



Anal. Bioanal. Chem. Res., Vol. 2, No. 1, 1-12, June 2015.

Application of Sulfur Nanoparticles as a Solid Phase Extraction Sorbent for the Preconcentration of Lead(II) and Palladium(II) in Environmental Samples Prior to Flame Atomic Absorption Spectrometry Determination

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(Received 26 August 2014, Accepted 10 March 2015)

The application of sulfur nanoparticles as an efficient adsorbent for the solid-phase extraction and determination of the trace amounts of Pb and Pd ions was investigated in environmental samples using flame atomic absorption spectrometry. Effects of various parameters such as pH, flow rate of sample and eluent, type and concentration of eluent, sample volume, amount of adsorbent and interfering ions were investigated and optimized. The results showed that the optimal conditions for quantitative recovery of the metal ions by adsorption and elution on the sulfur nanoparticles were achieved by employing a flow rate of 2 ml min⁻¹, a pH of 9.5 for the sample solutions, and an eluent composed of 4.0 M HNO₃ in ethanol. The maximum adsorption capacity of SNPs as sorbents at optimum conditions for lead and palladium ions was found to be 2.80 mg g⁻¹ and 2.87 mg g⁻¹, respectively. At optimum conditions, the detection limits of this method were 0.3 and 2.5 ng ml⁻¹ for Pb(II) and Pd(II), respectively. The proposed procedure was applied to the determination of the metal ions in soil and water samples.

Keywords: Solid phase extraction, Preconcentration, Palladium, Lead, Sulfur nanoparticle, Flame atomic absorption spectrometry

INTRODUCTION

In recent years, pollution of the environment by heavy metals has received considerable attention. The toxic heavy metals could gradually accumulate in the human body through the food chain and cause damage to human health. Lead is a neurotoxin and can be accumulated in skeleton, thus it can lead to behavioural abnormalities, retarding intelligence and mental development [1].

Because of their chemical properties, the use of Platinum Group Metals (PGMs) is a key factor for several industrial applications. Due to excellent chemical and physical characteristics of palladium such as resistance to corrosion and oxidation, electrical conductivity, catalytic activity, and high melting point, its application has been growing during the last few decades [2]. Similarly, Pd(II)

can bind to thiol-containing amino acids, proteins, DNA, and several biomolecules and adversely affect the cellular processes [3]. Furthermore, the release of Pd(II) and its accumulation in the environment can cause the human health problems such as eye irritation, skin problems, rhinoconjunctivitis, asthma, *etc.* [4,5]. Consequently, the development of reliable methods for the determination of Pb(II) and Pd(II) in environmental and biological samples is of particular significance.

In routine laboratory measurements, several analytical techniques such as flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), spectrophotometric and electrochemistry methods have been proposed for the determination of the trace and toxic metals in different environmental sample. However, direct determination of the trace amounts of these compounds in complicated materials is usually difficult owing to the matrix interferences and

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insufficient detection power. Monitoring of the trace element concentrations in complicated materials might be considered as a difficult analytical task, mostly owing to the complexity of the matrix and the low concentration of these compounds, which requires sensitive instrumental techniques and often a preconcentration step [6-9]. Many methods, either on-line or batch systems, have been developed for the preconcentration of the trace metals from various samples, including precipitation/co-precipitation [10-13], liquid-liquid extraction (LLE) [14-16], solid phase extraction (SPE) [17-21], flotation [22], ion exchange [23,24], biosorption [25], and cloud point extraction (CPE) [26-29]. Among these techniques, SPE is one of the most important preconcentration methodologies because of its several major advantages; such as higher enrichment factor, simple operation, safety with respect to hazardous samples, consumption of small volumes of organic solvent, high selectivity, lower cost, less time and the ability to combine with different modern detection techniques [30]. Various solid phase adsorbent materials like activated carbon [31], Amberlite XAD resins [32,33], chromosorb resins [34] and silica gel [35,36] have been successfully used for the preconcentration and separation of heavy metal ions at the trace level. However, the development of new SPE preconcentration and separation systems has been growing [37]. An actual tendency in the field of solid phase extraction is related to the use of the new sorbent materials with good performance, such as high resistance to acids and bases, selective for analytes, large surface area and high adsorption capacity [38,39]. Recently reported the use of several nano-sized SPE adsorbents such as nanoparticles (NPs) and carbon nanotubes have been proposed as a novel solid phase extractor for various inorganic and organic materials at trace levels [40,41]. Nano-sized sulfur particles are another class of NPs, being widely applied in pharmaceuticals, synthesis of nano-composites for lithium batteries, and modification of carbon nanotubes [42]. Sulfur is a non-metal, tasteless, odorless, and a non-toxic element. Some outstanding features of this adsorbent are its low cost, readily availability, and long-term stability; these make it suitable for routine SPE procedures [43,44]. In this work, sulfur nanoparticles (SNPs) were synthesized and used as a sorbent for separation and preconcentration of the trace amounts of Pb(II) and Pd(II) ions prior to its determination

by flame atomic absorption spectroscopy (FAAS). All of the factors affecting the preconcentration of heavy metals such as pH of sample, eluent and interfering ions, were studied and optimized. The final results demonstrate that sulfur nanoparticles are useful, convenient, new non-toxic and non-expensive materials as adsorbents for Pb(II) and Pd(II) ions. The validity of the proposed method was examined for spiked water samples.

