Magnetic Solid-Phase Extraction Based on APTS/Fe₃O₄ Nanoparticles for the Determination of Trace Cu and Pb in Environmental Samples Coupled With Graphite Furnace Atomic Absorption Spectrometry

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INTRODUCTION

Copper is an essential element and plays an important role in the glucose, lipid, and protein metabolism, while lead is an extremely toxic element (1,2). The determination of trace amounts of Cu and Pb in environmental samples is of great significance from the public health and environmental point of view. Direct determination of trace metal ions in environmental samples is difficult and due to various factors, particularly their low concentrations and matrix effects. Under these circumstances and in order to determine trace levels of Cu and Pb, a separation and enrichment step prior to their determination is the choice.

Recently, magnetic nanocomposite particle (MNP) materials have attracted much attention due to their unique physical and chemical properties and high potential applications in separation and preconcentration of target analytes from environmental or biological samples (3-5). Several groups (6-9) have synthesized various MNPs with special functional ligands bound onto the surface and applied them to the extraction of different analytes from water samples. The main advantage of using magnetic functionalized materials as adsorbent makes the sample pretreatment simple. The adsorbent need not be packed into the solid-phase extraction (SPE) cartridges as in traditional SPE, and phase separation could be

ABSTRACT

A new APTS-modified Fe₃O₄ magnetic nanoparticle is synthesized, and characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), vibrating sample magnetometer (VSM), and Fourier transform infrared spectroscopy (FT-IR). The prepared material was used to separate/preconcentrate trace amounts of Cu and Pb in environmental water samples and their determination by graphite furnace atomic absorption spectrometry (GFAAS).

The optimum experimental conditions, including pH, sample volume, eluent concentration, volume, and co-existing ions, were investigated. The detection limits for Cu and Pb (with enrichment factors of 121 and 136) were 1.8 ng L⁻¹ and 2.5 ng L⁻¹ and the relative standard deviations (RSD) were 4.8% and 5.5% (c=5.0 ng L⁻¹, n=5), respectively. The developed method was applied to the determination of trace Cu and Pb in water samples and reference materials with satisfactory results.

conveniently realized by applying an external magnetic field.

N-(β-ethylenamine)-γ-propylamine trimethoxysilane (APTS) is a kind of coupling agent that can form a stable complex with Cu and Pb under optimal conditions. This procedure has often been used to modify the surface of inorganic materials. In this work, we successfully synthesized APTS/Fe₃O₄ magnetite nanoparticles and employed

them as an SPE adsorbent for the separation and preconcentration of trace amounts of Cu and Pb from seawater samples.

EXPERIMENTAL

Instrumentation

The magnetic nanoparticles were characterized by using the following instrumentation:

Model FT-IR Varian 640 (Varian, USA), Model JEM 2100 TEM transmission electron microscopic system (JEOL Ltd., Japan), Model XRD X-ray diffraction system (Bruker, Germany), and magnetic particle measurement system Model VSM vibrating sample magnetometer (Quantum Design, USA). A Model SY1200 ultrasonicator (Shengyuan Instrument Factory, Shanghai, P.R. China) was used to disperse the nanoparticles in solution. A Model TAS-990 atomic absorption spectrometer was used (Beijing Puxi Instrument Factory, Beijing, P.R. China), equipped with deuterium lamp background correction and transversely heated graphite atomizer, including pyrolytic graphite tubes (Beijing Puxi Instrument Factory, Beijing, P.R. China).

Copper and lead hollow cathode lamps were employed as radiation sources at 324.8 nm and 283.3 nm with a slit width of 0.2 nm. Argon (99.99 %) was used as a protective and purge gas. The integrated absorbance mode was used throughout. The instrumentation used and the graphite furnace temperature program for the determination of Cu is given in Table I.

