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Determination of Rhodium(III) Ions by Flame Atomic Absorption Spectrometry after Preconcentration with Modified Magnetic Activated Carbon

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A new method for analysis of trace amount of Rh(III) ions by magnetic activated carbon modified with 2,3,5,6-tetra(2-pyridyl)pyrazine (MAC/TPPZ) as the magnetic sorbent has been proposed. The proposed adsorbent was found to be advantageous over conventional solid phase extraction (SPE) in terms of operational simplicity and low time-consuming. The experimental parameters affecting the extraction/preconcentration and determination of the analyte were systematically examined. In order to investigate the selectivity of this magnetic sorbent, the effect of a variety of ions on preconcentration and recovery of Rh(III) ions were also investigated. Under optimum conditions, the calibration graph was linear for the concentration range of 0.8-650 $\mu\text{g l}^{-1}$. The limit of detection (LOD, $3S_b/m$) and the relative standard deviation (RSD, $n = 8$, $c = 50 \mu\text{g l}^{-1}$) were 0.1 $\mu\text{g l}^{-1}$ and 3.6%, respectively. The maximum sorption capacity of the adsorbent for rhodium was found to be 21.6 mg g^{-1} . The presented procedure was applied to monitoring rhodium in water and synthetic samples.

Keywords: Spectrometry, Magnetic activated carbon, Rhodium, Nanocomposite

INTRODUCTION

In recent years, pollution of the environment by various harmful heavy metal ions has attracted great attention [1,2]. Rhodium metal is known for its stability in corrosive environments, physical beauty and unique physical and chemical properties [3]. The determination of rhodium has been reported by means of a wide range of spectrometric methods such as inductively coupled plasma atomic-emission spectrometry (ICP-AES) [4], graphite furnace atomic absorption spectrometry (GF-AAS)[5], inductively coupled plasma-mass spectrometry (ICP-MS) [6] and flame atomic absorption spectrometry (FAAS) [7] because of the relatively simple and inexpensive equipment required [8]. However, it is difficult to determine directly the extremely low concentration of rhodium in the presence of a relatively

high concentration of other diverse ions. Hence, separation and preconcentration methods have been routinely used to eliminate matrix effects. Currently, the widely used techniques for preconcentration and separation of trace amount of rhodium include dispersive liquid-liquid microextraction (DLLME) [9], cloud point extraction (CPE) [3], liquid-liquid extraction (LLE) [10] and solid phase extraction (SPE) [11]. Recently, solid phase extraction technique has become increasingly important because it offers many practical and operating advantages over other preconcentration methods such as higher preconcentration factor, simple operation, rapid phase separation, lower cost and less time, and the ability of combination with different detection techniques in the form of on-line or off-line mode [12-15]. In SPE procedure, the choice of an appropriate adsorbent is a critical factor to obtain full recovery and high enrichment factor [16-18]. To date, many sorbents such as activated carbon [19], nanometer-sized materials [20-22], ion exchange resin [23] and modified silica gel [24] have

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been employed in SPE. Activated carbon (AC) is one of the most extensive adsorbents for the removal of metal ions from aqueous solution due to its high surface area and porosity, high adsorption capacity, negligible environmental toxicity, low cost, selective adsorption and high purity standards [25]. In order to improve the selectivity and adsorption capacity, activated carbon is normally modified by attaching organic and inorganic compounds comprising heteroatoms such as oxygen, nitrogen, sulfur and phosphorus to their surface [26].

As a particular kind of nanometer-sized materials, magnetic nanoparticles have magnetic property beside the general characteristics of nanometer-sized materials and have obtained extensive applications in bio-separation cell labeling, drug delivery, magnetic resonance imaging (MRI) during the past few years. Recently, there have been some developments in the SPE method, based on modifications to the sorbent materials using magnetic particles leading to the so-called magnetic solid phase extraction process (MSPE) [27]. The MSPE methodology shows excellent extraction efficiency and rapid separation from the crude sample matrix by an external magnetic field. The magnetic adsorbent does not need to be packed into the cartridge when using dynamic extraction mode, and no centrifugation or filtration of the sample is required after extraction when the static batch mode is applied [28]. Their separation and concentration are easier, more convenient and faster than conventional SPE methods. For example, Sun *et al.* reported a magnetic graphene oxide nanocomposite being successfully used for determination of trace cobalt(II), nickel(II), copper(II), cadmium(II) and lead(II) in biological samples [29].

