SEPARATION/PRECONCENTRATION AND DETERMINATION OF TRACE AMOUNTS OF PALLADIUM USING MODIFIED ALUMINA COATED MAGNETITE NANOPARTICLES WITHOUT CHELATING AGENT

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ABSTRACT

In the present article, a simple, rapid, selective, sensitive and economical method has been developed for the separation/preconcentration of the trace amounts of Pd(II) in different real samples using alumina coated magnetite nanoparticles modified by sodium dodecyl sulfate and its determination by flame atomic absorption spectrometry after eluting with 1.0 mol L⁻¹ thiourea. Under the optimal experimental conditions, the preconcentration factor, detection limit, linear range and relative standard deviation of Pd(II) were 280 (for 700 mL of sample solution), 4.3 ng mL⁻¹, 6.0 – 120.0 ng mL⁻¹ and 4.6% (for 10 ng mL⁻¹, n=10), respectively.

Keywords: Solid-phase extraction; Alumina-coated magnetite nanoparticles; Palladium(II); Flame atomic absorption spectrometry

1. INTRODUCTION

Palladium is widely used in metallurgy, in various chemical syntheses, production of dental alloys, heat and corrosion resistance apparatus, medicinal devices, jewelry manufacture, electronic, telephone circuits and electrodes for high quality spark plugs ¹⁻³. This noble metal is a metal of economic importance; however, as a new pollutant in the environment, all its compounds should be regarded as highly toxic and carcinogenic to humans ⁴. Therefore, separation/preconcentration and determination of Pd(II) is greatly interested in environmental compartments such as soil, road dust, wastewater and different water samples. Among various methods proposed for the separation and enrichment of Pd(II) solid phase extraction (SPE) is the most widely applied technique due to rapid phase separation, simple and higher preconcentration factor ⁵⁻¹³.

At present, nano-sized materials such as TiO₂, Al₂O₃, ZrO₂, SiO₂ and carbon nanotubes have more important in SPE due to their special property of high adsorption capacity ¹⁴⁻¹⁹. But separation of these particles from aqueous medium is difficult because of very small dimension and high dispersion. Combining nanoparticles adsorption with magnetic separation is good for avoid passing through the column in conventional SPE methods. Magnetite nanoparticles (MNPs) are suitable for this propose and surface modification of MNPs is a challenged key for this application ²⁰⁻³⁴. Several analytical methods such as spectrophotometry ³⁵, flame atomic absorption spectrometry (FAAS) ³⁶, inductively coupled plasma-mass spectrometry (ICP-MS) ³⁷, inductively coupled plasma-optical emission spectrometry (ICP-OES) ³⁸ and electrochemical methods ³⁹ have been used for determination of trace amounts of palladium.

In our previous works, the abilities of alumina coated magnetite nanoparticles (ACMNPs) for separation/preconcentration of Ag(I) and Pb(II) were investigated ⁴⁰⁻⁴². In this study, we will explore the possibility of only SDS immobilized on ACMNPs without chelating agent to act as SPE sorbent for the separation/preconcentration of trace level of Pd(II) from environmental samples prior to determination by flame atomic absorption spectrometry (FAAS).

2. EXPERIMENTAL

2.1 Apparatus and reagents

Scanning electron microscope (LEO 1455VP SEM), Fourier transform infrared spectrometer (FT-IR Prestige-21, Shimadzu) and vibrating sample magnetometer (VSM 7400 Model Lake-Shore) were used to characterize the structure of the prepared ACMNPs and SDS-ACMNPs. A flame atomic absorption spectrometer (PG Instrument, England) was used with a lead hollow-cathode-lamp at an operating current of 15 mA. Other instruments used were: ultrasonic bath (S60H Elmasonic, Germany), mechanical stirrer (Heidolph, RZR2020), orbital shaker (Ika, KS130 Basic), an electronic analytical balance (Adam, AA220LA) was used for weighing the solid materials. In addition, for magnetic separations a strong neodymium-iron-boron (Nd₂Fe₁₂B) magnet (1.2 T, 2.5cm × 5cm × 10cm) was used.

All reagents used were of analytical grade and all solutions were prepared

by using triple distilled and deionized water. A stock solution of 1000 µg mL⁻¹ of Pd(II) was prepared by dissolving 0.169 g of PdCl₂ in 10 mL of concentrate HCl and was diluted to 100 mL. Working solutions were obtained by further diluting the stock solution to the required concentrations before use. Sodium dodecylsulfate (SDS), ferrous chloride (FeCl₂·4H₂O), ferric chloride (FeCl₃·6H₂O), aluminum isopropoxide, ethanol, nitric acid, hydrochloric acid, thiourea and sodium hydroxide were used without further purification processes.

