

Alumina-coated magnetite nanoparticles for solid phase extraction of Cd in water samples

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Abstract: A new type of alumina-coated magnetite nanoparticles with sodium dodecyl sulfate and by the use of 1-(2-pyridylazo)-2-naphthol (PAN) as a new sorbent solid phase extraction (SPE) has been successfully for preconcentration and separation of Cd in water samples.

Compared with conventional SPE methods, the advantages of this new $\text{Fe}_3\text{O}_4/\text{Al}_2\text{O}_3$ NPs MHSPE method include easy preparation and regeneration of sorbents, short times of sample pretreatment, high extraction yields, and high breakthrough volumes. Various influencing parameters on the separation and preconcentration of trace metals, such as the amount of SDS, pH value, amount of nanoparticle, amount of PAN, sample volume, were studied. The detection limit of this method for Cd was $1.5 \mu\text{g L}^{-1}$ and the R.S.D. was 3.2% ($n = 10$). The proposed method has been applied to the determination of the metal ion at trace levels in water samples with satisfactory results.

1. Introduction

The determination of metal ions at trace level by flame atomic absorption spectrometry (FAAS) has a number of advantages which include high selectivity, speed and fairly low operational cost. Direct determination of trace elements at extremely low concentration is often very difficult due to the insufficient sensitivity of the methods and the matrix interferences. For these reasons, an efficient separation and preconcentration procedure is often required prior to the measurement step. 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 techniques [1,2].

Recently, magnetic materials have received increasing attention. Generally, magnetic materials are prepared by encapsulating inorganic magnetic particle with organic polymer or inorganics [3-6]. 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 [7]. Because of their large surface area and unique physical and chemical properties, they have been widely applied in many fields, e.g. protein separation [7-9], removal of metal ions and dyes [4, 10 and 11]. In recent years, many studies have been reported their application in the analytical chemistry field. These magnetic materials as adsorbents can be used for the extraction of organic contaminants from environmental samples [5, 6]. 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).

Due to the high surface area and the excellent adsorption capacity of these nano-magnetic adsorbents, satisfactory extraction recoveries of Cd (II) could be achieved in some water samples.

2. Experimental

2.1. Apparatus

The determination of Cd was carried out using a GBC model SensAA atomic absorption spectrometer with deuterium lamp background correction and hollow cathode lamp at respective wavelengths (resonance line) as radiation sources, was used throughout the measurements. An air acetylene flame was used for the determination of the metal 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 Cd (II) was 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 (FeCl₂·4H₂O), ferric chloride (FeCl₃·6H₂O), 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 nanoparticle adsorbents

The magnetic adsorbents, alumina-coated magnetite nanoparticles (Fe₃O₄/Al₂O₃ NPs), were synthesized by alkoxide hydrolysis precipitation method [12].

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 Fe₃O₄ 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. Aluminum isopropoxide (1.0 g) was dissolved in ethanol (60 mL) to form a clear solution. Fe₃O₄ 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 Fe₃O₄ 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 [13].

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 mixed hemimicelles particles

For the preparation of mixed hemimicelles particles firstly, 0.05 g Fe₃O₄/Al₂O₃ 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 Fe₃O₄/Al₂O₃ NPs were isolated by placing a strong magnet and the supernatant was poured away and there were washed with high purity deionized water.

2.5. Procedure

The target analyte a 250 ml of sample solution containing Cd(II) in the range of .5–280 µg L⁻¹ was 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 Fe₃O₄/Al₂O₃ NPs and then were shaken mechanically for 15 min. Subsequently, the SDS-PAN coated Fe₃O₄/Al₂O₃ NPs were isolated by placing a strong magnet and the supernatant was poured away. The preconcentrated target analyte absorbed on SDS-PAN coated Fe₃O₄/Al₂O₃ NPs was eluted with using 3 ml of 2 mol L⁻¹ HNO₃. The analytes in the effluent were determined by FAAS.

2.6. Water samples

Water samples were collected from KOR River (Sought of Iran). Waste waters were collected from Shiraz petrochemical industry. They were filtered through Watman No. 42 and stored in glass bottles at 4°C. Then the samples were ready for purposed procedure.