Herein, magnetic activated carbon nanocomposite (MAC) based on activated carbon/ γ -Fe₂O₃ was prepared by a coprecipitation method. Since the prepared MAC nanocomposite was not selective and not suitable for samples with complicated matrices, it was modified by 2,3,5,6-tetra(2-pyridyl)pyrazine (TPPZ). The novel synthesized sorbent is highly selective for separation of Rh(III) ions, and it has a good adsorption capacity under the optimized experimental conditions. To the best of our knowledge, this methodology has not been employed yet for the separation and determination of trace levels of rhodium

from aqueous samples.

EXPERIMENTAL

Apparatus

A Varian Spectra AA 220 atomic absorption spectrometer (Varian, Melbourne, Australia) was used for the measuring of Rh(III) in an air-acetylene flame. FT-IR spectra were recorded with a Tensor-27 spectrometer (Bruker, Ettlingen, Germany). The morphology of the synthesized composites was analyzed with a field emission scanning electron microscope (FE-SEM, CARL ZEISS-AURIGA 60 microscope, Jena, Germany). All pH values were measured with a Metrohm digital pH-meter model 827 (Herisau, Switzerland). The magnetic property was analyzed by using a vibrating sample magnetometer (VSM) (Meghnatis Daghigh Kavir Co., Kashan, Iran). X-ray diffraction (XRD) patterns of AC and MAC nanocomposite were obtained on a powder X-ray diffraction system from PANalytical model X'Pert PRO (PANalytical B.V., Almelo, The Netherlands). The magnetic separation was performed by a super magnet with 7,000 Gsmagnetic field (Nd-Fe-B, 10 × 5 × 4 cm). An ultrasonic bath at 35 kHz (Model Sonorex Digitec DT 255 H, Singen, Germany) was used to disperse the adsorbent in sample solutions. Ultra-pure water was obtained from a Milli-Q water purification system (Millipore Corporation, Milford, MA, USA).

Reagents and Materials

Reagents of analytical and spectral purity were used for all experiments. A stock solution of Rh(III) (1000 mg l⁻¹), ferrous chloride tetrahydrate (FeCl₂·4H₂O; 98%), ferric chloride hexahydrate (FeCl₃·6H₂O; 99%) and AC were purchased from Merck (Darmstadt, Germany). Reagent grade TPPZ, from Sigma-Aldrich (St. Louis, MO, USA), was used as chelating agent. Buffer solutions were prepared from 0.5 M acetic acid and 0.5 M sodium acetate for pH 3.0-6.0.

Preparation of MAC/TPPZ Nanocomposite

To remove adsorbed impurities, AC powder soaked in 10% (v/v) hydrochloric acid solution for 2 days and then washed with water and dried in an oven at a temperature of 110 °C for 24 h. The pretreating step was used to modify the

AC with carboxyl functional groups. For this purpose, 10 g of purified activated carbon reacted with 100 ml 5 M nitric acid solution and refluxed for 5 h at 70 °C to achieve oxidized AC. The mixture was filtered and washed with deionized water and dried at 70 °C overnight.

MAC nanocomposite was synthesized by coprecipitation method. In brief, 4.2 g of oxidized AC, 21.6 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (99%) and 8.0 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (98%) were dissolved in 100 ml of 2 M HCl (37%). Then, $\text{NH}_3 \cdot \text{H}_2\text{O}$ (25-30%) solution (4 M) was added dropwise to this solution (250 ml) under vigorous stirring at room temperature for 2 h. The resultant product was collected by filtration, followed by repeated washing with deionized water and absolute ethanol (99.9%), and then dried at 70 °C for 24 h.

TPPZ loaded MAC was prepared by dissolving 0.1 g of TPPZ in 200 ml of methanol/acetonitrile (30/60 ml) under stirring; then 2.00 g of MAC nanocomposite was added to the mixture. The mixture was stirred at room temperature for 24 h. The resulting solid phase was separated using a magnet, washed with highly purified and then dried at 70 °C overnight.

