

Determination of Pb (II) in some real samples based on alumina-coated magnetite nanoparticles solid phase extraction method

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Abstract: In this study, a new type of alumina-coated magnetite nanoparticles ($\text{Fe}_3\text{O}_4/\text{Al}_2\text{O}_3$ NPs) with sodium dodecyl sulfate- 1-(2-pyridylazo)-2-naphthol (SDS-PAN) as a new sorbent solid phase extraction (SPE) has been successfully synthesized and applied for preconcentration and separation of Pb (II).

The metal was eluted with 3 mL HNO_3 2 mol L^{-1} directly and detected by flame atomic absorption spectrometry (FAAS). Various influencing parameters on the separation and preconcentration of analytes, such as amount of SDS, pH, amount of nanoparticle and PAN, were studied. The detection limit of this method for Pb (II) was 8 $\mu\text{g L}^{-1}$ and the R.S.D. was 2.7% ($n = 10$). The proposed method has been applied to the determination of the metal ion at trace levels in water and soil samples with satisfactory results.

1. Introduction

Heavy metals released into the environment have posed a significant threat to the environment and public health because of their toxicity and persistence in environment [1-2].

The contamination of wastewaters and surface waters by toxic heavy metals is a worldwide environmental problem. Direct determination of heavy metals appears to be a difficult task as the concentration of them is close to or below the detection limits of most of the analytical instruments besides the real sample matrix may cause serious interference for their determination during the process. Separation and preconcentration methods can solve these problems. Solid-phase extraction (SPE) is the most common technique used for preconcentration of analytes because of high concentration factor, simple operation, the ability to handle large volume samples in a closed system free from contamination, rapid phase separation, and the

possibility of combination with different analytical technique [3,4].

Everyone is exposed to trace amounts of lead through air, soil, household dust, food, drinking water and various consumers. Inorganic lead arising from a number of industrial and mining sources occurs in water in the +2 oxidation state. Lead from leaded gasoline used to be a major source of atmospheric and terrestrial lead, much of which eventually entered natural water system.

Recently, magnetic materials have received increasing attention. Generally, magnetic materials are prepared by encapsulating inorganic magnetic particle with organic polymer or inorganics [5-7]. Magnetic materials as adsorbents have several advantages in comparison with traditional adsorbents. The separation process can be performed directly in crude samples containing suspended solid material without additional centrifugation or filtration, which makes separation easier and faster [8].

In this study, alumina-coated magnetite nanoparticles ($\text{Fe}_3\text{O}_4/\text{Al}_2\text{O}_3$ NPs) as magnetic adsorbents were synthesized by alkoxide hydrolysis precipitation on the surface of magnetite nanoparticles (Fe_3O_4 NPs) and applied for preconcentration of Pb (II) prior to determination by FAAS. Compared with conventional SPE methods, the advantages of this new $\text{Fe}_3\text{O}_4/\text{Al}_2\text{O}_3$ NPs mixed hemimicelles solid-phase extraction (MHSPE) method still include easy preparation and regeneration of sorbents, short times of sample pretreatment, high extraction yields, and high breakthrough volumes.

2. Experimental

2.1. Apparatus

The determination of Pb was carried out using a GBC model SansAA atomic absorption spectrometer with deuterium lamp background correction and hollow cathode lamps at respective wavelengths (resonance line) as radiation sources, was used throughout the measurements. An air acetylene flame was used for the determination of the metals ions. All instrumental settings were those recommended by the manufacturer. A Metrohm 692 pH/Ion meter with a combined glass-calomel electrode was used for adjustment of test solution pH.

A KQ 2200E ultrasonic bath (Ultrasonic Instrument, Kunshan, China) was employed in this process. The operating frequency of the ultrasonic bath was constant and fixed at 40 kHz. The output power was 100 W. The ultrasonic assisted extraction was performed at room temperature.