EXPERIMENTAL

Apparatus

The determination of Pb and Pd was carried out using A Chemtech Analytical Instrument model CTA-2000 (Bedford, England) atomic absorption spectrometer equipped with an air-acetylene burner. Hollow cathode lamps were used as radiation source, and the operational conditions of the equipment were established according to the manufacturer's recommendations for each element. The instrumental parameters were adjusted according to the manufacturer's recommendations. The crystalline structure of the SNPs was characterized using a PANalytical X'Pert PRO MPD system (PANalytical B.V., The Netherlands) with Cu K α radiation ($\lambda = 1.542 \text{ \AA}$). The X-ray generator was set to an acceleration voltage of 40 kV and a filament emission of 30 mA. The morphology of SNPs was also determined by scanning electron microscopy (SEM, Philips XLC30). The particle size distribution was determined by using a dynamic laser light scattering (LLS) technique (Zetasizer, MS2000). A Metrohm 780 (Herisau, Switzerland) pH/ion meter furnished with a combined glass-saturated calomel electrode was used for pH measurements. A vacuum pump model Rocker 400 (Tarson, India) was used to control the flow rate. A funnel-tipped glass tube (4 mm i.d. and 7 cm length) was used as a column for the preconcentration.

Chemicals and Reagents

Reagents of analytical and spectral purity were used for all experiments and doubly distilled deionized water was used throughout. Standard lab ware and glassware used were repeatedly cleaned with HNO₃ and rinsed with double distilled water, according to a published procedure [45]. The

stock standard solutions containing 1000 mg l⁻¹ of Pb(II) and Pd(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. Hydrochloric acid (HCl), nitric acid (HNO₃) and ethanol of 99.5% purity were purchased from Merck. The pH was adjusted with the NH₃/NH₄Cl buffer solution.

Synthesis and Characterization of SNPs

Sulfur nanoparticles in liquid phase were synthesized according to a previously reported procedure [46]. For this purpose, 20 ml of thiosulfate solution (0.01 M) and 20 ml of a solution containing HCl (0.02 M) and SDBS (0.01 M) were combined and mechanically stirred at 1500 rpm for 30 min. After equilibration, the sample was sonicated for 2 min to prevent any possible agglomeration. After several times of rinsing the precipitate with acetone and deionized water, SNPs was dried at room temperature for 48 h.

Figure 1 shows the XRD patterns of SNPs. The positions and intensities of the diffraction peaks were in good agreement with the literature values for monoclinic phase sulfur according to JCPDS N34-0941 (JCPDS = Joint Committee on Powder Diffraction Standards).

The particle sizes of the prepared SNPs were analyzed by the LLS technique (Fig. 2). It reveals that the distribution size of most of the SNPs was in the range of 75-85 nm.

Figure 3 shows the SEM image of the prepared SNPs. From the figure it is clear that the sulfur nanoparticles are almost spherical shape and uniform size.

Column Preparation

0.5 g nano-sized sulfur was conditioned by 5.0 ml of methanol and 10 ml of water and then poured into a funnel-tipped glass (7 cm long and 0.4 cm internal diameter). A small amount of glass wool was used to prevent adsorbent leakage. The column was connected to a vacuum pump *via* a büchner system.