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Reagents and Standard Solutions

N-(β -ethylenamine)- γ -propylamine trimethoxysilane (AAPTS) and tetraethoxysilane (TEOS) were obtained from Wuhan University Silicone New Material (P.R. China). Deionized water ($18 \text{ M}\Omega \text{ cm}^{-1}$) was obtained with a Milli-Q™ system (Millipore Corporation, Bedford, MA, USA). The $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, absolute ethanol and $\text{NH}_3 \cdot \text{H}_2\text{O}$ were purchased from Tianjin Chemical (P.R. China). Stock standard solutions (1.0 mg mL^{-1}) of Cu and Pb were prepared in accordance with the routine method.

Working standard solutions were obtained by appropriate dilution of the stock standard solution just before use. The certified reference materials seawater GBW(E)080040 (National Institute of Standards and Technology, Beijing, P.R. China) was used for checking the accuracy of the developed method. All reagents used were of analytical reagent grade.

Preparation of Fe_3O_4 MNPs

The method of preparation was according to that of Massart et al.

(10). The typical procedure was as follows: 8.8 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 3.96 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ dissolved in 120 mL deionized water with about 5 minutes of ultrasonication. Then the solution was purged with argon to agitate the mixture and to prevent oxidation of the Fe^{2+} ions. After 30 minutes of purging, 300 mL of $0.7 \text{ mol L}^{-1} \text{NH}_4 \cdot \text{OH}$ was added dropwise into the above Fe^{2+} solution, and the alkaline solution purged for an additional 60 minutes. During the addition of $\text{NH}_4 \cdot \text{OH}$, it was noticed that the solution changed color from the original brown to dark brown and then to black. As expected, the black iron oxide product responded to a magnetic field. Then the product was washed with deionized water several times and put into a vacuum drying oven at 30°C for 24 hours.

Preparation of AAPTS/ Fe_3O_4 MNPs

The AAPTS/ Fe_3O_4 MNPs were prepared according to Li et al. (11) with some little modifications. Briefly, 2.32 g of Fe_3O_4 MNPs and 80 mL of absolute ethanol were mixed and ultrasonicated for about 10 minutes at 40°C . Then, under

mechanical stirring, 4.0 mL of 21% ammonia, 7.5 mL of deionized water, 0.1 mL of TEOS and 0.56 mL of AAPTS were added in sequence to the Fe_3O_4 MNPs mixture. After stirring vigorously with a magnetic stirrer for 2 hours, the mixture was again ultrasonicated for 1 hour. The MNPs were separated from the liquid by magnetic attraction and dispersed in 80 mL of ethanol. The same procedure was repeated two times. The particles were finally separated from the liquid by a magnetic field and vacuum-dried.

Sample Collection and Preparation

Seawater (Dalian, P.R. China) was acidified to a pH of about 2.0. Artificial seawater (250 mL) was prepared by dissolving 0.3675 g of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 3.275 g of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, and 6.975 g of NaCl in doubly deionized water (12).

Analysis Procedure

A portion of the sample solution was transferred to a 250-mL beaker, and the pH adjusted to 7.0 with $0.1 \text{ mol L}^{-1} \text{HNO}_3$ and aqueous ammonia. Then, 50 mg AAPTS/ Fe_3O_4 MNPs adsorbent was added, the solution ultrasonicated for 5 minutes, and the magnetic adsorbent isolated from the suspension with a magnet. The magnet was removed, a solution containing $0.01 \text{ mol L}^{-1} \text{HNO}_3$ added as eluent and ultrasonicated for 2 minutes, and the magnet used again to settle the magnet adsorbent. Finally, 20 μL of eluate was injected into the GFAAS system for analysis.

