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Solid phase extraction of trace amounts of palladium in environmental water samples on multi-walled carbon nanotubes as a new sorbent: comparison with activated carbon

Nahid Tavakkoli*, Saeed Habibollahi, Marzieh Keshavarzianpour

Chemistry Department, Payame Noor University, Tehran 19395-4697, Iran
Tel. +98 311 3650073; Fax: +98 311 7391500/7381002; email: Tavakkolinahid@yahoo.com

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ABSTRACT

A solid phase extraction procedure is proposed for the separation and preconcentration trace amounts of Pd (II) in aqueous medium by using a column of multi-walled carbon nanotubes (MWCNTs) modified with 1-(2-pyridylazo)-2-naphtol (PAN). The elution was carried out with 5.0 mL of 2 mol L^{-1} thiourea in 4 mol L^{-1} HCl. The amount of eluted Pd (II) was measured using flame atomic absorption spectrometry. The influences of the various experimental parameters, including pH, eluent type, concentration of eluent, amount of sorbent, and interfering ions on the recovery of palladium ions were investigated. The detection limit for palladium under the optimum condition was 1.0 ng mL^{-1} with enrichment factor of 100 and the relative standard deviation was 1.89% ($n = 6$, $C = 0.5\ \mu g\ mL^{-1}$). The method was applied for the determination of Pd (II) in water samples. The enrichment performance of the method using modified MWCNTs as preconcentration sorbent was also compared with PAN-modified activated carbon.

Keywords: Multi-walled carbon nanotubes; Palladium; Preconcentration; Flame atomic absorption spectrometry; Solid phase extraction

1. Introduction

Palladium is used in different areas of science and technology, including coating agents, brazing alloys, petroleum, electrical industries, and catalytic chemical reactions [1,2]. Thus, due to its increasing usage on one hand, and the toxicity of palladium (II) compounds to mammals, fish, and higher plants on the other hand, concerns about human health have been growing [3]. Since palladium has not the effect biological role, all palladium compounds should be regarded as of palladium on highly toxic [4]. Therefore, determination and purification of palladium in waste water could be crucial.

Even with the high sensitivity and selectivity of modern analytical techniques such as atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry, inductively coupled plasma mass spectrometry, and neutron activation analysis, a separation/preconcentration procedure is often required due to the matrix effect of foreign ions and low concentration of metal ions in the samples [5–10].

For this purpose, liquid–liquid extraction [11], co-precipitation [12,13], ion- exchange [14], and solid

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*Corresponding author.

phase extraction (SPE) [15–17] techniques have been widely used. In fact, SPE has become known as powerful tool for separation and enrichment of various inorganic and organic analytes. It has several advantages over other techniques, including stability and reusability of the solid phase, easiness of separation and enrichment under dynamic conditions, no need for organic solvents, and minimal costs due to low consumption of reagents.

Nowadays, in the SPE, the choice of materials as solid phase extractor is important. At this point, carbon nanotubes (CNTs) have been proposed as a novel solid phase extractor for various inorganic and organic materials at trace levels [18–21]. CNTs are one of the most commonly used building blocks of nanotechnology. CNTs are divided into multi-walled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes (SWCNTs) according to the carbon atom layers in the wall of the nanotubes [22–27]. MWCNTs have many applications in analytical sciences [28,29]. They have been widely used for preconcentration of organic pollutants such as phenolics and phthalate compounds [30,31], chlorobenzenes [32], chlorophenols [33], polybrominated diphenyl ethers in milk samples [34], and sulfonamides in eggs and pork [35]. MWCNTs were also applied for preconcentration of metal ions. Liang et al. have studied on the adsorption of rare earth elements [36] Cd, Ni, Mn [37], and Cu [21] on CNTs.

The purpose of this study is separation/preconcentration of palladium ion on MWCNTs modified with PAN prior to determination by FAAS. The preconcentration efficiency of modified MWCNTs was also compared with PAN-modified activated carbon (PAN-AC) as a sorbent for preconcentration of Pd (II).

