

## Pyridine-Functionalized TiO<sub>2</sub> Nanoparticles as a Sorbent for Preconcentration and Determination of Ultra-Trace Palladium Ions

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### ABSTRACT

In this work, TiO<sub>2</sub> nano-particles were modified by pyridine group and characterized by scanning electron microscopy (SEM), X-Ray diffraction (XRD), FT-IR and elemental analysis (CHN). This sorbent was applied for pre-concentration of ultra-trace amount of palladium prior to its determination by flame atomic adsorption spectroscopy (FAAS). Through this study, different factors such as sample pH, sample flow rate, eluent parameters (type, concentration and volume), and eluent flow rate were optimized. Also effects of the selectivity of sorbent toward Pd(II) was investigated by palladium determination in presence of various interfering ions. The limit of detection was 3.8 ng mL<sup>-1</sup> and recovery was 99.1 % with a relative standard deviation of 2.5%. Finally the method was validated using standard reference material which their palladium concentrations are certified.

**Key words:** Palladium determination; Pyridine-functionalized TiO<sub>2</sub> nanoparticles; solid phase extraction; Flame atomic absorption spectrometry.

### INTRODUCTION

Increasing demand for noble metals, particularly platinum group metals (PGM), such as palladium(II), platinum(IV), ruthenium(III), rhodium(III) has been recently observed because of their wide range of industrial applications, e.g. as catalysts in organic processes, value added components in metal alloys and vehicle catalytic converter systems, in chemical, pharmaceutical, petroleum and electronic industries and also in jewellery making.

These applications of PGMs have increased the demand for these metals, whereas the natural resources are limited<sup>1-3</sup>.

Flame atomic absorption spectrometry (FAAS) is one of the most popular techniques for determination of metal ions because of its high

specificity and low cost. However its sensitivity is usually insufficient for determination of trace metal ions in environmental samples. In order to overcome this problem and prevent interference effects, those who use this method usually include an efficient preconcentration step<sup>4-5</sup>.

Solid-phase extraction (SPE) is one of the most common methods for preconcentration of noble metals. It has the advantages of flexibility, economical and environmental-friendly, simplicity, and being fast and safe.<sup>5</sup> Since the key point in SPE is choosing adsorbent, several SPE methods based on sorbents such as different polymers<sup>7</sup>, silica<sup>8</sup> and Fe<sub>3</sub>O<sub>4</sub><sup>9</sup> have been developed. Compared to the other sorbents TiO<sub>2</sub> has attracted more attention due to its high surface area<sup>10-12</sup>.

In this work, a novel sorbent based on functionalization of TiO<sub>2</sub> nano-particles by pyridine

group is constructed. This sorbent was applied for preconcentration of Pd(II) ions in aqueous samples after characterization by FT-IR, XRD pattern, elemental analysis and SEM micrograph.

## EXPERIMENTAL

### Reagents and Materials

The standard solution of Pd(II), 1000 mg L<sup>-1</sup>, was purchased from Aldrich Company (Milwaukee, WI, USA). TiO<sub>2</sub> nano-particles with 10-15 nm in diameter were purchased from Neunano Company (Tehran, Iran). All reagents includes solvents, acids, 3-aminopropyltriethoxysilane, triethylamine, dichloromethane, oxalyl chloride and 4-pyridine carboxylic acid were of analytical grade and purchased from Merck Company (Darmstadt, Germany). The standard reference material (NIST SRM 2557) was purchased from National Institute of Standards.

### Apparatus

The atomic absorption spectrometer (AAS) used in this experiment was a Shimadzu AA-680 equipped with a single element hollow cathode lamp (6.0 mA for palladium). Burner head was 50 mm and air acetylene burner head was used during the experiment. Resonance line for palladium is 244.8 nm, so the wavelength was set at this value. The spectral band width was set at 0.5 nm and the ratio of air-acetylene was set at 4.7. The pH was measured at 25 ± 1 °C with a digital WTW Metrohm 827 Ion analyzer (Herisau, Switzerland) equipped with a combined glass-calomel electrode. The Fourier Transform Infrared (FT-IR) spectrum was recorded on a BOMEM MB-Series FT-IR spectrometer in the form of KBr pellets. The elemental analyses (CHNS) were performed on a Thermo Finnigan Flash-2000 microanalyzer (Italy). The SEM micrograph was recorded by a Vega-TeScan scanning electron microscope.