Magnetic Solid-phase Extraction Procedure

Figure 1 shows the extraction procedure for MSPE of rhodium using MAC/TPPZ sorbent. Firstly, 100 ml aqueous sample solution containing analyte ions was transferred to a 250 ml Erlenmeyer flask; pH value was adjusted to 4.0 with acetate buffer. Secondly, the solution was ultrasonicated for 3 min to facilitate adsorption of the Rh(III) onto the nanocomposite, and then the sorbent isolated from the suspension with a Nd-Fe-B strong magnet and the clear supernatant was directly decanted. Thirdly, the adsorbed analytes were desorbed from the isolated adsorbent with 2

ml of 0.1 M thiourea/0.1 M HCl by ultrasonication for 3 min. Finally, the magnet was used again to settle the magnetic nanocomposite and the eluent was introduced into FAAS for subsequent determination.

Sample Preparation

Water samples were collected from two primary sources: (1) well water (Shahid Bahonar University of Kerman, Kerman, Iran) and (2) aqueduct water (Sirjan, Kerman, Iran). The only pretreatment was acidification to pH 2 with nitric acid, performed immediately after collection, to prevent adsorption of the metal ions on the flask walls. These samples were filtered through a 0.45 μm pore size filter (Millipore Corporation, Bedford, MA, USA) to remove suspended particulate matters, stored at 4 °C in a refrigerator and the proposed method was applied for the determination of rhodium(III) ions.

The rhodium content in the synthetic sample was determined for accuracy evaluation. An aliquot of the synthetic sample (Composition: K(I) = 100.0, Mg = 100.0, Cd = 75.0, Pd = 75.0, Pb = 50.0, Mn = 50.0, Cr = 50.0, Fe = 50.0 and Rh = 20.0 $\mu\text{g l}^{-1}$) was applied to the determination of Rh(III) ions. The samples analyzed in this work were digested in triplicate.

To verify the validity of the proposed procedure, this method was applied for the determination of the content of rhodium in a platinum-iridium alloy (Composition: Pt = 55, Ir = 28, Cu = 3.0, Fe = 3.5, Pd = 3.5, Rh = 7%). For doing so, 7 ml of aqua regia was added to 5.0 mg of the alloy and the solution was evaporated. Then, 5 milliliters of concentrated hydrochloric acid was added, and the solution was warmed, transferred to a 100 ml volumetric flask, and made up to mark with distilled water. An aliquot of this

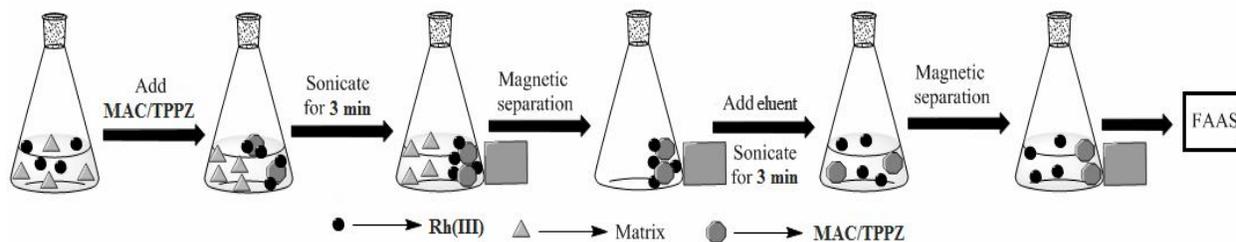


Fig. 1. Schematic illustration of the MSPE procedure.