2. Experimental

2.1. Instrumentation

A Philips PU 9100X flame atomic absorption spectrometer (Holland) was used for the determination of palladium. It was equipped with a hollow cathode lamp and an air-acetylene flame. The operating conditions were as follows: wavelength 247.6 nm, lamp current 15 mA, slit width 0.2 nm. The flow rates of air and acetylene were set as recommended by the manufacturer. The pH measurement was carried out using a Metrohm digital pH meter (Model 827, Switzerland) with a combined pH glass electrode calibrated against two standard buffer solutions at pH 4.0 and 7.0. The polypropylene columns (10×80 mm) were used as columns for preconcentration.

2.2. Reagents and solutions

All the chemicals were of analytical reagent grade. A standard 1,000 $\mu g\, mL^{-1}$ Pd (II) solution (Merck, Darmstadt, Germany, and No. 64271) was used. This solution was stored in a polyethylene bottle. Working standard solution of Pd (II) was prepared daily by serial dilution of the stock standard. Deionized water (Milli-Q) was used for all dilutions. The pH adjustments were made with 1 $mol\, L^{-1}$ HNO_3 or NaOH.

A 0.05% solution of PAN (Merck, Germany) was prepared by dissolving it in ethanol (Merck, Germany). MWCNTs with diameter of 110–170 nm and length of 5–9 μm were purchased from Aldrich, USA. Activated carbon (Q.P, Espanish) with 30 mesh size was used as a sorbent after modifying with PAN.

2.3. Preparation of modified MWCNTs and modified activated carbon

Raw MWCNTs were heated at 300˚C for 40 min to remove amorphous carbon. MWCNTs were oxidized with concentrated nitric acid. The treatment was carried out by dispersion of 25 mL concentrated nitric acid to 1 g of MWCNTs, and then refluxing for 6 h at 100˚C. Then the solution was filtered through a 0.45 μm membrane filter and the MWCNTs were washed with distilled water until the pH was neutral. Afterwards, 100 mL of a 0.05% solution of PAN was added to 1 g of MWCNTs and stirred for 3 h. The produced modified MWCNTs were dried at 100˚C and stored until use. The amount of PAN deposited on the MWCNTs was estimated by spectrometric measurements from the residual amount of PAN in solution. Forty grams of activated carbon was immersed in 200 mL of 1.0 $mol\, L^{-1}$ NaOH and 200 mL 0.5 $mol\, L^{-1}$ HCl for 24 h, respectively, filtered, and washed with double-distilled water until neutral, then immersed in 50 mL of ethanol for 12 h, and finally dried prior to storage. For the preparation of PAN-AC, 5 g of the above activated carbon was added to 50 mL of 0.05% (W/V) of PAN solution and the resulting mixture was stirred for 5 h, and deposited for 24 h. Then the PAN-AC was filtered, dried at room temperature prior to storage for use in the preconcentration of the Pd (II).

2.4. Preconcentration procedure

The polyethylene columns were packed with 100 mg of MWCNTs or PAN-AC and sealed from both ends with glass wool. The columns were conditioned by passing 5 mL of distilled water through it. 50 mL of an aqueous solution containing 1 $\mu g\, mL^{-1}$ palladium ion was taken and the pH was adjusted to about 2.0.

The resulting solution was passed through the column at flow rate of about 1 mL min^{-1}. After the solution passed completely, the column was rinsed with 5 mL of water. The adsorbed Pd (II) was eluted with 5 mL of 2 mol L^{-1} thiourea in 4 mol L^{-1} HCl at an elution rate of 1 mL min^{-1}. The Pd (II) concentration in the final solution was determined by flame atomic AAS.

2.5. Application to natural water samples

Tap water, river water, and waste water were collected in prewashed polyethylene bottles. The water samples were filtered through a cellulose membrane (Millipore) of 0.45 μm pore size. The pH of the samples was adjusted to 2.0 with HNO_3 solution. Then the preconcentration procedure given above was applied to the samples.

3. Results and discussion

In preliminary experiments, it was observed that the preconcentration of palladium with the MWCNTs is not suitable (70%). Recent work [34,35,38] indicated that the MWCNTs can adsorb organic materials, and therefore, since PAN is good reagent complexing with Pd (II), it was added to MWCNTs. Modified MWCNTs were capable of retaining Pd (II) in the sample solution (>90%). Thus, the adsorption of PAN on the surface of MWCNTs had an effective role in the sorption of Pd (II). In order to obtain quantitative recoveries of Pd (II) ion on modified MWCNTs, the enrichment/ separation procedure was optimized for various analytical parameters, such as pH, amount of sorbent, type and concentration of the eluent, the effect of sample volume, matrix effects, etc. The percent of metal adsorbed on nanotubes was calculated from the amount of metal ion in the starting sample and the amount of metal ion in the final solution.