2.2. Reagents

All chemicals used were of analytical-reagent grade. The stock standard solutions containing 1000 mg L^{-1} of Pb (II) were prepared by dissolving appropriate amounts of their nitrate salts in distilled water and working standard solutions were obtained by appropriate stepwise dilution of the stock standard solutions. Working solutions were obtained daily by appropriately diluting the stock solution with pure water.

Ferrous chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), sodium dodecyl sulfate, were supplied by Guangfu Fine Chemical Research Institute (Tianjin, China). Aluminum isopropoxide was obtained from Sinopharm Chemical Reagent Co. (Shanghai, China). The pure water was prepared by Milli-Q water purification system (Millipore, Bedford, MA, USA). SDS (Schuchardt, Germany) was used without further purification. The chelating solution was prepared by dissolving 0.25 g of PAN in 100 mL of 95% ethanol.

2.3. Preparation of magnetic adsorbents

The magnetic adsorbents, alumina-coated magnetite nanoparticles ($\text{Fe}_3\text{O}_4/\text{Al}_2\text{O}_3$ NPs), were synthesized by alkoxide hydrolysis precipitation method similar to our previous method [9].

Ferrous chloride (2.0 g), ferric chloride (5.2 g), and hydrochloric acid (12 mol L^{-1}) (0.85 mL) were dissolved in 25 mL pure water. The mixture was added dropwise into 250 mL NaOH solution (1.5 mol L^{-1}) under vigorous stirring with nitrogen gas passing continuously through the solution during the reaction. After the reaction, the obtained Fe_3O_4 NPs precipitate was separated from the reaction medium under the magnetic field, and rinsed with 200 mL pure water four times. Then, the product was oven dried at 80°C . The $\text{Fe}_3\text{O}_4/\text{Al}_2\text{O}_3$ nanoparticles ($\text{Fe}_3\text{O}_4/\text{Al}_2\text{O}_3$ NPs) were prepared according to Li et al. [10] with minor modification. Aluminum isopropoxide (1.0 g) was dissolved in ethanol (60 mL) to form a clear solution. Fe_3O_4 NPs (0.1 g) were then dispersed in the freshly prepared solution for 5 min with the aid of ultrasonic. A mixture of water and ethanol (1:5, v/v) was added drop wise to the suspension of Fe_3O_4 NPs with vigorous stirring. The mixture was stirred for half an hour after the addition. Subsequently, the suspension was standing for one hour before separating and washing with ethanol.

After five cycles of separation/washing/redispersion with ethanol, the powder obtained was oven dried and calcined at 500°C for three hours.

2.4. Preparation of hemimicelles

The mixed hemimicelle solid phase extraction procedure was carried out as follows. Firstly, 0.05 g $\text{Fe}_3\text{O}_4/\text{Al}_2\text{O}_3$ NPs and 40 mg SDS and 9.0 mg L^{-1} PAN solution were added into 250 mL water and the pH was adjusted to 2–2.5 with 3 mol L^{-1} HCl solutions and then were shaken mechanically for 15 min to form mixed hemimicelles assemblies. Subsequently, the on SDS-PAN coated $\text{Fe}_3\text{O}_4/\text{Al}_2\text{O}_3$ NPs were isolated by placing a strong magnet and the supernatant was poured away and they were washed with high purity deionized water.

2.5. Procedure

The target analyte a 250 ml of sample solution containing Pb(II) in the range of 20–300 $\mu\text{g L}^{-1}$ were prepared and the pH value was adjusted to 2 with 0.1 mol L^{-1} HCl and NaOH solutions was added into the SDS-PAN coated $\text{Fe}_3\text{O}_4/\text{Al}_2\text{O}_3$ NPs and then were shaken mechanically for 15 min. Subsequently, the SDS-PAN coated $\text{Fe}_3\text{O}_4/\text{Al}_2\text{O}_3$ NPs were isolated by placing a strong magnet and the supernatant was poured away. The preconcentrated target analyte absorbed on SDS-PAN coated $\text{Fe}_3\text{O}_4/\text{Al}_2\text{O}_3$ NPs was

eluted with using 3 ml of 2 mol L⁻¹ HNO₃. The analytes in the effluent were determined by FAAS.