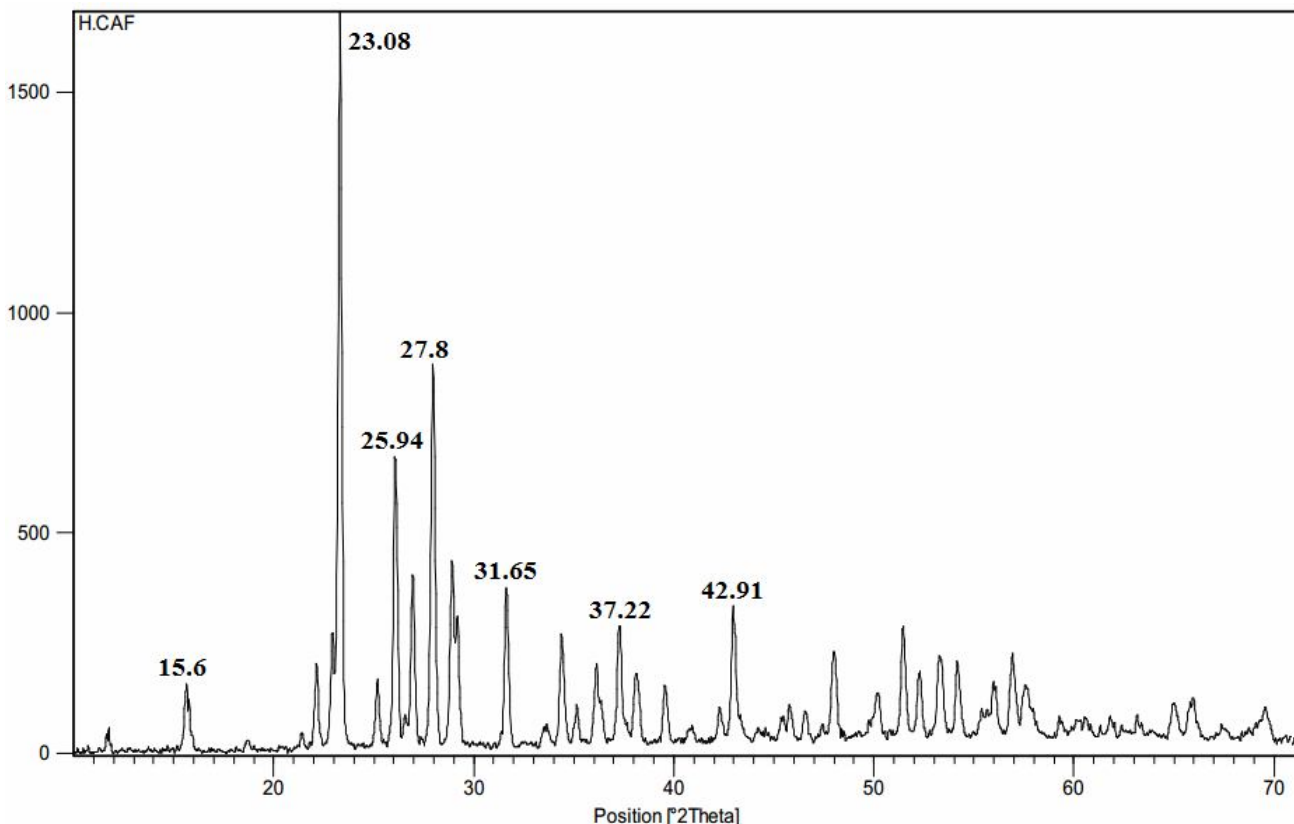


Fig. 1. XRD patterns of SNPs.