3.1. Effect of pH

The pH of working solution is the main factor in the SPE for the quantitative adsorption of analytes on solid phase. In order to study the effect of pH on the recovery of Pd (II) with modified MWCNTs, the pH of 50 mL of sample solution containing 1 μg mL^{-1} palladium was adjusted in the range of 1.0–8.0. The pH was adjusted using HNO_3 or NaOH. As can be seen from Fig. 1, the percent sorption of Pd (II) depends on the pH of the sample solution and is about 98% in the pH range 1.5–3.5. Therefore, a pH of 2.0 in the middle of the pH range was considered as being the optimum value to avoid an abrupt change in adsorption which may occur due to minor changes in the pH.

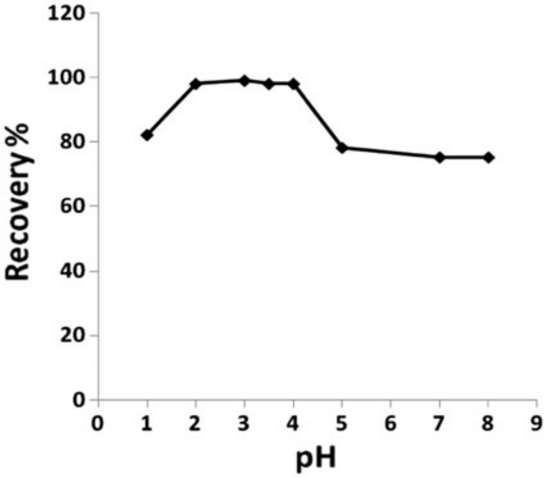

Fig. 1. Effect of initial sample pH on the percent sorption of Pd (II). Volume of sample solution: 50 mL, palladium concentration in sample solution 1 μg mL^{-1}.

3.2. Effect of the amount of MWCNTs

In the adsorption step, an appropriate amount of sorbent should be used in order to obtain quantitative retention of the metal. On the other hand, an excess amount of the sorbent also prevents the quantitative elution of the retained metal by a small volume of eluent. In order to determine the effect of amount of modified MWCNTs on the preconcentration of Pd (II), the amount of adsorbent varied in the range of 100–400 mg. The recovery values for Pd (II) were found quantitative in the adsorbent amounts of 100–200 mg. In all further studies, the column was filled with 100 mg of modified MWCNTs.

3.3. Choice of eluent

Another important factor which affects the preconcentration procedure is the type, volume, and concentration of the eluent used for the removal of metal ions from the sorbent. Optimization of the elution conditions were performed in order to obtain the maximum recovery with minimal concentration and volume of the elution solution. A series of selected eluents, such as HCl, acetone, ethanol, thiourea, thioacetamide, ethylendiamine, and HNO_3 were used and the results were compared. An aliquot of 1.0 μg mL^{-1} Pd (II) solution was passed through a series of columns containing 100 mg of sorbent at pH 2. The adsorbed palladium ion was eluted by passing through the above- mentioned selected eluents by means of 5.0 mL of each eluent in various concentrations. The amount of palladium ion hence extracted into the liquid phase by each eluent was measured to

Table 1
Effect of various eluents on the recoveries of Pd (II). (Eluent volume: 5 mL, $N = 3$)

Eluents	Recovery (%)
Ethanol	12 ± 2[a]
Acetone	18 ± 2
4 mol L^{-1} HCl	23 ± 1
4 mol L^{-1} HNO_3	10 ± 2
Thioacetamide	17 ± 2
Ethelendiamine	26 ± 1
Thiourea 0.5 mol L^{-1} + HCl 4.0 mol L^{-1}	77 ± 1
Thiourea 1.0 mol L^{-1} + HCl 4.0 mol L^{-1}	80 ± 2
Thiourea 2.0 mol L^{-1} + HCl 4.0 mol L^{-1}	97 ± 1
Thiourea 3.0 mol L^{-1} + HCl 4.0 mol L^{-1}	99 ± 2

[a] Mean ± standard.

using FAAS and the percent recoveries of Pd (II) were calculated in each case. The results given in Table 1 indicate that the highest recovery values are obtained with 5 mL of 2 mol L^{-1} thiourea in 4 mol L^{-1} HCl. Different volumes of selected eluents (1.0–7.0 mL) were tested and volume of 5 mL was the best (Fig. 2).