3. Results and discussion

3.1. Effect of the amount of SDS on adsorption of Pb (II)

The outer surface of hemimicelles is hydrophobic whereas that of admicelles is ionic, which provides different mechanisms for retention of organic compounds and both are suitable for the SPE method. In mixed hemimicelles phase, the adsorption is driven by both hydrophobic interactions and electrostatic attraction because of the formation of hemimicelles and admicelles on the surface of mineral oxides [11]. In Fig. 1, shows that in the presence of SDS, the Pb (II) was hardly adsorbed onto the surface of Fe₃O₄/Al₂O₃ NPs. The adsorption amount of the Pb (II) increased remarkably with the increasing amount of SDS. Given these findings, 40mg was selected as the final addition amount of SDS in the studies.

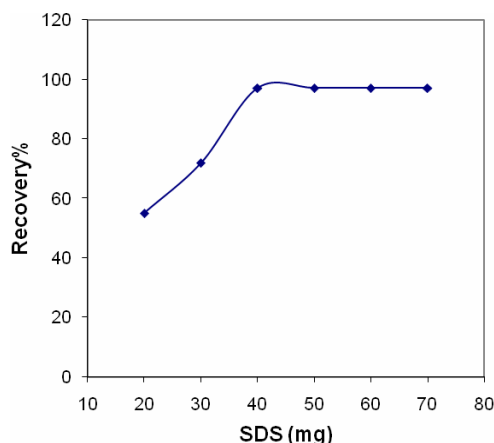


Fig.1.Effect of amount of SDS added on the adsorption of the Pb (II).

3.2. Effect of pH

pH is one of the factors influencing the adsorption behavior of mixed hemimicelles system due to the change of the charge density on the Fe₃O₄/Al₂O₃ NPs surface. As shown in Fig. 2, maximum adsorption of Pb (II) was obtained when pH was 2.0. The adsorption amount decreased when the pH increased from 2.0 to 6.0. This can be attributed to the fact that the positively charged surface of Fe₃O₄/Al₂O₃ NPs was favorable for the adsorption of anionic surfactants. When pH value was higher, the positive charge density of Fe₃O₄/Al₂O₃

NPs surface was lower. The electrostatic attraction between negative charges of SDS and positive charges of the surface of Fe₃O₄/Al₂O₃ NPs was not strong enough to produce hemimicelles, which made against the great adsorption of Pb (II). The pH of 2.0 was selected for the next studies. When solution was acidified, SDS would form hemi-micelles on Fe₃O₄/Al₂O₃ NPs by strong sorption. The micelles could trap PAN molecules homogeneously, which cause Fe₃O₄/Al₂O₃ NPs to change in colorless from white to orange.

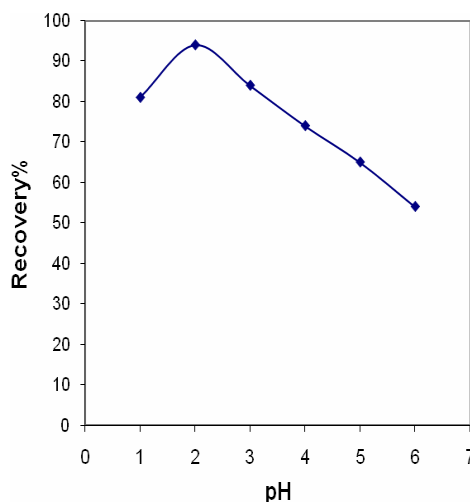


Fig. 2. Effect of pH on the adsorption of Pb (II).