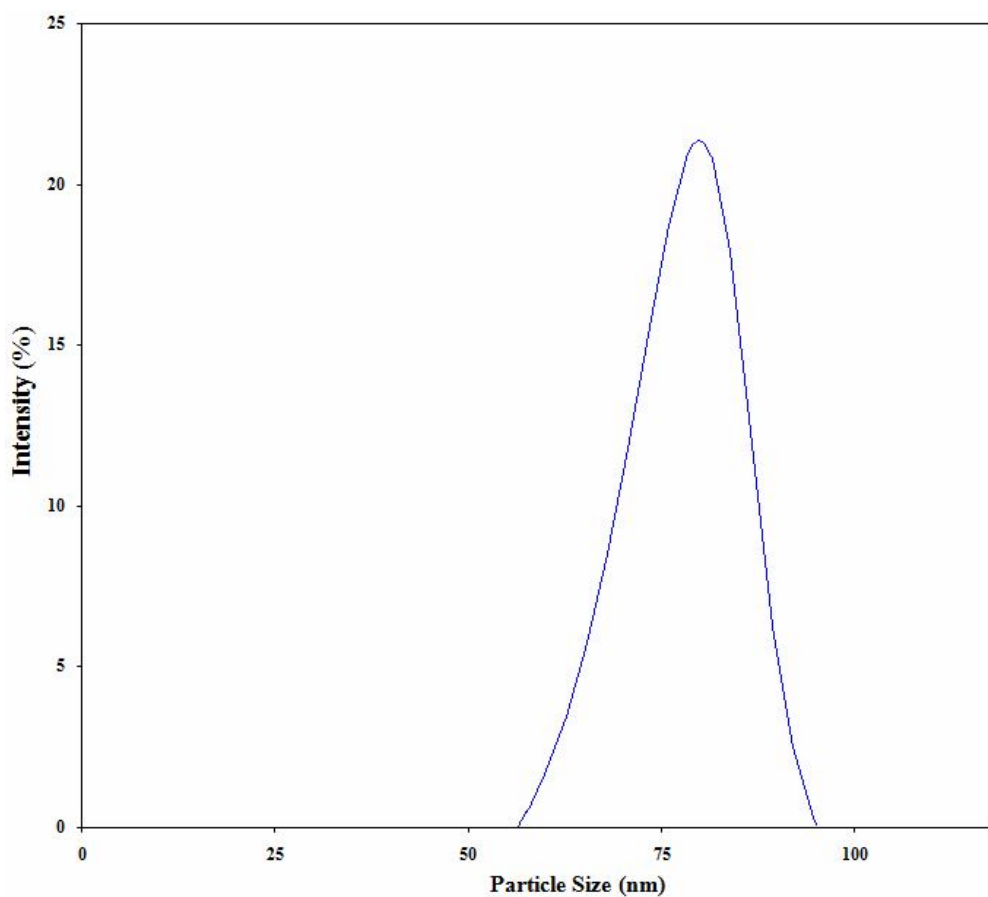


Fig. 2. Particle size distribution of SNPs.

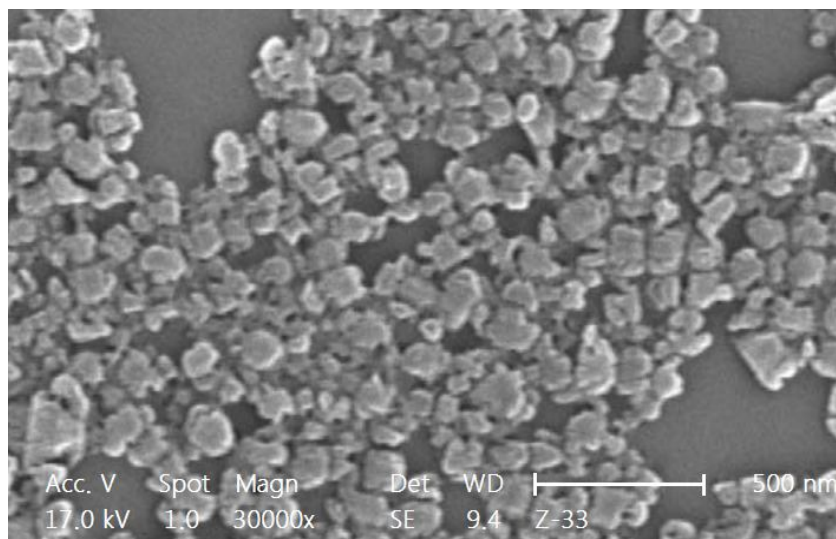


Fig. 3. SEM image of SNPs.

Applications to Real Samples

Water samples were collected from three main sources: (1) tap water (Damghan drinking water, Iran), (2) river water from Kardeh, a village near Mashhad (Iran), (3) wastewater from copper factory (Sarcheshmeh, Kerman, Iran). Water samples were acidified with nitric acid and stored in polyethylene bottles thoroughly washed with detergent, tap water and distilled water. The water samples were kept in the refrigerator and filtered prior to analytical procedure.

For the preparation of soil samples, amounts of about one gram of the soil sample was dried at 100 °C for 4 h. Based on the Tsopelas Method, the cold acidic digestion of soil samples was performed [47]. The storage period was kept as short as possible. The acidic digested soil was centrifuged to remove suspended particles at 2000 rpm for 10 min and then filtered through a cellulose membrane filter with a pore size of 0.45 μm .

Preconcentration Procedure

An off-line column procedure was applied for the preconcentration process. 250 ml of the sample solution containing 8-160 ng ml^{-1} of lead, 16-120 ng ml^{-1} of palladium and buffered at pH 9.5 was passed through the column at a flow rate of 2 ml min^{-1} using a vacuum pump *via* a büchner system. The retained metal ions were eluted from the column by 2 ml of 4 M of HNO_3 in ethanol solution and the concentrations of metal ions were determined by FAAS. A blank solution was also run under the same conditions without adding the analytes.

RESULTS AND DISCUSSION

Sulfur forms over 30 solid allotropes, more than any other element [48]. Orthorhombic and monoclinic sulfur are the most stable forms containing crown-shaped S_6 , S_8 and S_{12} molecules [49]. Therefore, it is suggested that the interaction between solid sulfur and M^{n+} is probably similar to the host-guest interaction such as those occurring between crown ethers and metal ions.

In order to obtain optimum separation and/or preconcentration conditions and maximum recoveries, some experimental parameters such as the pH of sample solution, type and concentration of eluent, the flow rates of the eluent

and sample solutions, and the effect of different coexisting ions were optimized. The analytical parameters such as limit of detection (LOD), precision, accuracy and linear working range were determined at optimal experimental conditions.