3.4. Effect of flow rates of sample and eluent solution

The flow rate of the sample and eluent solution is a measure of the contact time between the sample solution and the sorbent. Thus, the flow rate was adjusted simply by connecting the adsorbing column to a flask, which had a controllable vacuum. It was found that retention and recovery of the ions was independent of flow rate in a range of 0.5–1.5 mL min^{-1}. Therefore, a flow rate of 1.0 mL min^{-1} was applied for the sample and eluent solutions in all experiments.

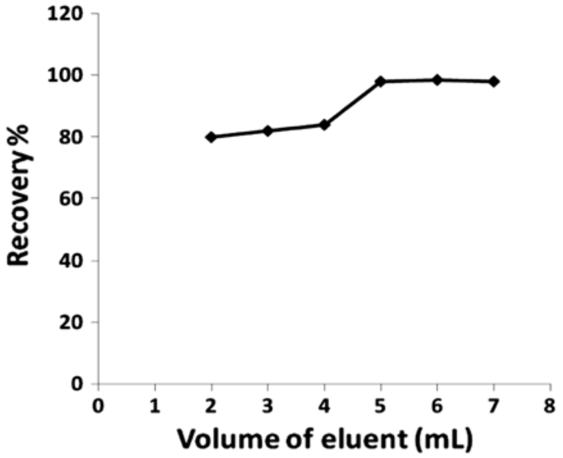

Fig. 2. Effect of the volume of eluent on the recovery of Pd (II). Volume of sample solution: 50 mL, palladium concentration in sample solution 1 μg mL^{-1}; eluent concentration 2 mol L^{-1} thiourea in 4 mol L^{-1} HCl.

3.5. Effect of sample volume

In order to explore the possibility of enriching low concentration of analytes from large volumes, the maximum applicable sample volume must be determined. For this purpose, 50–1,000 mL of sample volume were adopted to test the effect of sample volume. Sample solutions containing 1.0 μg Pd (II) at pH 2.0 were passed through the column. The results indicate that the quantitative recoveries of Pd (II) are 92.1–103.1% with 50–500 mL sample volume.

As described previously, 5.0 mL of 2.0 mol L^{-1} thiourea in 4.0 mol L^{-1} HCl is enough to elute the analyte adsorbed on the column. The preconcentration factor was calculated to be 100 as the ratio of the highest sample volume for the analyte (500 mL) and the lowest eluent volume (5.0 mL) with no decrease in recovery. This trait gives the feasibility for the determination of samples with different analytes' concentration levels.

3.6. Adsorption capacity

The adsorption capacity is an important factor because it determines how much sorbent is required to quantitatively concentrate the analytes from a given solution. 0.1 g sorbent was added to 50 mL of solution containing 1.0 mg of Pd (II) at pH 2.0. After shaking for 40 min, the mixture was filtered to study the adsorption capacity of sorbent. Ten milliliters of the supernatant solution was diluted to 100 mL and determined by flame atomic AAS. The experimental results demonstrated that the adsorption capacity of Pd (II) was 10.6 mg g^{-1} for modified MWCNTs.

3.7. Interferences

The interferences of coexisting ions binary mixtures of Pd (II) with foreign ions were studied on the percent recovery of palladium (0.5 μg mL^{-1}). After introducing the binary solution into a column, the adsorbed palladium ion was eluted by a 5.0 mL of 2.0 mol L^{-1} thiourea in 4.0 mol L^{-1} HCl solution. The content of palladium ions in effluents was determined using FAAS and the recoveries were calculated. The results summarized in Table 2 clearly indicate that most of the tested ions do not interfere with the determination of palladium.