### Preparation of Pyridine functionalizing agent

Pyridine functionalizing agent was synthesized according to earlier report<sup>12</sup> and characterized by <sup>1</sup>H NMR. Briefly, 1.0 g of 4-pyridine carboxylic acid was suspended in 100 mL of dried CH<sub>2</sub>Cl<sub>2</sub> under nitrogen atmosphere and 10 mL of oxalyl chloride was slowly added to the mixture and was stirred for 12 h. Then CH<sub>2</sub>Cl<sub>2</sub> was removed

under reduced pressure, and the residue was suspended again in 100 mL of dried CH<sub>2</sub>Cl<sub>2</sub>. After addition of 17 mL triethylamine to reaction mixture, 4.0 g 3-aminopropyltrimethoxysilane was slowly added. The reaction mixture was stirred at room temperature for further 4 h. Then the solvent was removed under reduced pressure to obtain brownish viscose oil.

### Preparation of pyridine functionalized TiO<sub>2</sub> nano-particles

In a typical reaction, 1.0 g TiO<sub>2</sub> nano-particles were suspended in 50 mL toluene, and 2 mL pyridine functionalization agent was added and the mixture was refluxed for 24 h under nitrogen atmosphere. Then the solid was collected by filtration and washed with methanol and acetone and then dried at room temperature. Formation of pyridine functionalized TiO<sub>2</sub> nano-particles (Py-TiO<sub>2</sub> NPs) was confirmed by FT-IR spectroscopy, XRD pattern, elemental analyses and SEM micrograph.

### Column preparation

A glass column, 120 mm in length and 20 mm in diameter, was blocked by polypropylene filters at the ends, filled with 200 mg of the Py-TiO<sub>2</sub> nano-particles, and then used for the experiments. Before extraction, the column was treated with 5 mL hydrochloric acid (1 M), 5 mL nitric acid (1 M), 5 mL toluene, 5 mL ethanol and 20 mL distilled water to remove organic and inorganic contaminants.

### Preconcentration procedure

A solution containing 1 µg mL<sup>-1</sup> of palladium with pH=7.0 was prepared. The pH was adjusted with Na<sub>2</sub>HPO<sub>4</sub>/NaH<sub>2</sub>PO<sub>4</sub> buffer solution and then 50 mL of solution was passed through the column at a flow rate of 8 mL min<sup>-1</sup>. The column was eluted by 12 mL of 1 mol L<sup>-1</sup> thiourea in 0.1 mol L<sup>-1</sup> HCl solution, then the eluent was analyzed by FAAS.

### Standard reference materials pretreatment

Auto-catalyst NIST SRM 2557 of 0.1000 g were mixed with about 5.0 mL aqua regia and 1.0 mL HF (48–51%, v/v) in a Teflon vessel, and heated until the sample was completely decomposed. Then the solutions were evaporated in a water bath. The residues were dissolved with 0.05 mol L<sup>-1</sup> HCl and diluted to the appropriate volume with distilled water<sup>13</sup>.

## RESULTS AND DISCUSSION

### Sorbent Characterization

Modification of TiO<sub>2</sub> nano-particles have been performed according to previous report<sup>14</sup>. Reaction of pyridine functionalizing agent with active hydroxyl group on the surface of TiO<sub>2</sub> leads to formation of this sorbent (Fig. 1). Formation of this sorbent was confirmed by FT-IR spectroscopy, XRD pattern, elemental analyses and SEM micrograph. The presence of peaks at 3027 (CH, aromatic), 2953 (CH, aliphatic), 1561&1470 (C=C, aromatic) and 1402 (C=N) in IR spectrum confirm presence of pyridine in this sorbent. Also the amount of grafted pyridine was calculated by elemental analysis. According to the elemental analysis results (%C= 6.74, %H= 0.69, %N= 1.73), approximately 0.61 mmol pyridine is grafted on each gram of TiO<sub>2</sub> nano-particles. In order to confirm remaining TiO<sub>2</sub> nano-particles unchanged after functionalization (no decomposition or converting to the other oxides), XRD pattern of final product was recorded. Comparing to reference pattern (JCPDS file, No. 86-0147), the results show the TiO<sub>2</sub> nanoparticles structure has not been changed after functionalization (Fig. 2). Finally in order to

investigate the size and morphology of this sorbent, SEM micrograph of Py-TiO<sub>2</sub> nano-particles was recorded. As it can be seen in Fig. 3, spherical nanoparticles with approximately 15-20 nm in diameter were obtained.