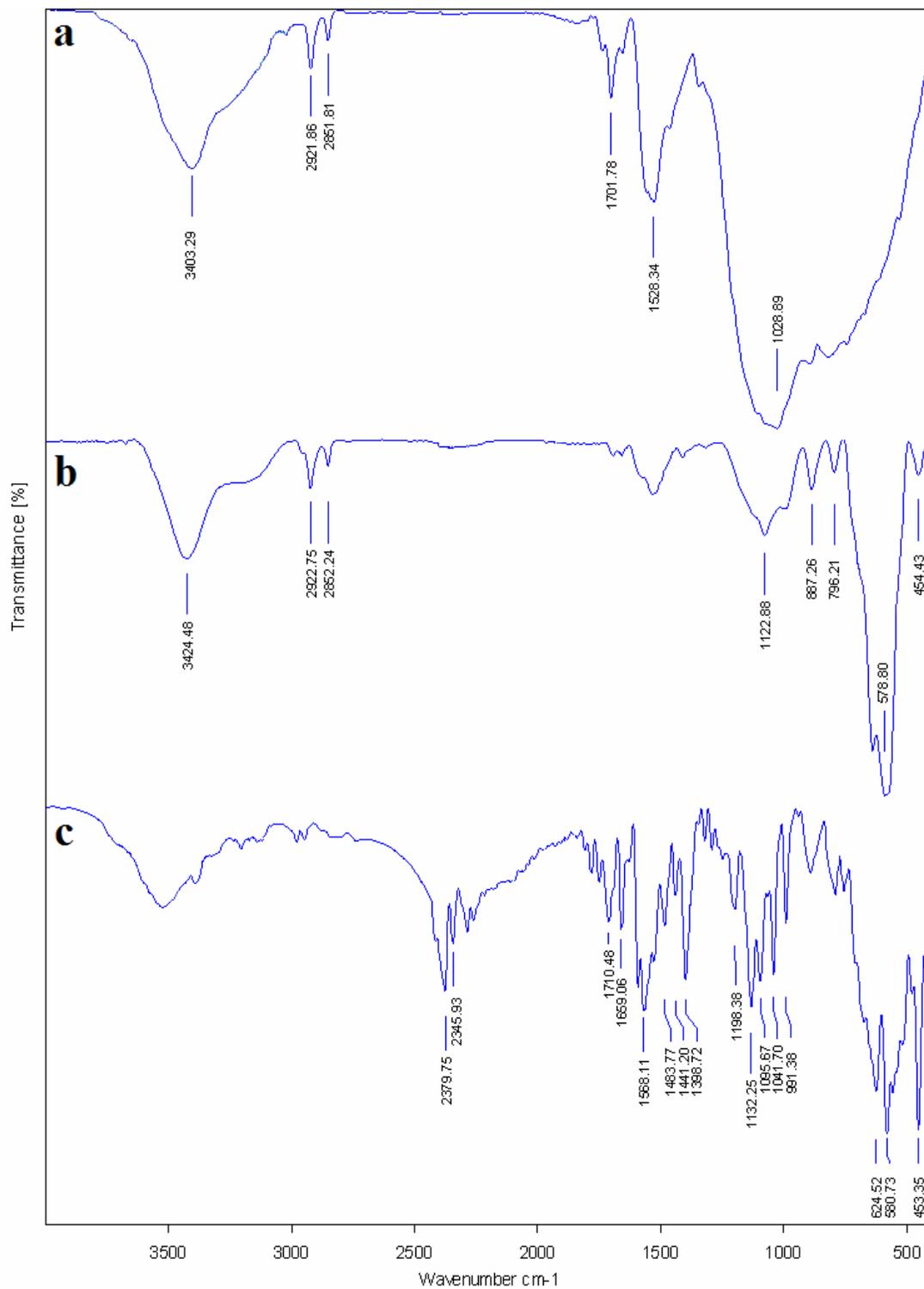


Fig. 2. FT-IR spectra of (a) AC, (b) MAC and (c) MAC/TPPZ nanocomposite

solution was taken and rhodium was determined by the general procedure.

RESULTS AND DISCUSSION

Characterization of Proposed Nanocomposite

FT-IR spectra were taken using KBr to observe the functional groups of oxidized AC, MAC and MAC/TPPZ (Fig. 2). According to the literature [30], the broadband at 3403 is related to O-H stretching vibration of hydroxyl groups in adsorbed water molecules and carboxylic acid groups of oxidized AC. For the oxidized AC, the characteristic vibration of carboxyl group is shown as a peak of COO⁻ stretching at 1701.78 cm⁻¹, it confirms that carboxylic derivative of activated carbon was prepared successfully. The characteristic peak around 1528.34 cm⁻¹ is