The tolerance limit was defined as the ion concentration causing a relative error less than 5% relative

Table 2
Influence of some foreign ions on the recovery of Pd (0.5μgmL^{-1})

Ion	Concentration (μg mL^{-1})	Recovery (%)
Na^+	500	103.1
K^+	300	99.7
Ca^{2+}	400	103.1
Mg^{2+}	400	96.3
Al^{3+}	25	98.1
Fe^{3+}	25	96.3
Zn^{2+}	50	102.6
Cu^{2+}	50	94.9
Co^{2+}	50	102.1
Cl^-	500	103.1
Pt^{4+}	50	95.2
Au^{3+}	50	96.7

Table 3
Analytical results for the determination of Pd in water samples

Samples	Concentration (μgmL^{-1})		
	Pd (II) added	Founded[a]	Recovery (%)
River water	0	nd[b]	
	0.5	0.53 ± 0.03	101
Tap water	0	nd	
	0.5	0.47 ± 0.02	94
Waste water	0	4.52 ± 0.08	
	1.0	5.48 ± 0.09	96

[a] Mean ± standard deviation ($n = 3$); [b] Non detected.

to the preconcentration and determination of the analytes.

3.8. Analytical performance

The detection limit (DL) of the presented SPE study was calculated under optimum conditions after the application of the preconcentration procedure to blank solutions. The DL defined as the concentration equivalent to three times the standard deviations of nine runs of the blank to the slope of plot was 1.0 ngmL^{-1}. The recommended procedure was repeated six times to find the relative standard deviation (RSD) in the determination of 0.5 μg mL^{-1} of Pd (II) ion. The RSD was found to be 1.89%.

The calibration curve was obtained using the general procedure and it was found to be linear in the range of 0.1–2 μgmL^{-1} of palladium in the initial solution. The regression equation for Pd was $A = 0.2499\ C—4.9 \times 10^{-3}$ with $r^2 = 0.999$, where C is the concentration of metal ion in the initial solution and A is the absorbance value of the eluent.

3.9. Analytical application

The method was applied for the determination of Pd (II) in river water (Zayande-rood River, Isfahan, Iran), tap water, and waste water samples. Various amounts of palladium ions were also spiked in these water samples. The results are given in Table 3. A good agreement was obtained between the added and measured analyte amounts. These results confirm the validity of the proposed method. The results indicated that the recoveries were reasonable for the determination of Pd (II) in a range of 94–105%.

3.10. Comparing the enrichment efficiency of modified MWCNTs with modified activated carbon

For the purpose of comparison, modified MWCNTs and PAN-AC were used separately for the preconcentration of Pd (II) ion. In preliminary experiments, it was observed that the preconcentration of Pd (II) ion with untreated AC is not suitable (10%). Therefore, PAN-AC seems to be a better sorbent in sorption of Pd (II). Optimization of the various experimental parameters gave similar procedures that are described in sections 3.1–3.4. Based on the experi-

Table 4
Comparison of the present sorbents for preconcentration and determination of palladium ion

Sorbent	Preconcentration factor	Detection limit, ng mL^{-1}	Ref.
Fullerene C60	66.5	0.04	[39]
Exfoliated graphite	80	1.0	[40]
Silica gel	75	1.2	[41]
Nanoparticles of Alumina Functionalized with pyridine groups	60	0.6	[42]
Present work	100	1.0	

mental results, the optimal parameters were determined as the same as that of modified MWCNTs. Under the optimum condition, the best recovery of Pd (II) on PAN-AC was achieved to about 70% at pH 2. The enrichment performance of Pd (II) with modified MWCNTs was excellent relative to PAN-AC. Due to the highest recoveries achieved with modified MWCNTs sorbent at pH 2.0, this sorbent was selected for the subsequent optimization of the preconcentration SPE procedure of Pd (II).

4. Conclusion

The present study demonstrates the use of a sorbent based on the modification of MWCNTs with PAN. The modification of MWCNTs is simple and low cost. The procedure offers a useful, simple, and rapid enrichment technique for preconcentration of trace palladium in real samples with acceptable accuracy and precision. Also, the preconcentration factor of the sorbent is found to be higher than some of the other sorbents (Table 4). The preconcentration efficiency of the modified MWCNTs was compared with the modified AC sorbent at pH 2. The PAN-AC sorbent did not give satisfactory percentage recovery.

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