2.2 Preparation of SDS-ACMNPs

ACMNPs were prepared according to our previous works. ⁴⁰⁻⁴² A SDS solution was prepared by dissolving 200.0 mg SDS in 100 mL deionized water. Ten milliliters of this solution was added to 10 mL water containing 0.2 g of ACMNPs. The pH of this suspension was adjusted to 2.0 by drop-wise addition of HNO₃ (0.1 mol L⁻¹) solution. The mixed solution was shaken for 15 min and then separated from the reaction medium under the magnetic field, and rinsed with 10 mL pure water. This product was used as sorbent for palladium ions.

2.3 General procedure

The procedure for the magnetic SPE of Pd(II) is as follows: 10 mL of Pd(II) solution (5 µg mL⁻¹) was added to SDS/ACMNPs from above section, subsequently the pH value was adjusted to 6.0 with phosphate buffer and the solution was shaken for 15 min to facilitate adsorption of the palladium ions onto the NPs. Then the magnetite adsorbents were separated easily and quickly using magnet and decanted directly. Subsequently, 2.0 mL of thiourea solution (1.0 mol L⁻¹) as eluent was added. Finally, the magnet was used again to settle the magnetic nanoparticles and the eluate was separated for FAAS analysis.

2.4 Sample preparation procedure for water

Water samples (*i.e.*, tap water, spring water and river water), were filtered after collection through filter paper (Whatman, no. 4) to remove suspended particulate matter and basicified to a pH of about 9.5 with ammonia/ammonium chloride buffer prior to storage in polyethylene containers for use. The SPE procedure was carried out as described in the general procedure.

2.5 Sample preparation procedure for road dust

The four to 10 grams of road dust samples were collected from four different roadsides with dense traffic in Sirjan. The samples were digested with a mixture of 20 mL concentrated HCl and 5 mL of concentrated HNO₃ at room temperature, then they were heated to 100 °C for 5 h. The mixtures were evaporated to dryness and then 10 mL of above acid mixture was added to the residue and evaporated to dryness again. After this, 20 mL of deionized water were added to the beaker and the insoluble parts were filtered. The pH was adjusted to 9.5 with ammonia/ammonium chloride buffer and the total volumes were made up to 20 mL with deionized water in four beakers and the solutions were taken for separation/preconcentration procedure.

3. RESULTS AND DISCUSSION

3.1 Characterization of ACMNPs and SDS-ACMNPs

It is most important that the ACMNPs as sorbent should possess suitable magnetic property. This was studied by measuring the hysteresis and remanence curve by means of a vibrating sample magnetometer (VSM). The curve shows that ACMNPs with value of large saturation magnetization of 9.34

emu g^{-1} exhibit typical superparamagnetic behavior due to no hysteresis (Fig. 1). Therefore, sorbent of ACMNPs is sufficient for magnetic separation with a conventional magnet.

Fig. 1. The magnetic behavior of ACMNPs.

A scanning electron microscope (SEM) was used to examine the surfaces of the MNPs and ACMNPs as adsorbent (Fig. 2). The image of Fig. 2b illustrates a highly porous morphology of adsorbent with uniform size distribution of the nanospheres.

Fig. 2. SEM images of MNPs (a) and ACMNPs (b).

The XRD pattern for the ACMNPs showed eight characteristic peaks for Fe_3O_4 and Al_2O_3 according to the software database file. The average crystallite size (D) is calculated to be 18.9 ± 2 nm for ACMNPs using the Debye-Scherrer formula of $D = K\lambda/(\beta \cos\theta)$, where K , λ , β and θ are the Scherrer constant ($K=0.89$), the X-ray wavelength ($\lambda=1.5406 \text{ \AA}$), the full peak width at half maximum (FWHM) and the Bragg diffraction angle, respectively⁴³. The result is well consistent with that of SEM analysis.

Fig. 3. XRD patterns for the naked Fe_3O_4 (a) and alumina coated Fe_3O_4 nanoparticles (b).

3.2 Effect of pH and SDS amount

ACMNPs have positively charged surfaces in highly acidic solutions that can strongly adsorb a negatively charged surfactant such as SDS. The SDS would form hemimicelles or admicelles on alumina by strong adsorption and it can strongly adsorb on the positively charged ACMNPs surface to form aggregates⁴⁴. A concentration of SDS, below its critical micellar concentration (CMC, 8 mmol L^{-1}), was used. Above this concentration, the excess of SDS would form micelles in the aqueous solution, which were not adsorbed on alumina surfaces. When the solution was acidified, the ad-micelles could trap Pd(II) . Therefore influence of various amounts of 25, 50, 60, 75, 90, 100, 125, 150 and 200 mg SDS on adsorption of palladium ions through the ACMNPs substrate was investigated. The results showed that maximum adsorption was obtained when 100 mg SDS used. Thus, this amount was selected as the optimum concentration of SDS for further studies.

