisms for retention of compounds and are both suitable for the SPE method. In the mixed hemimicelles phase, both hemimicelles and admicelles are formed in the surface of mineral oxides and the adsorption is driven by both hydrophobic interaction and electrostatic attraction. The effect of CTAB amounts on the extraction efficiency was considered in the ranges of 0–100 mg. Based on the obtained results (Fig. 4), increasing the amount of CTAB up to 25 mg resulted an increase in the extraction recovery; after that, it decreased due to unsuitable interactions. So, 25 mg of CTAB was chosen as optimum amount in order to achieve the highest possible extraction efficiency.

3.5. Effect of the adsorbent amount and extraction time

In comparison with the traditional sorbents (micro size sorbents), NPs offer a significantly higher surface area-to-volume ratio. Therefore, satisfactory results can be achieved with fewer amounts of NPs. In order to study the effect of the adsorbent,

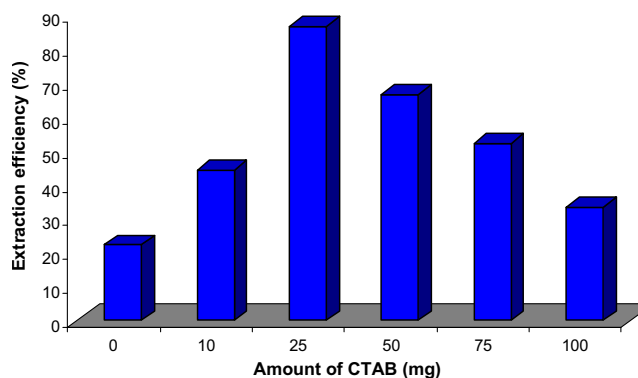


Figure 4 Effect of CTAB amount on extraction efficiency. Conditions: 500 mL of 50 ng mL^{-1} of lead; sample's pH = 9.0, 2.0 mL of 0.001 mol L^{-1} 359 PAN solution ($L/M = 16$); 100 mg Fe_3O_4 NPs; 50 mg CTAB; 5 min stirring, elution with 1.0 mL methanol.

10–150 mg of the Fe_3O_4 NPs was added to 500 mL of the sample solution. The obtained results showed that by increasing the adsorbent amounts from 25 up to 100 mg; extraction efficiency was increased slowly due to the increasing of accessible sites, and remained constant. So, a 100 mg of the Fe_3O_4 NPs was selected for all subsequent experiments.

Also, the effect of the extraction time on the extraction recovery of lead was investigated. Due to the shorter diffusion route for NPs plus the magnetically assisted separation of the magnetic NPs from the sample solutions, extraction of lead can be achieved in less time even for larger volumes of samples. The effect of the extraction time on the extraction recovery was investigated in the range of 1–5 min. Based on the obtained results, extraction recovery increased up to 2 min and then remained constant. Therefore, 2 min was chosen as optimum value in order to obtain a shorter analysis time.

3.6. Desorption conditions

Organic solvents are known to disrupt surfactant aggregates and were used to elute lead complex from the CTAB-coated Fe_3O_4 NPs surface (Zhao et al., 2008a,b; Sun et al., 2009). So, acetone, ethanol and methanol were selected as eluent. Among these eluents, methanol showed better desorption ability. In continue, effect of methanol's acidity on desorption efficiency was considered. Results showed that desorption ability of methanol containing 0.5% HCl was found to be superior to that without adding HCl. Lead complex was quantitatively eluted from CTAB aggregates by using 1.0 mL of 0.5% HCl in methanol. This can be attributed to the fact that when the pH level was below or around its isoelectric point, charge density in Fe_3O_4 NPs surface was weak and favorable for the disruption of CTAB aggregates. Thus, 1.0 mL of 0.5% HCl in methanol was selected for desorption. On the other hand, in order to obtain maximum desorption efficiency, effect of the desorption time was investigated in the range of 1–5 min. Based on the obtained results, a time of 2 min was chosen for further studies. Moreover, further studies showed that the adsorbent can be used for at least five successive analyses without a considerable change.