Effect of pH

pH is one of the most important factors affecting the adsorption process. According to the batch procedure, the effect of the pH on adsorption of Pb(II) and Pd(II) was investigated in the pH range of 2-11 and then analyzed by FAAS. The adsorption experiments were in triplicates and the respective results are depicted in Fig. 4. As can be seen, Pb(II) and Pd(II) were quantitatively (above 95%) recovered at the pH 9.5. At higher pH values the recovery efficiency was probably reduced due to the formation of $\text{M}(\text{OH})_n$ or $\text{M}(\text{OH})^+$. Therefore, pH adjustment in each sample was carried out by adding 5 ml of $\text{NH}_3/\text{NH}_4\text{Cl}$ buffer (pH 9.5). Experimental evidence showed that the addition of 5.0 ml of this buffer solution to 250 ml of the sample solution had no effect on the recovery of the metal ions. Under these conditions, the metal ions could form stable cationic ammonia complexes, which in turn could prevent heavy metal ion precipitation under alkaline conditions.

Choice of Eluent and Flow Rate

The type, amount, and concentration of eluent are other important parameters for this kind of studies. For selection of the best eluent, various acidic solutions on the preconcentration yields of the metals were studied under the optimum conditions. Especially, the acids with ethanol provided higher recovery efficiency compared to the acids in aqueous solutions (Table 1). Quantitative recoveries for both metals were obtained with HNO_3 in ethanol and therefore it was selected as an eluent for further applications. After the findings above, the experiments were carried out for selecting the concentration of nitric acid solution in ethanol. From Table 1, it is clear that the maximum quantitative recovery of lead and palladium was obtained with 4.0 M HNO_3 in ethanol eluent, while the minimum was obtained with 4.0 M CH_3COOH in water. Subsequent experiments indicated that 2.0 ml of the eluent solution was sufficient for the quantitative elution of metal ions and the ensuing FAAS measurement. Consequently, 2.0 ml of 4 M HNO_3 in ethanol was selected as the optimum

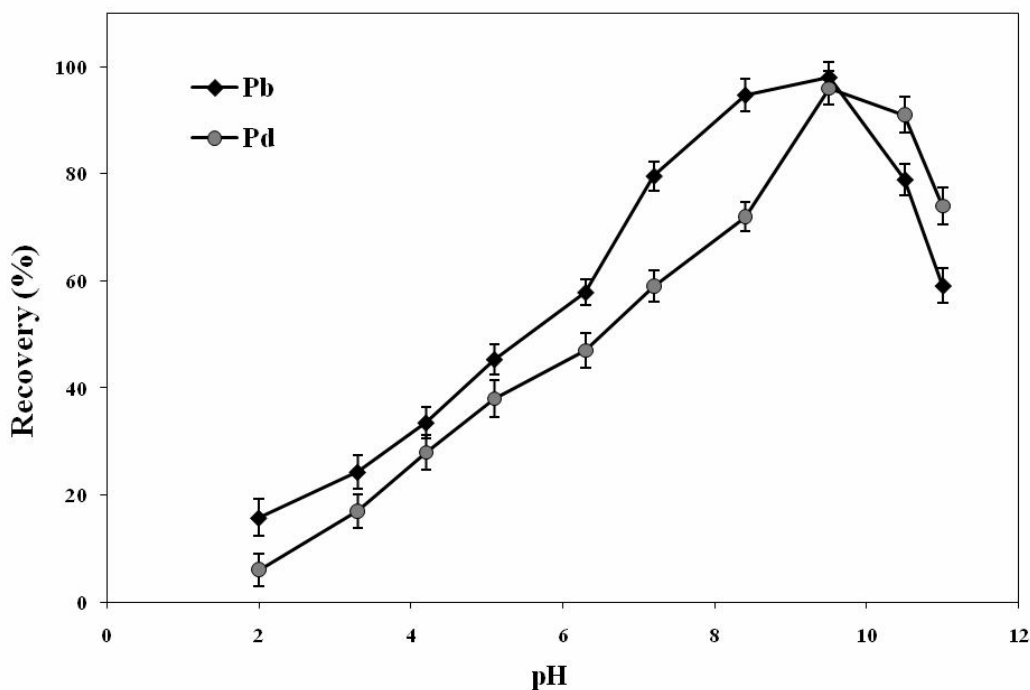


Fig. 4. Effect of the pH on adsorption of $40 \text{ ng ml}^{-1} \text{ Pb}^{2+}$ and Pd^{2+} on SNPs. Other conditions: sample volume 250 ml, sample solution flow rate 2 ml min^{-1} , HNO_3 concentration 4 M.