3. Results and discussion

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

From Fig. 1, we can see that in the presence of SDS, the Cd (II) was hardly adsorbed onto the surface of Fe₃O₄/Al₂O₃ NPs. The adsorption amount of the Cd (II) increased remarkably with the increasing amount of SDS. Given these findings, 40 mg was selected as the final addition amount of SDS in the studies.

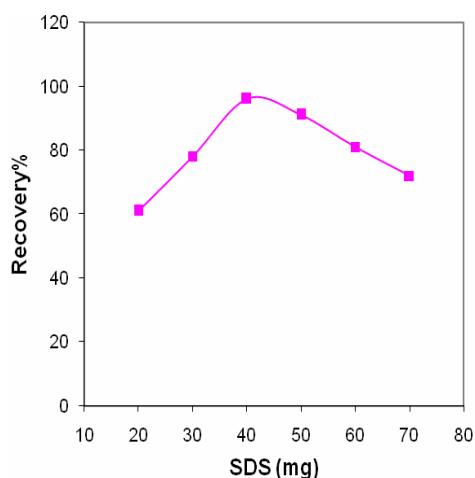


Fig.1.Effect of amount of SDS added on the adsorption of the Cd (II)

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 Cd (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 Cd (II). The pH of 2.0 was selected for the next studies.

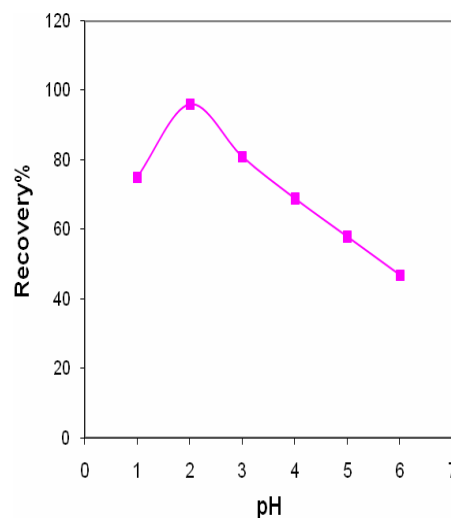


Fig. 2. Effect of pH on the adsorption of Cd (II)

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 Cd, 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 Cd was obtained with increasing of modified Fe₃O₄/Al₂O₃ NPs amount of 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.

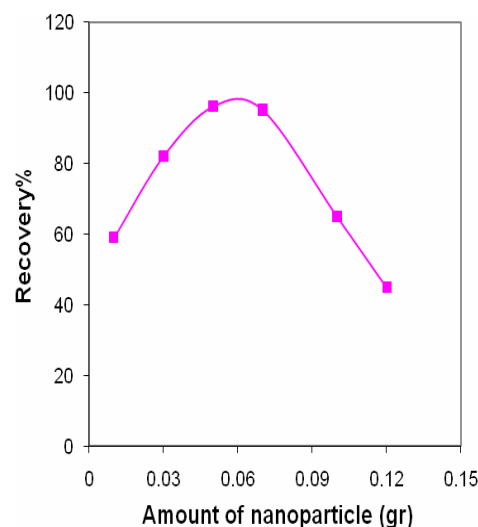


Fig. 3. Amount of modified Fe₃O₄/Al₂O₃ NPs on the adsorption of Cd (II)

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

To investigate the optimum amount of PAN on the quantitative extraction of understudy metals ions by the SDS coated on $\text{Fe}_3\text{O}_4/\text{Al}_2\text{O}_3$ 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.