3.3. Effect of the amount of modified Fe₃O₄/Al₂O₃ NPs

In order to investigate the effect of the amount of modified Fe₃O₄/Al₂O₃ NPs on the quantitative extraction of Pb, the extraction was conducted by varying the amounts of the modified Fe₃O₄/Al₂O₃ NPs from 10 to 120 mg. As shown in Fig. 3, the results indicated that the quantitative recovery (>95%) of Pb was obtained with increasing of modified Fe₃O₄/Al₂O₃ NPs amount up to 50 mg. Hence, 50 mg of the modified nanometer sized of modified Fe₃O₄/Al₂O₃ NPs was used for further experiments due to the greater availability of the surface area at high amounts of the sorbent and to account for other extractable species.

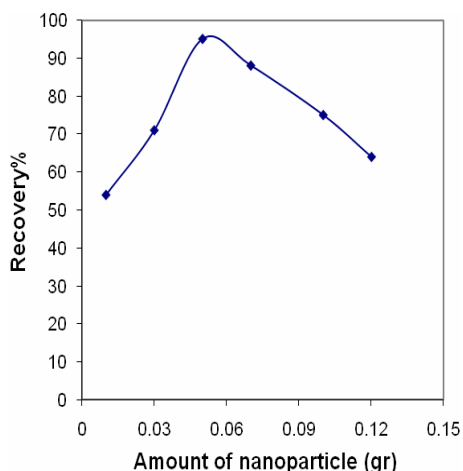


Fig.3. Amount of modified Fe₃O₄/Al₂O₃ NPs on the adsorption of Pb (II).

3.4. Effect of the amount PAN on adsorption of Pb (II)

To investigate the optimum amount of PAN on the quantitative extraction of understudy metals ions by the SDS coated on Fe₃O₄/Al₂O₃ NPs, these ions extraction was conducted by varying the amount of PAN from 1.5 to 7.5 mg L⁻¹. The results are shown in Fig. 4 with increasing amount of PAN up to 4.5 mg L⁻¹ an increase in recoveries can be achieved and further increase does not mentionable change in efficiency. Quantitative recoveries for the analytes were obtained after 4.5 mg L⁻¹ of PAN. Subsequent studies for further experiments were carried out with 4.5 mg L⁻¹ of PAN.

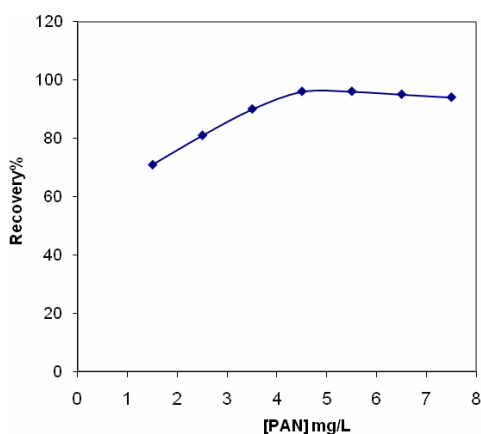


Fig. 4. Effect of the amount PAN on the adsorption of Pb (II).

3.5. Desorption conditions

Some experiments were carried out in order to choose a proper eluent for the adsorbed Pb ions by SDS-PAN coated Fe₃O₄/Al₂O₃ NPs. The Pb ions were stripped with different concentrations (0.1–4 mol L⁻¹) of

various acids. From given data, it is observed that 3.0 mL of 2.0 mol L⁻¹ nitric acid could accomplish the quantitative elution of Pb from the SDS-PAN coated Fe₃O₄/Al₂O₃ NPs. Thus, we selected 3.0mL of 2.0 mol L⁻¹ nitric acid as eluent for stripping of studied metal ions.

3.6. Maximal extraction volume

The maximal enrichment volume of water sample for Pb(II) was determined using a series of different volume aqueous solutions (100–500 mL) of Pb(II) in the optimal conditions.