Table 1. Effect of the Eluting Solution (2 ml) on Lead and Palladium Recovery

Eluent	Recovery (%)	
	Pb	Pd
4.0 M CH_3COOH in water	45.7 ± 3.4	48.4 ± 3.2
4.0 M CH_3COOH in methanol	53.1 ± 3.6	56.7 ± 3.1
4.0 M CH_3COOH in ethanol	55.9 ± 2.9	58.2 ± 3.5
4.0 M HCl in water	57.7 ± 2.8	54.9 ± 2.3
4.0 M HCl in methanol	65.6 ± 2.8	63.8 ± 2.6
4.0 M HCl in ethanol	71.3 ± 3.0	68.1 ± 2.7
4.0 M HNO_3 in water	69.8 ± 2.5	71.1 ± 2.9
4.0 M HNO_3 in methanol	76.1 ± 2.2	76.4 ± 2.3
4.0 M HNO_3 in ethanol	98.7 ± 2.0	97.5 ± 1.9
3.0 M HNO_3 in ethanol	81.2 ± 1.9	94.7 ± 2.1
2.0 M HNO_3 in ethanol	66.0 ± 2.4	74.3 ± 1.8

eluting condition.

The effect of the elution flow rate was also investigated in the range of 0.3-3.0 ml min⁻¹. After 1 ml min⁻¹ of eluent solution, the recovery values of the analytes were not quantitative. For the all experiments, 0.5 ml min⁻¹ was selected as eluent flow rate.

Sample Flow Rate and Sample Volume

The retention of metal ions on the sorbent depends on the flow rate of the metal ions solution. The influence of metal ions sorption on SNPs was investigated by varying the flow rate of the sample solution in the range of 0.5-5.0 ml min⁻¹, and passing the solution through the column using a vacuum pump. The effect of the flow rate on the sorption of metal ions is shown in Fig. 5. The recoveries of the analytes decreased with increasing the flow rate more than 3.0 ml min⁻¹. Hence, a flow rate of 2.0 ml min⁻¹ was employed in this work.

Sample volume is one of the important parameters for obtaining high preconcentration factor. Therefore, the volumes of sample solution containing 4.0 µg of Pb(II), and Pd(II) were varied from 200 to 400 ml. The metals were preconcentrated on the nano-sized sulfur by applying the

proposed procedure. As shown in Fig. 6, quantitative recovery (>95%) of Pd and Pb was obtained up to 250 ml of sample solution. At volumes higher than 250 ml, because of passing excess water through the column, effectiveness of the analyte ions is not likely retained [44]. As stated previously, the final solution volume, after eluting the metal ions, was 2 ml, therefore the preconcentration factors of 125 was obtained for both analytes.

Effect of the Mass of Sorbent

The amount of solid phase extraction material is also another important factor on the column studies for the quantitative recoveries of metal chelates [50]. The effect of the amount of SNPs on the sorption of metal ions at pH 9.5 was examined in the range of 0.05-1.0 g. The results demonstrated that quantitative recoveries (>95%) of the working elements are observed when the resin used was above 0.5 g. Therefore, in the proposed procedure, 0.5 g of this sorbent was selected as the optimum value.

Adsorption Capacity

The capacity of the adsorbent is an important factor because it determines how much adsorbent is required to

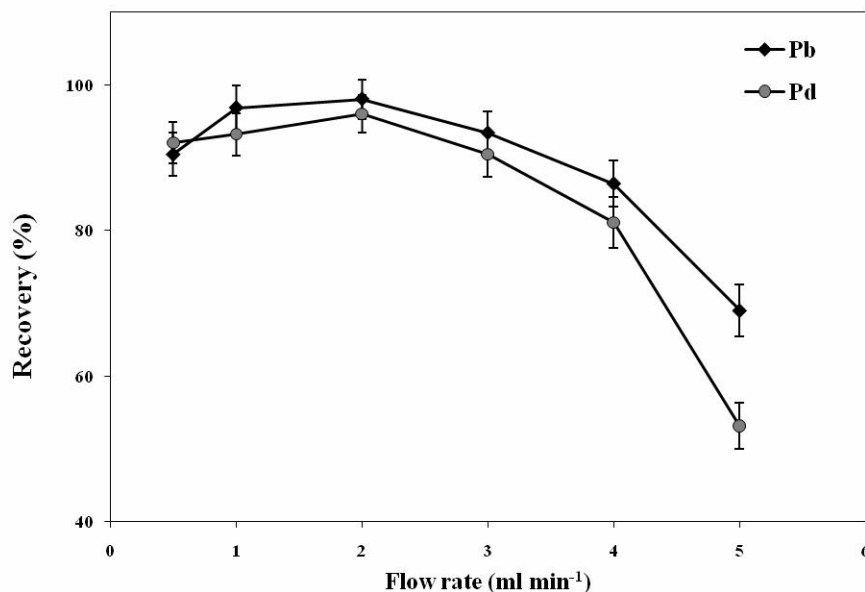


Fig. 5. Effect of the flow rate on the recoveries. Experimental conditions were the same as in Fig. 4, except the flow rate (pH, 9.5).