3.7. Effect of sample volume

In order to obtain a higher enrichment factor, a larger volume of sample solution is required. Fortunately, due to the magnetically assisted separation of the adsorbent (Fe_3O_4 NPs), it is possible to collect the adsorbent from larger volumes of the sample solution. Thus the extraction of 25 μg of lead from different volumes of the water samples ranging from 500 to 1500 mL was investigated (Fig. 5). It was found that the best quantitative recovery (>90%) was obtained when the sample volumes were less than 1000 mL. However, the extraction efficiency would slightly decrease when the sample volumes were more than 1000 mL. Hence, a sample volume of 1000 mL was selected as the ideal volume for trace analysis of lead in water samples.

3.8. Interference studies

In view of the high selectivity provided by FAAS, the only interference may be attributed to the preconcentration step,

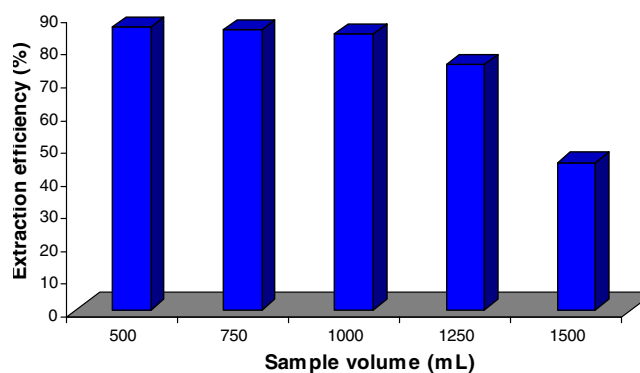


Figure 5 Effect of sample volume on extraction efficiency. Conditions: 500 mL of 50 ng mL^{-1} of lead; sample's pH = 9.0, 2.0 mL of 0.001 mol L^{-1} 364 PAN solution ($L/M = 16$); 100 mg Fe_3O_4 NPs; 25 mg CTAB; 2 min stirring, elution with 1.0 mL of 0.5% HCl in methanol.

in which the cations may react with PAN which may lead to a decrease in extraction efficiency. So, interference of co-existing ions on the preconcentration of lead was investigated. In order to investigate the effect of foreign ions on the extraction efficiency, solutions (500 mL) containing 50 ng mL^{-1} of lead ions and various amounts of foreign ions were prepared and were extracted according to the procedure described in the experimental section. The deviation of $\pm 10\%$ from the recovery of the standard solution was taken as interference. The results are shown in the Table 1. It can be seen that a very good selectivity was achieved.

3.9. Analytical features

The analytical features of the proposed method such as precision, linear range of calibration curve and limit of detection were also examined. The results are summarized in Table 2. Precision of the method was estimated by applying successive retention and elution cycles with 1000 mL of a sample solution containing 10 μg of lead under the optimum conditions. The recovery of lead was quantitative (>95%) and the precision of the method was very good (RSD = 2.1%). The linear calibration range for measurements under the optimum conditions was $0.05\text{--}100 \text{ ng mL}^{-1}$ ($R^2 = 0.9996$) for 1000 mL of solution.

Table 1 Tolerance limit of interfering ions.

Interference	Interference to metal ion ratio	Recovery (%)
Na^+	10,000	100
K^+	10,000	90
Ba^{2+}	250	95
Ca^{2+}	100	91
Mg^{2+}	750	96
Mn^{2+}	1000	108
Hg^{2+}	Saturated solution	107
Al^{3+}	Saturated solution	94
Cu^{2+}	20	100
Cd^{2+}	50	95
Co^{2+}	50	91
Ni^{2+}	20	94
Zn^{2+}	20	97

Table 2 Figures of merit of the proposed method for the extraction and determination of the lead.

Enhancement factor	Limit of detection (ng mL ⁻¹)	RSD % ($n = 6$) (10 ng mL ⁻¹)	Dynamic linear range (ng mL ⁻¹)	Calibration equation	R ²
1050	0.005	2.1	0.05–100	$I = 516 c + 761$	0.9996

Table 3 Determination of lead in different water samples by applying the proposed method.