### Optimization studies

#### Influence of pH

In order to study the effect of pH on the Pd(II) extraction, the pH of 50 mL of different sample solutions containing 1 mg L<sup>-1</sup> palladium were adjusted in the range of 2-9. The samples were passed through the column at a flow rate of 8 mL min<sup>-1</sup>. Then the column was eluted by 12 mL of 1 mol L<sup>-1</sup> thiourea in 0.1 mol L<sup>-1</sup> HCl solution and the Pd(II) content in eluent was analyzed by FAAS. As the results in Fig. 4 show, the highest palladium recovery is at pH=7.0. The best recovery at neutral pH may be attributed to the presence of free lone pair of electrons on the nitrogen atoms which are suitable donors for coordination to the palladium ions.

#### Effect of type, concentration and volume of eluent

Different eluent solutions including different HCl solutions and their mixture with

**Table 1: The effect of diverse ions on recovery of palladium(II) on Py-TiO<sub>2</sub> nano-particles**

Interfering ion	Concentration( $\mu\text{g mL}^{-1}$ )	Recovery(%)
Na <sup>+</sup>	1000	98.3
K <sup>+</sup>	1000	98.9
Cs <sup>+</sup>	1000	98.6
Ca <sup>2+</sup>	1000	98.1
Mg <sup>2+</sup>	1000	98.3
Fe <sup>2+</sup>	250	96.4
Pb <sup>2+</sup>	100	91.8
Mn <sup>2+</sup>	250	95.7
Cd <sup>2+</sup>	100	92.3
Cr <sup>3+</sup>	250	96.1

**Table 2: The analysis of standard reference materials (NIST SRM 2557)**

Sample Name	Certified value ( $\text{ng g}^{-1}$ )	Obtained value ( $\text{ng g}^{-1}$ )	Recovery (%)	RSD (%) (n=10)
NIST SRM 2557	239.8	235.9	98.3	3.2

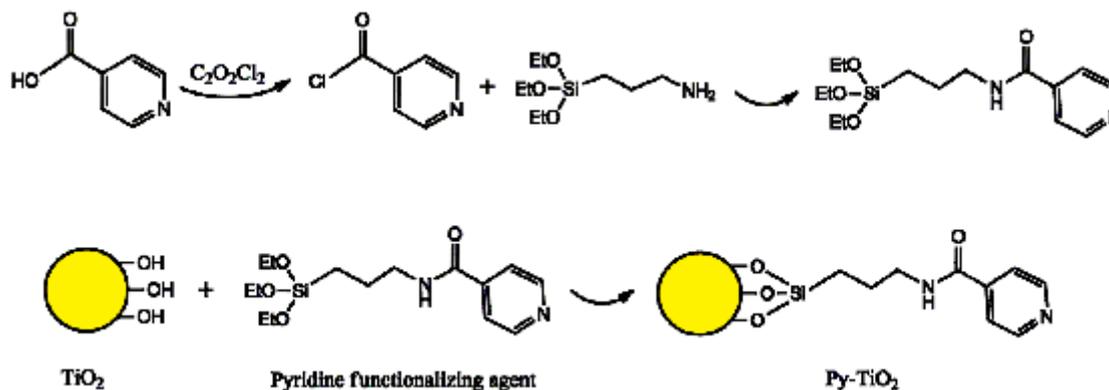


Fig. 1: A schematic diagram for synthesis of pyridine functionalized  $\text{TiO}_2$  nanoparticles

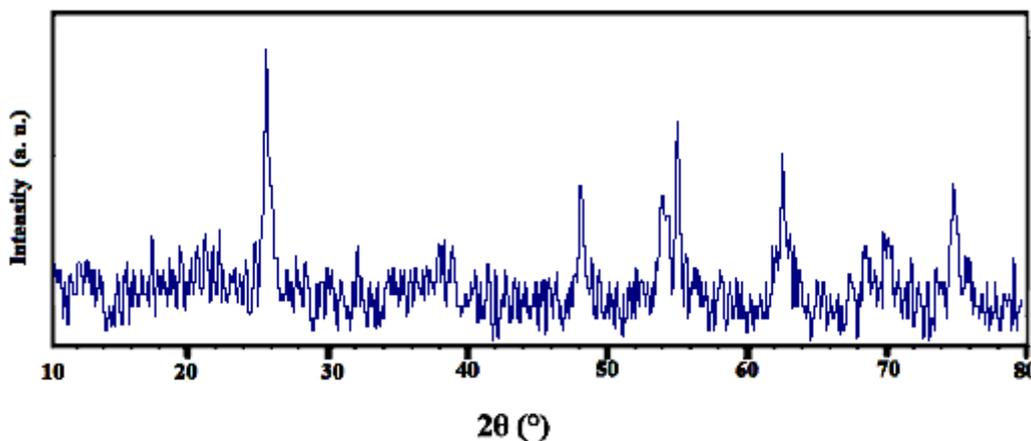


Fig. 2: The XRD pattern of pyridine functionalized  $\text{TiO}_2$  nanoparticles