The recoveries of Pb (II) (98 %) were satisfactory with the water sample volume ranging from 100 to 500 mL. When above 250 mL, recoveries decreased quickly and insufficient recovery was considered to occur. Thus, 250mL was considered to be the maximal enrichment volume for water samples.

3.7. Analytical parameters

A calibration curve was constructed by pre concentrating 250 ml of sample which contain standard solutions. Table 1 shows the analytical characteristics of the method. Under the optimum experimental conditions, the calibration curve for cadmium was linear from 20 to 300 µg l⁻¹ with a correlation coefficient of 0.9998. The preconcentration factor of about 83 obtained by preconcentrating a 250 ml of sample volume can be considered highly satisfactory compared with other methods. The limit of detection was sufficiently low (8 µg l⁻¹).

Table 1. Properties of merit obtained by the proposed method

Parameters	Pb
Linear Range (µg L ⁻¹)	20-300
Correlation Coefficient	0.9998
Detection Limit (µg L ⁻¹) (n=5)	8
Preconcentration factor ^a	83
RSD % (n=5)	2.7
Recovery %	97

a) The preconcentration factors as the ratio of initial volume to final volume.

3.8. Interference effects

Some cations and anions were added individually to sample solutions containing 80 µg L⁻¹ of Pb in order to examine the effect of common coexisting ions on the sorption of analyte ions. The tolerance limit was considered if it resulted in a ±5% variation in sorption efficiency of Pb. As can be seen in Table 2, most of examined cations did not interfere with the extraction and determination. It has been found that recovery of Pb(II) was almost quantitative in the presence of foreign ions and therefore useful for the analysis of Pb in real samples.

3.9. Analytical applications

In order to test the reliability of the proposed methodology suitable for the assaying of lead in soil, waste water samples. For this purpose, 250 ml of each

of the samples were pre-concentrated by the proposed procedure and determined. The results are shown in Table 3.

Conclusions

The modified Fe₃O₄/Al₂O₃ NPs are highly monodisperse and magnetically separable, and shown to be an efficient, simple, easy, safe, rapid, inexpensive and versatile pre-concentration technique to determine pb by FAAS. In this method PAN is a reagent selectivity and sensitivity for determination of lead in soil, water samples. The nanoparticles can rapidly and quantitatively adsorb Pb from 250 mL of aqueous solution in 15 min. The proposed method has promising application in environmental analysis for trace lead.

Table 2. Investigation of other ions on the perposed method

Foreign ions	analyte / ion
K ⁺ , Na ⁺ , Li ⁺ , Ce ⁴⁺ , Mg ²⁺ , NO ₃ ⁻	> 1000
HPO ₄ ²⁻ , ClO ₃ ⁻ , IO ₃ ⁻ , Mg ²⁺ , Ca ²⁺ , F ⁻ , Cl ⁻ , Br ⁻ , CH ₃ COO ⁻ , Ni ⁺ , Pd ²⁺	500
SCN ⁻ , Mn ²⁺ , Al ³⁺ , Cr ³⁺ , Zn ²⁺ , CrO ₄ ²⁻ , Fe ³⁺	300
Sn ²⁺ , Ti ³⁺ , Cu ²⁺ , Co ²⁺	200

Table 3. Determination of pb in soil and water samples

Sample	Pb ²⁺ (µg L ⁻¹)		% Recovery
	Added	Found	
Waste water ^a 1	-	15.60±0.3	-
	20	37.32±0.3	108.6
	50	69.50±0.4	107.8
Waste water 2	-	ND ^d	-
	20	22.23±0.3	111.1
	50	54.51±0.4	109.0
Soil ^b	-	20.41± 0.4	-
	20	44.73±0.3	121.6
	50	76.24±0.4	111.6
Water ^c	-	ND	-
	20	19.00±0.5	95.0
	50	51.30±0.3	102.6

a) From Shiraz petrochemical center

b) From near Shiraz petrochemical center

c) From Kor river water (local river)

d) No detected

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