RESULTS AND DISCUSSION

Characterization of AAPTS/ Fe_3O_4 MNPs

The particle size and morphology of magnetite particles were investigated by TEM, as shown in Figure 1. Particles with an approximate spherical shape and an average diameter of Fe_3O_4 MNPs of

TABLE I
Instrumental and Operating Conditions

Instrumentation	Operating Conditions				
FT-IR	KBr powder to form pellets; Resolution: 2 cm^{-1}				
XRD	Voltage: 40 kV; Current: 40 mA; Cu K α radiation				
TEM	Accelerating voltage: 200 kV; Energy slit: 10eV; 100 mesh copper grids				
VSM	Magnetic field: 10 kOe; Room temperature				
GFAAS					
Step	Temperature ($^\circ\text{C}$)		Ramp Time (s)		Ar Flow (mL min^{-1})
	Pb	Cu	Pb	Cu	
Drying	100	100	10	10	250
Pyrolysis	700	900	10	15	250
Atomization	1200	2100	0	3	0
Cleaning	1400	2300	1	2	250

13.6 nm and APTS/Fe₃O₄ MNPs of 19.8 nm were observed. In the images, core and shell can be seen clearly.

The X-ray diffraction patterns of Fe₃O₄ MNPs and APTS/Fe₃O₄ MNPs are shown in Figure 2. The patterns (XRD) of ferrite oxide were consistent with Fe₃O₄ (JCPDS-75). The same characteristic peaks can also be found in Figure 2, which illustrate that the characteristic peaks did not change, only the peak intensity and width after coating with APTS. This shows that the crystalline structure of the modified nanoparticles was not varied.

The magnetic properties of nanoparticles were characterized by vibrating the sample in a vibrating sample magnetometer (VSM). Figure 3 shows the typical room temperature magnetization curves of bare Fe₃O₄ and APTS/Fe₃O₄ MNPs. As shown in this figure, the saturation magnetization of samples is 66.3 and 48.1 emu/g, respectively. The APTS/Fe₃O₄ MNPs show a typical superparamagnetic behavior, which is strong enough to be easily separated by an external magnetic field. The saturation magnetization of APTS/Fe₃O₄ MNPs is significantly smaller than that of Fe₃O₄ MNPs, which is due to the rather small size of the Fe₃O₄ MNPs

and the added mass of the monolayer (13).

The successful coating of the APTS was verified by the FT-IR spectra of Fe₃O₄ MNPs and APTS/Fe₃O₄ MNPs (Figure 4). As can be seen, the adsorption peaks at around 589 cm⁻¹ are related to the absorption of the Fe—O band which confirms the presence of magnetite nanoparticles. The bands at 1105 cm⁻¹, 1635 cm⁻¹, 1397 cm⁻¹, and 2854–2924 cm⁻¹ can be attributed to C—N, N—H, O—Si—C, and C—H, respectively. A comparison of these characteristic spectral bands indicates that the APTS coupling agent had been introduced onto the Fe₃O₄ MNPs surface.

Fig. 1. TEM images of (a) Fe₃O₄ MNPs and (b) APTS/Fe₃O₄ MNPs.

Fig. 2. XRD images of Fe₃O₄ MNPs and APTS/Fe₃O₄ MNPs.

Fig. 3. Magnetization curves obtained by VSM at room temperature.

Fig. 4. Infrared spectra of the Fe₃O₄ MNPs and APTS/Fe₃O₄ MNPs.

Optimization of Extraction Conditions

The effect of sample pH on the extraction of Cu and Pb was studied in the pH range from 1 to 8. As can be seen in Figure 5, Cu and Pb was quantitatively adsorbed at the pH range of 4 to 8. In this work, a pH of 7.0 was selected for further studies.

In order to study the recovery of target analytes from the magnetic particles, HNO_3 was employed as an eluent. The experimental results indicated that quantitative recovery of both analytes was obtained with 1.0 mL of 0.01 mol L^{-1} HNO_3 .

The effect of sample volume on the recoveries of Cu and Pb was examined by preconcentration of different volumes (10–250 mL) containing 20 ng of the target analyte. It was found that quantitative recoveries for both target analytes were obtained when the sample volume was less than 200 mL. Hence, a sample volume of 150 mL was selected for subsequent experiments.

Ultrasonic time for adsorption and elution was also investigated. The results showed that quantitative recovery of both analytes was obtained when greater than 5 min-

utes was used for adsorption and greater than 2 minutes for elution. Therefore, in further experiments, an ultrasonic time of 5 minutes was used for adsorption and 2 minutes for elution.