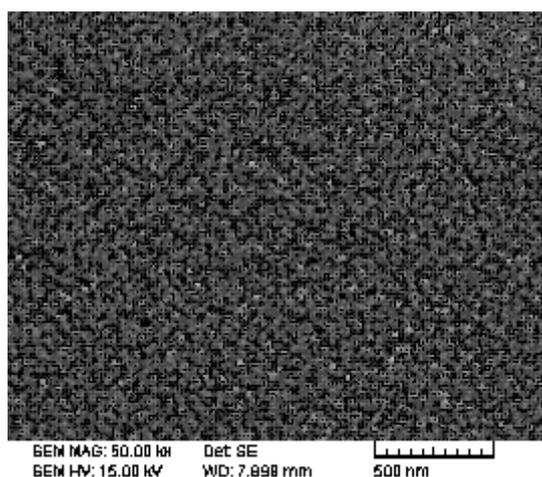


Fig. 3: SEM micrograph of pyridine functionalized  $\text{TiO}_2$  nanoparticles

thiourea with different concentrations were used for desorption of palladium from Py- $\text{TiO}_2$  nanoparticles. In this approach, a solution containing  $1 \mu\text{g mL}^{-1}$  of palladium with  $\text{pH}=7.0$  was passed through the column at a flow rate of  $8 \text{ mL min}^{-1}$ . Then the adsorbed ions were desorbed by 20 mL of each eluent. Then the palladium content in each eluent was analyzed by FAAS. According to these results the best eluent is a solution of  $1 \text{ mol L}^{-1}$  thiourea in  $0.1 \text{ mol L}^{-1}$  HCl. Moreover in order to study the effect of eluent volume, different volume of  $1 \text{ mol L}^{-1}$  thiourea in  $0.1 \text{ mol L}^{-1}$  HCl solution (2, 4, 6, 8, 10, 12, 14, 16 and 18 mL) was used for palladium desorption. The results show that at least 12 mL of this eluent is needed for complete palladium desorption from the column.

**Sample and eluent flow rates**

In order to study sample and eluent flow rates, the pH of 100 mL of 1  $\mu\text{g mL}^{-1}$  palladium (II) solution was adjusted to 7 and the solution was passed through the column with different flow rates in the range of 1-10  $\text{mL min}^{-1}$  using a peristaltic pump. As Fig. 5 show, the maximum flow rate for complete adsorption is 8  $\text{mL min}^{-1}$ . Also same experiments were performed by different eluent

flow rates. As it is shown in Fig. 5, at the flow rates more than 2  $\text{mL min}^{-1}$ , the Pd(II) desorption will be decrease. So in the further experiments, 8 and 2  $\text{mL min}^{-1}$  were chosen as optimum sample and eluent flow rates, respectively.

**Influence of interference ions**

To investigate the selectivity of the sorbent, the effect of different cations such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$ ,

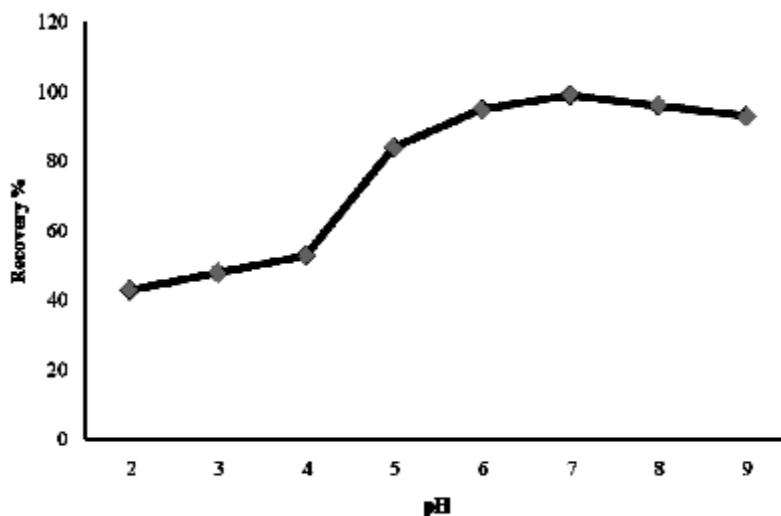


Fig. 4: The effect of pH on adsorption of palladium on pyridine functionalized  $\text{TiO}_2$  nanoparticles