Sample	Added (ng mL ⁻¹)	Found (ng mL ⁻¹) ^a	Relative recovery (%)
Tap water	0.00	–	–
	2.00	1.93 ± 0.09	95
	10.00	9.78 ± 0.35	97
Well water	0.00	0.21 ± 0.01	–
	2.00	2.01 ± 0.05	91
	10.00	10.34 ± 0.45	101
Mineral water	0.00	–	–
	2.00	2.13 ± 0.21	105
	10.00	9.92 ± 0.15	99
Wastewater sample	0.00	4.80 ± 0.08	–
	2.00	6.40 ± 0.35	94
	10.00	14.10 ± 0.62	95

^a Mean ± SD ($n = 3$).

Table 4 Comparison of the proposed method with some of the methods reported in the literature for extraction and determination of lead.

Metal ions	System	Technique	EF	DLR ^a	DL ^b	RSD %	Detection	References
Pb, Cu, Ni, Co, Cd	Modified silica gel with aminothioamidoanthraquinone	Batch SPE	^c	^c	0.95–22.5	<9	FAAS	Tuzen and Soylak, 2009
Cd, Co, Ni, Pb	Black stone (Pierre noire)	On-line SPE	20	^c	0.3–1.1	1.1–5.9	ICP-OES	Suleiman et al., 2008
Cd, Cr, Ni, Mn, Pb	Cu(II)-dibenzylthiocarbamate	Coprecipitation	50	^c	0.3–0.87	<10	FAAS	Tuzen et al., 2005
Cd, Co, Cr, Cu, Fe, Mn	TTA/TritonX-114	On-line CPE	42–97	0.5–100	0.1–2.2	2.2–4.6	ICP-OES	Yamini et al., 2008
Pb	5-Br-PADAP/ Triton X-1 14	Off-line CPE	50	0.1–30	0.08	2.8	ET-AAS	Chen et al., 2005
Pb	CTAB-coated Fe ₃ O ₄ nanoparticles	Batch SPE	1050	0.05–100	0.005	2.1	FAAS	This work

^a Dynamic linear range (ng mL⁻¹).

^b Detection limit (ng mL⁻¹).

^c Data not reported.

The detection limit based on three-times of the standard deviation of the blank solution (3Sb/m) was found to be 0.005 ng mL⁻¹. Also, an enhancement factor of 1050 was calculated as the ratio between the slopes of the calibration curve submitted by the SPE procedure (for $V = 1000$ mL) and the direct calibration curve (without preconcentration).

3.10. Analysis of environmental water samples

In order to check the applicability of the proposed method for various water samples, lead ions were determined in different water samples including Tehran tap water, well water (Jaber Ebne Hayyan Pharmaceutical Company), mineral water (Damavand Brand) and wastewater sample collected around Tehran Refinery. An appropriate volume of sample solutions was adjusted to the optimum pH and subjected to the recommended procedure with external calibration method. Low concentrations of lead ions were found in the well water and

wastewater samples. Reliability was checked by spiking samples. 1000 mL of the water samples spiked with 2.0 and 10.0 ng mL⁻¹ of lead ions was extracted by the proposed SPE procedure. Table 3 lists the recoveries and concentrations found for lead, expressed as the mean value ($n = 3$). Recoveries of lead ranged between 91% and 105% for the all four water samples. The results demonstrate the applicability of the proposed method to water analysis.

3.11. Comparison of the proposed method with other methods

The proposed method was compared with a variety of methods reported recently in the literature for the preconcentration and determination of lead. The distinct features of the proposed method are summarized in Table 4. As can be seen from Table 4, it is evident that the enhancement factor obtained with the CTAB-coated Fe₃O₄ NPs is very high in comparison with other methods. Large dynamic linear range, also, very

low LOD and RSD are the other significant features of the method which are comparable to or even better than off-line cloud point extraction (CPE) followed by the very sensitive detection method (ET-AAS) (Chen et al., 2005).

4. Conclusion

A new SPE method based on CTAB-coated Fe_3O_4 NPs was developed for the preconcentration of lead ions in environmental water samples. The use of NPs endowed the SPE method with high extraction capacity and preconcentration factors. The magnetic separation greatly improved the separation rate while avoided the time-consuming column passing or filtration operation. The results obtained in this work demonstrate the applicability of the proposed procedure for preconcentration and determination of traces of lead ions. The recoveries of analytes were nearly quantitative (> 95%). The developed method is simple, rapid and sensitive and very suitable for rapid adsorption of heavy metals from large volume of sample solution.

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