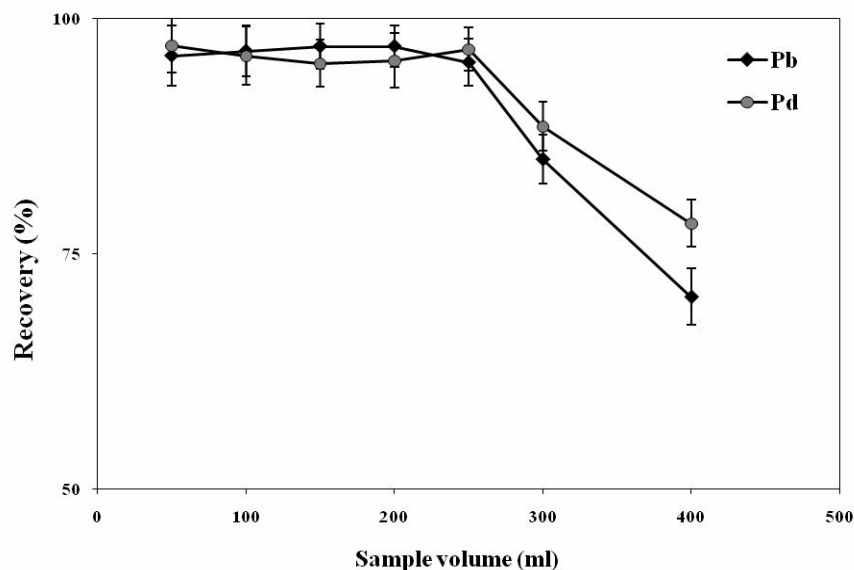


Fig. 6. Effect of the sample volume. Experimental conditions were the same as in Fig. 5, except the sample volume.

Table 2. Tolerance Limits for Coexisting Ions in Adsorption of 40 ng ml⁻¹ of Pb and Pd

Foreign ions	Tolerance limit (mg l ⁻¹)
Na ⁺ , K ⁺ , SCN ⁻	1000
NO ₃ ⁻	800
Ca ²⁺ , Mg ²⁺ , Ba ²⁺	750
F ⁻ , Br ⁻	500
CH ₃ COO ⁻ , SO ₄ ²⁻ , S ₂ O ₃ ²⁻	150
Ni ²⁺ , Cd ²⁺ , Zn ²⁺	100
Au ³⁺ , Ag ⁺	40
Fe ³⁺ , Al ³⁺ , Cu ²⁺ , Cr ³⁺ , Co ²⁺ , Sn ²⁺ , Mn ²⁺	20
Pt ⁴⁺	10

quantitatively remove a specific amount of metal ions from the solutions [51]. The loading capacity of SNPs was determined by the batch method. 1.0 g of sorbent was placed in contact with 250 ml of a 12 µg ml⁻¹ solution of metal ions for 1 h while stirring. After filtration lead and palladium in the filtrate were determined by FAAS. The loading capacity was 2.80 mg g⁻¹ for Pb and 2.87 mg g⁻¹ for Pd.

Evaluation of Interferences

The preconcentration procedures of the trace metal can

be strongly affected by other ions. For this reason, Metal cations and anions were added individually to sample solutions containing 40 ng ml⁻¹ of Pb and Pd to examine the effect of common coexisting ions on the sorption of the studied metal ions. The tolerance limit was considered if it resulted in a ±5% variation in sorption efficiency of Pb and Pd. As seen in Table 2, most of the examined cations and anions do not interfere with the extraction and determination, indicating that recovery of Pb(II) and Pd(II) is almost quantitative in the presence of foreign ions and therefore useful for the analysis of Pb and Pd in real

samples.

Characteristics of the Method

Under the optimum conditions described above, calibration curves were constructed for the determination of Pb(II) and Pd(II) ions according to the general procedure. The results summarized in Table 3 indicate that the calibration graph is linear in the range of 1-160 and 8-120 ng ml⁻¹ of lead and palladium, respectively. The limit of detection, defined as $LOD = 3 S_b/m$ (where S_b is the standard deviation of the blank and m is the slope of the calibration graph), was calculated to be 0.3 ng ml⁻¹ for Pb

and 2.5 ng ml⁻¹ for Pd. A good correlation coefficient was obtained and relative standard deviation (R.S.D.) for 10 replicate measurements of 70 ng ml⁻¹ Pb(II) and Pd(II) was 3.1 and 3.7% respectively. As the amount of Pb and Pd in the sample solution was measured after a final volume of nearly 2 ml, the solution was concentrated by a factor of 125. A comparison of the proposed system with other preconcentration procedures is given in Table 4. Some obtained parameters were comparable to those presented by other methods described in the literature. As seen from the data in Table 4, the proposed method shows comparable results in terms of preconcentration factor and sensitivity.