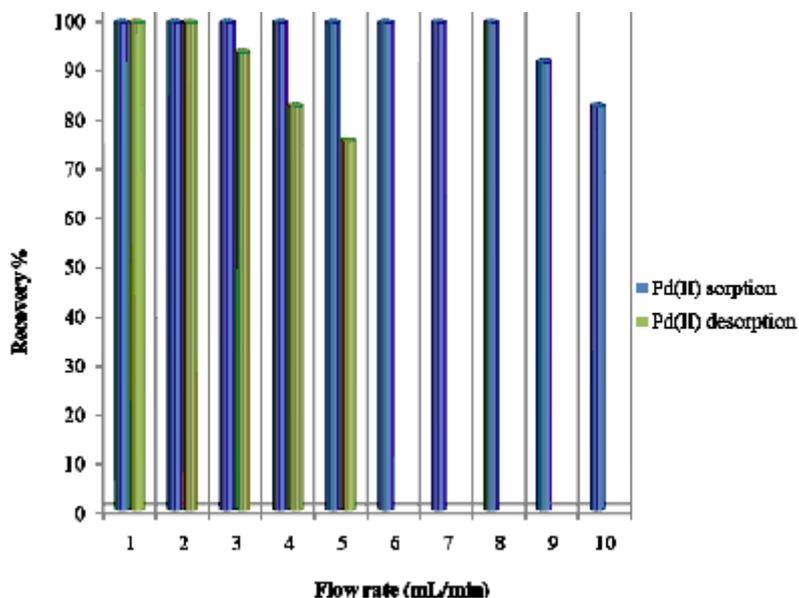


Fig. 5: Investigation of adsorption and desorption time of palladium on pyridine functionalized  $\text{TiO}_2$  nanoparticles

Mg<sup>2+</sup>, Ca<sup>2+</sup>, Fe<sup>2+</sup>, Pb<sup>2+</sup>, Mn<sup>2+</sup>, Cd<sup>2+</sup> and Cr<sup>3+</sup> in the Pd(II) determination was studied. The cations of as their chloride salts with various concentrations were added to a 100 mL of single solution containing 1 µg mL<sup>-1</sup> palladium (II) and the extraction procedure was followed. As can be seen from Table 1, a good selectivity for palladium extraction was observed in pH=7.0 and this sorbent could be used as a selective Pd(II) extractor in natural samples with diverse interfere ions.

#### Maximum adsorption capacity

In order to determine the maximum adsorption capacity of this sorbent, 500 mL of a solution containing 100 mg palladium was treated with the extraction procedure and the maximum capacity was calculated by analyzing the adsorbed palladium in eluent. The maximum adsorption capacity for three replicates was found to be 61 mg g<sup>-1</sup> (0.57 mmol g<sup>-1</sup>).

#### Analytical performance

In order to determine the detection limit (DL) of the presented method, 500 mL of ten blank solutions were passed through the column under the optimal conditions. The LOD values of 3.8 ng

mL<sup>-1</sup> was obtained for palladium with Py-TiO<sub>2</sub> nanoparticles from  $C_{LOD} = K_b S_b / m$  using a numerical factor of  $k_b = 3$ . The analytical values of the proposed method were calculated from the data obtained under the optimum conditions. The recovery of the extraction of palladium ion on Py-TiO<sub>2</sub> was determined to be 99.1 % with a relative standard deviation of 2.5 % for ten replicated analysis.

#### Method validation

The method validation was done by analyzing a standard reference material. NIST SRM 2557 was analyzed by this method and the results of this study are presented in Table 2. The obtained results were in a good agreement with the certified value of the standard reference material.

#### CONCLUSION

The proposed solid phase extraction procedure based on TiO<sub>2</sub> functionalized with pyridine group shows a good selectivity for preconcentration and determination of palladium ions in trace levels. The low detection limit, palladium at trace level can be determined by this rapid and selective proposed method.

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