In order to establish the effect of pH on the adsorption of Pd(II) , the batch equilibrium studies at different pH values were carried out in the range of 2.0–11.0. Results show that the maximum removal of Pd(II) on the adsorbents was observed at range of 3.5–7.5 by shaking the solution containing SDS and ACMNPs for 10 min. When solution was acidified, SDS would form hemimicelles on ACMNPs by strong sorption and this micelles could trap Pd(II) ions. At $\text{pH} > 7.5$ the metal complex forms and results in precipitation and therefore the separation may not be due to adsorption. Therefore, the pH value of 6.0 was used as pH optimum for further study.

3.3 Standing and magnetic separation time

The effect of time on the adsorption of palladium on the SDS-ACMNPs was studied. When the ACMNPs were isolated immediately without a standing process, the recovery of Pd(II) was 67%. But, when the standing time was adjusted to 5, 10, 15, 20 and 30 min, recoveries were improved to 87, 93, 96, 96 and 96%. Therefore, standing times of 15 min was selected as the optimum time to achieve satisfactory adsorption and better recovery of palladium ions.

3.4 Effect of sample volume, nanoparticles amount and desorption conditions

In order to obtain a preconcentration factor, a larger volume of sample solution is required. For study the effect of sample volume on the recovery of palladium ions, the sample solutions in the range of 50–800 mL containing $5.0 \mu\text{g}$ of palladium ions were operated according to the general procedure and eluted using 2.0 mL of thiourea (1.0 mol L^{-1}). In the sample volumes higher than 700 mL, the recovery decreased. Consequently, a preconcentration factor of 280 could be attained for quantitative recovery of $95 \pm 2 \%$ of Pd(II) when the sample volume was 700 mL.

The effect of nanoparticles amount on the quantitative extraction of Pd(II) was studied by applying various amounts of SDS/ACMNPs (from 10 to 300

mg). The extraction was found to be quantitative when 200 mg or more. Experiments were carried out with 200 mg modified nanoparticles.

Different eluents of thiourea, thiosulphate, acetate, HCl, HNO₃, H₂SO₄ and NaOH at various concentrations were tested in order to elute the adsorbed palladium from the sorbent. It was found that 2.0 mL of thiourea with a concentration of 1.0 mol L⁻¹ was sufficient for quantitative recovery of adsorbed Pd(II).

Table 1 Comparison of the characteristic data between typical published methods and the proposed method for separation/preconcentration and determination of Pd(II).

Sorbent	Detection method	Preconcentration factor	Sorbent capacity (mg g ⁻¹)	RSD (%)	Linear range (ng mL ⁻¹)	Detection limit (ng mL ⁻¹)	Ref
Saccharomyces cerevisiae/ calcium alginate beads	GFAAS ^a	N.R. ^b	10.0	4.6	N.R.	7.0	[5]
Thiophene-2-carbaldehyde/Silica	ICP-OES ^c	100	5.0	3.2	1-1000	0.2	[6]
5(p-dimethylaminobenzylidene) rhodanine/Silica gel-polyethylene glycol	FAAS	125	0.99	4	2-80	0.54	[7]
Pyridine/ Nano alumina	FAAS	60	37	0.8	N.R.	0.6	[8]
Aspergillus sp./Cellex-T resin	ETAAS ^d	11.5	1.24	5.0	0.5-5.6	0.012	[9]
Cysteine/Silica gel	ICP-OES	100	N.R	6-8	N.R	0.02	[10]
Murexide/Halloysite nanotubes	ICP-OES	120	42.86	3.1	N.R.	0.29	[11]
Oxidized MWCNTs ^e	FAAS	165	15.7	5.3	1-200	0.3	[12]
2,6-Diaminopyridine /Activated carbon	ICP-AES ^f	150	38.5	<3	N.R.	0.33	[13]
SDS/ACMNPs	FAAS	280	8.3	4.6	6.0-120.0	4.3	This work

^a Graphite furnace atomic absorption spectrometry; ^b Not reported; ^c Inductively coupled plasma-optical emission spectrometry; ^d Electrothermal atomic absorption spectrometry; ^e Multi-walled carbon nanotubes; ^f Inductively coupled plasma-atomic emission spectrometry

Table 2 Recoveries results for Pd(II) determination in different real samples of road dust, river, tap and spring waters.