Table 3. Analytical Features of the Proposed Method at the Optimum Conditions

Features	Pb	Pd
Linear range (ng ml ⁻¹)	1-160	8-120
Regression equation	$A = 0.0018C + 0.0286$	$A = 0.0019C + 0.0367$
R ²	99.89	99.91
LOD (ng ml ⁻¹) (n = 10)	0.3	2.5
RSD (%) (n = 10)	3.1	3.7
Preconcentration factor	125	125

Table 4. Comparison of the Proposed Method with some Recent Studies

System	PF ^a or EF ^b	Detection	Linear range (µg l ⁻¹)		Detection limit (µg l ⁻¹)		Ref.
			Pb	Pd	Pb	Pd	
Cloud Point Extraction	39	FAAS	-	-	2.8	1.6	[52]
Coprecipitation	25	FAAS	-	-	2.6	2.1	[53]
Cloud Point Extraction	23	FAAS	18-260	20-270	2.6	2.4	[54]
Polyamine Metalfix-Chelamine Resin	35	ICP-OES ^c	0-20000	-	-	2.5	[55]
Coprecipitation	50	FAAS	-	-	0.86	-	[56]
Nanosized Sulfur Adsorbent	125	FAAS	1-160	8-120	0.30	2.5	This work

^aPreconcentration factor. ^bEnrichment factor. ^cInductively coupled plasma-optical emission spectrometry.

Table 5. Concentration of Analyte Ions in Solid Samples (N = 3)

Sample	Analyte	Added ($\mu\text{g g}^{-1}$)	Found ($\mu\text{g g}^{-1}$)	RSD (%)	Recovery (%)
Soil (1)	Pb	0	0.875	3.5	-
		0.2	1.091	3.2	101.5
	Pd	0	0.046	2.9	-
		0.2	0.242	3.1	98.8
Soil (2)	Pb	0	0.745	3.0	-
		0.2	0.968	3.3	102.4
	Pd	0	0.027	3.6	-
		0.2	0.222	3.4	97.8

Table 6. Recovery of Analytes from Spiked Samples by Using the Proposed Method (N = 3)

Sample	Analyte	Added (ng ml^{-1})	Found (ng ml^{-1})	RSD (%)	Recovery (%)
Tap water	Pb	0	ND ^a	-	-
		20	20.9	2.2	104.5
		30	30.8	3.6	102.7
		40	39.3	3.9	98.2
	Pd	0	ND ^a	-	-
		20	19.3	2.7	96.5
		30	31.1	2.5	103.7
		40	40.5	3.1	101.2
River water	Pb	0	3.3	1.8	-
		20	22.8	4.4	97.5
		30	34.6	4.2	104.3
		40	43.1	3.7	99.5
	Pd	0	ND ^a	-	-
		20	20.8	4.0	104.0
		30	29.1	3.5	97.0
		40	39.3	3.4	98.2
Wastewater	Pb	0	19.1	2.9	-
		20	40.1	2.8	102.5
		30	50.5	3.2	102.8
		40	59.7	4.2	101.0
	Pd	0	ND ^a	-	-
		20	20.8	2.8	104.0
		30	31.1	3.6	103.6
		40	41.0	3.8	102.5

^aNot detected.

The stability and potential regeneration of the column packed with SNPs were also important factors in evaluating the adsorbent and the method. It was found that the SNPs show good stability. After four repeated cycles, the average recoveries of Pb(II) and Pd(II) were $95.4 \pm 3.8\%$, and $96.0 \pm 3.5\%$, respectively.

Application of the Method

The proposed preconcentration method was applied for determination of lead and palladium in tap water and river water samples. For accuracy and reliability of the proposed method, spiking experiments and independent analysis were used. The percentage of recoveries and relative standard deviation for each element in spiked water and soil samples are given in Tables 5 and 6. A good agreement was obtained between the added and measured amounts of analyte ions. These results confirm the validity of the proposed method. The mean recoveries of Pb(II) and Pd(II) in spiked samples were found to be 96.5-104.5% with relative standard deviation below 4.4%, confirming the good accuracy of proposed method and its independence from the matrix effects.

CONCLUSIONS

In this study a new application of SNPs as the sorbent for the determination of Pb and Pd was described. The use of nano-sized sulfur as the adsorbent for lead and palladium preconcentration possessed several advantages such as simplicity, high preconcentration factor and low cost. The SNPs adsorbent showed high affinity, selectivity and good accessibility for Pb(II) and Pd(II). Furthermore, this new developed method has been successfully applied to determine the trace of Pb(II) and Pd(II) in soil and water samples with satisfactory results. The proposed procedure indicates that the nano-sized sulfur is very suitable for further development of SPE techniques.

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