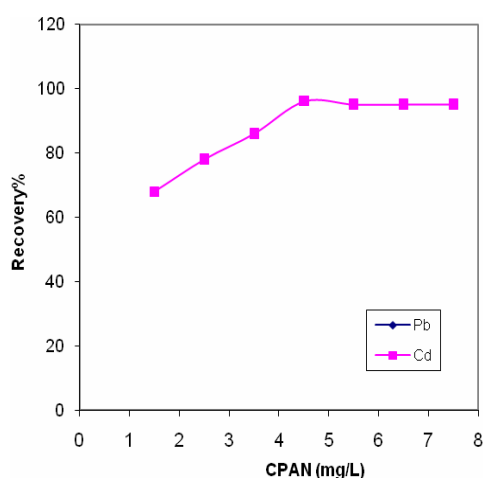


Fig. 4. Effect of the amount PAN on the adsorption of Cd (II)

3.5. Desorption conditions

Some experiments were carried out in order to choose a proper eluent for the adsorbed Cd ions by SDS-PAN coated $\text{Fe}_3\text{O}_4/\text{Al}_2\text{O}_3$ NPs. The Cd ions were stripped with different concentrations (0.1–4 mol L^{-1}) of various acids. It is observed that 3.0 mL of 2.0 mol L^{-1} nitric acid could accomplish the quantitative elution of Cd from the SDS-PAN coated $\text{Fe}_3\text{O}_4/\text{Al}_2\text{O}_3$ NPs.

3.6. Maximal extraction volume

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

The recoveries of Cd (II) ($\geq 96\%$) was 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, 250 mL was considered to be the maximal enrichment volume for water samples.

3.7. Analytical parameters

A calibration curve was constructed by preconcentrating 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 5 to 280 $\mu\text{g l}^{-1}$ 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 (1.5 $\mu\text{g l}^{-1}$).

Table 1. Properties of merit obtained by the proposed method

Parameters	Cd
Linear Range ($\mu\text{g L}^{-1}$)	5-280
Correlation Coefficient	0.9998
Detection Limit ($\mu\text{g L}^{-1}$) (n=5)	1.5
Preconcentration factor ^b	83
RSD % (n=10)	3.2
Recovery %	96

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

3.10. Interference effects

Metal cations and anions were added individually to sample solutions containing 80 $\mu\text{g L}^{-1}$ of Cd in order to examine the effect of common coexisting ions on the sorption of studied metal ion. The tolerance limit was considered if it resulted in a $\pm 5\%$ variation in sorption efficiency of Cd. 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 Cd (II) was almost quantitative in the presence of foreign ions and therefore useful for the analysis of Cd in real samples.

3.11. Analytical applications

In order to test the reliability of the proposed methodology suitable for the assaying of lead in water samples. The results are shown in Table 3.

Table 2. Investigation of other ions on the perposed method

Foreign ions	analyte / ion
K^+ , Na^+ , Li^+ , Ce^{4+} , Mg^{2+} , NO_3^- , Ca^{2+} , F^- , Cl^- , Br^-	> 1000
HPO_4^{2-} , ClO_3^- , IO_3^- , $Mg^{2+}CH_3COO^-$, Ni^{2+} , Pd^{2+}	500
SCN^- , Mn^{2+} , Al^{3+} , Cr^{3+} , Zn^{2+} , CrO_4^{2-} , Fe^{3+}	300
Cu^{2+} , Co^{2+}	200

Table 3. determination of pb in soil and waste water samples.

Sample	Cd^{2+} ($\mu g L^{-1}$)		% Recovery
	Added	Found	
Waste water ^a 1	-	ND	-
	20	21.32±0.3	106
	50	52.50±0.4	105
Waste water 2	-	ND	-
	20	21.23±0.3	107
	50	52.51±0.4	105
Water ^b	-	ND	-
	20	19.00±0.5	95
	50	48.30±0.3	97

a) from Shiraz petrochemical center

b) From Kor river water (local river).

Conclusions

The modified Fe_3O_4/Al_2O_3 NPs are highly monodisperse and magnetically separable, and they have high adsorptive capacities. The nanoparticles can rapidly and quantitatively adsorb Cd from 250 mL of aqueous solution. Further study reveals that these magnetic nanoparticles can be used as adsorbent for

magnetic solid phase extraction FAAS determination of trace amounts of Cd in water samples. Compared with established methods, the method described here has a high enrichment factor and very low LODs. In addition, it is suitable for rapid adsorption of heavy metals from large volumes of solution.

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