Sample	Pd(II) /μg mL ⁻¹		Recovery (%)
	Added	Found ^a	
River water (Tezerg, Hajiabad)	0	N.D	-----
	5	5.20 (±0.3)	104.0
	10	9.80 (±0.3)	99.8
Tap water (Sirjan)	0	N.D	-----
	5	4.70 (±0.1)	94.0
	10	9.35 (±0.2)	93.5
Spring water (Saadatabad, Sirjan)	0	N.D	-----
	5	4.87 (±0.4)	97.4
	10	9.91 (±0.3)	99.1
Road dust (Sirjan-Bandar Abbas) No. 1	0	0.21	-----
	5	5.44 (±0.4)	104.6
	10	10.37 (±0.2)	101.1
Road dust (Sirjan-Bandar Abbas) No. 2	0	0.27	-----
	5	5.42 (±0.3)	105.0
	10	10.30 (±0.3)	103.0
Road dust (Sirjan-Bandar Abbas) No. 3	0	0.36	-----
	5	5.36 (±0.2)	100.0
	10	10.55 (±0.3)	101.9
Road dust (Sirjan-Bandar Abbas) No. 4	0	0.26	-----
	5	5.44 (±0.4)	103.6
	10	10.76 (±0.4)	105.0

^a Average of three determination ± standard deviation.

3.5 Interference study

The study of interference was performed by a standard mixture solution containing 5.0 μg mL⁻¹ of Pd(II) and a certain amount of foreign ions. The following excesses of ions do not interfere (i.e., caused a relative error of less than 5%): less than a 1000-fold (largest amount tested) amount of Na⁺, K⁺, F⁻, Cl⁻, Br⁻, NO₃⁻, SO₄²⁻, ClO₄⁻; a 500-fold amount of NH₄⁺, Ba²⁺, Ca²⁺, Ni²⁺, Zn²⁺, Co²⁺, Mg²⁺, Cu²⁺, Pb²⁺, Fe²⁺; a 50-fold amount of Cr³⁺, Fe³⁺, Al³⁺ and a 10-fold amount of Zr⁴⁺.

3.6 Adsorption capacity and adsorbent regeneration

Adsorption capacity study used here was adapted from the method recommended by Maquieira et al.⁴⁵. The static sorption capacity of SDS/ACMNPs was found to be 8.3 mg g⁻¹ for palladium ions. In this research, it also was found that the adsorbent can be reused up to three times without loss of analytical performance. Considering that 4.0 g of modified ACMNPs could be prepared in one batch and only 200 mg of ACMNPs was used for one extraction operation, this reusability time is acceptable.

3.7 Analytical performance and method validation

Under the optimal experimental conditions, the analytical features of the method such as limit of detection (LOD), linear range of the calibration curve and precision were examined. The LOD of the proposed method based on three times the standard deviation of the blank (3S_b) was 4.3 ng mL⁻¹. The linear range of calibration curve for Pd(II) was 6.0 – 120.0 ng mL⁻¹ with a correlation coefficient of 0.9915. The regression equation was $A = 0.0238 C_{Pd} + 0.0366$ ($n = 7$), where C_{Pd} is the concentration of Pd (II) in ng mL⁻¹ and A is the absorbance. The relative standard deviation (RSD) for 10 replicate measurements of 10.0 ng mL⁻¹ of palladium ions was 4.6% which indicated a reproducible response. Table 1 shows a comparison of the proposed method with other reported SPE methods. It could be seen that some obtained values for the proposed method are as or better than some of the previously reported methods.

3.8 Analytical Applications

The performance and reliability of the method for the analysis of real samples was checked by determination of Pd(II) content in different waters and road dust samples (Table 2). According to these results, the added Pd(II) can be quantitatively recovered from different waters and road dust samples by the extraction procedure. These results demonstrate the applicability of the extraction procedure for palladium in real samples.

4. CONCLUSIONS

It has been demonstrated that the modified ACMNPs provides a new and fast route for separation/preconcentration and determination of Pd(II) using FAAS technique in different samples. This sorbent was successfully applied for convenient, fast, simple and efficient enrichment of trace amounts of palladium ions from road dust and different water samples. The main benefits of this methodology are: no use of toxic organic solvents, simplicity and high capacity of sorbent, preconcentration factor, fast adsorption and low cost. Magnetic separation greatly shortened the analysis time of the method. Furthermore, it avoids the time-consuming column passing (about 1 h in conventional SPE method) and filtration operation, and no clean-up steps were required.

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