Interferences

The potential interference due to the competition of other metal ions for the adsorption agent and their subsequent co-extraction with Cu and Pb was investigated. A solution containing 2.0 ng L^{-1} of Cu, Pb, and the interfering ions was treated according to the analysis procedure. The tolerance limits of the coexisting ions (defined as the recovery of Cu and Pb) were less than 90%. The results showed that at least 5000 $\mu\text{g mL}^{-1}$ of K^+ and Na^+ , 2000 $\mu\text{g mL}^{-1}$ of Ca^{2+} and Mg^{2+} , 100 $\mu\text{g mL}^{-1}$ of Al^{3+} , Zn^{2+} , and Fe^{3+} showed no substantial interferences.

Analytical Performance

Under the optimal experimental conditions, the detection limits for Cu and Pb were 1.8 ng L^{-1} and 2.5 ng L^{-1} , with enrichment factors of 121 and 136, respectively. The enrichment factor was calculated as the concentration ratio of analytes after preconcentration and in the initial solution. The relative stan-

dard deviations (RSDs) were 4.8% and 5.5% ($n=5$, $c=5.0$ ng L^{-1} , sample volume=150 mL), respectively.

Analytical Application

The proposed method was applied to the separation and determination of Pb and Cu in different seawater samples. The analytical results are given in Table II. The recoveries for the spiked samples were in the acceptable range of 92.5–103%.

To further verify the accuracy of the developed method, it was applied to the determination of Pb and Cu in the certified reference material GBW(E)080040 seawater. The analytical results for Pb of 9.79 ± 0.90 $\mu\text{g L}^{-1}$ and for Cu of 5.08 ± 0.43 $\mu\text{g L}^{-1}$ are in good agreement with the certified value of 10.0 ± 0.6 $\mu\text{g L}^{-1}$ for Pb and 5.0 ± 0.4 $\mu\text{g L}^{-1}$ for Cu. No significant differences were observed (t -test, $P = 0.05$).

CONCLUSION

N-(β -ethylenamine)- γ -propylamine trimethoxysilane (AAPTS)/ Fe_3O_4 MNPs are highly monodisperse and magnetically separable. They have been successfully employed for the magnetic solid-phase extraction of trace Cu and Pb from environmental water. Under the optimal experimental conditions, the detection limits for Cu and Pb, with enrichment factors of 121 and 136, were found to be 1.8 ng L^{-1} and 2.5 ng L^{-1} , and the relative standard deviations (RSDs) were 4.8% and 5.5% ($c=5.0$ ng L^{-1} , $n=5$), respectively.

The developed method has been applied to the determination of trace Cu and Pb in water samples and reference materials with satisfactory results. This method is simple, rapid, and sensitive and very suitable for the rapid adsorption of heavy metals from large volumes of sample solutions.

Fig. 5. Effect of pH on sorption of Pb and Cu. The concentration of Pb and Cu: 5.0 ng L^{-1} .

TABLE II
Analytical Results for Seawater Samples (mean $\pm$ S.D., n = 3)

Sample	Element	Added (ng L ⁻¹)	Found (ng L ⁻¹)	Recovery (%)
Seawater	Cu	0.0	31.2 $\pm$ 1.9	
		10.0	40.8 $\pm$ 2.4	96.0
	Pb	0.0	3.9 $\pm$ 0.2	
		4.0	7.6 $\pm$ 0.5	92.5
Artificial Seawater	Cu	0.0	–	
		10.0	10.3 $\pm$ 1.8	103
	Pb	0.0	–	
		10.0	9.69 $\pm$ 0.63	96.9
Seawater GBW(E) 080040		Certified Value (μ g L ⁻¹)	Found (μ g L ⁻¹)	
	Cu	5.0 $\pm$ 0.4	5.08 $\pm$ 0.43	
	Pb	10.0 $\pm$ 0.6	9.79 $\pm$ 0.90	

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