due to C=C stretching vibrations in aromatic rings. Moreover, a broadband in the region 800-1300 cm⁻¹ can be assigned to the stretching vibration of C-C and C-O in AC. In MAC spectrum (Fig. 2b), the absorption bands appeared at 454, 578, 796 and 887 cm⁻¹ are attributed to γ -Fe₂O₃ nanoparticles existing in the activated carbon [31]. Compared to the FT-IR spectrum of MAC/TPPZ (Fig. 2c), extra new peaks are observed in MAC spectrum. The peak at 1659.06 cm⁻¹ is due to C=N stretching vibration. The bands around 1398.72 and 1483.77 are due to the characteristic vibrations of benzene ring in TPPZ. Consequently, the above experimental results suggest that activated carbon is successfully modified by ligand.

Figure 3 shows the XRD patterns of AC and MAC nanocomposite. The result (Fig. 3a) shows that AC exhibit diffraction peaks at around 2 θ values of 23.98 and 43.79,

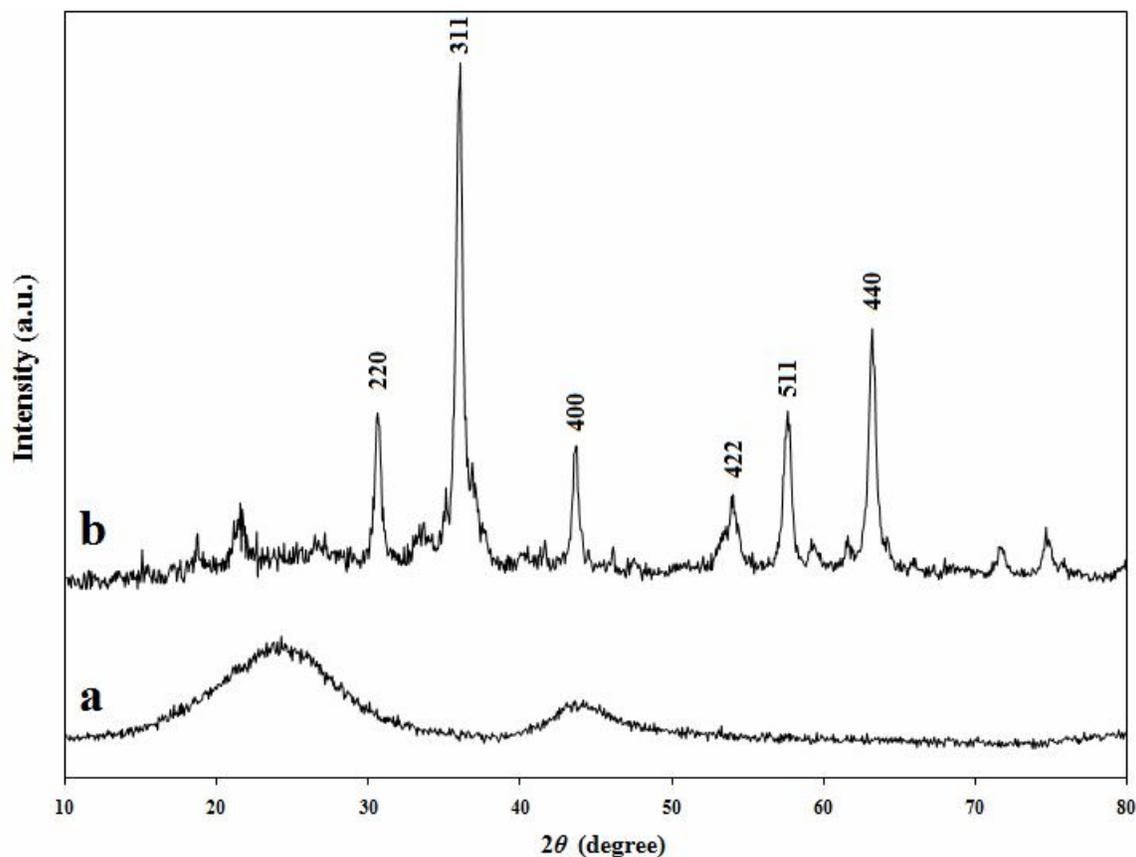


Fig. 3. XRD patterns of (a) AC and (b) MAC nanocomposite.

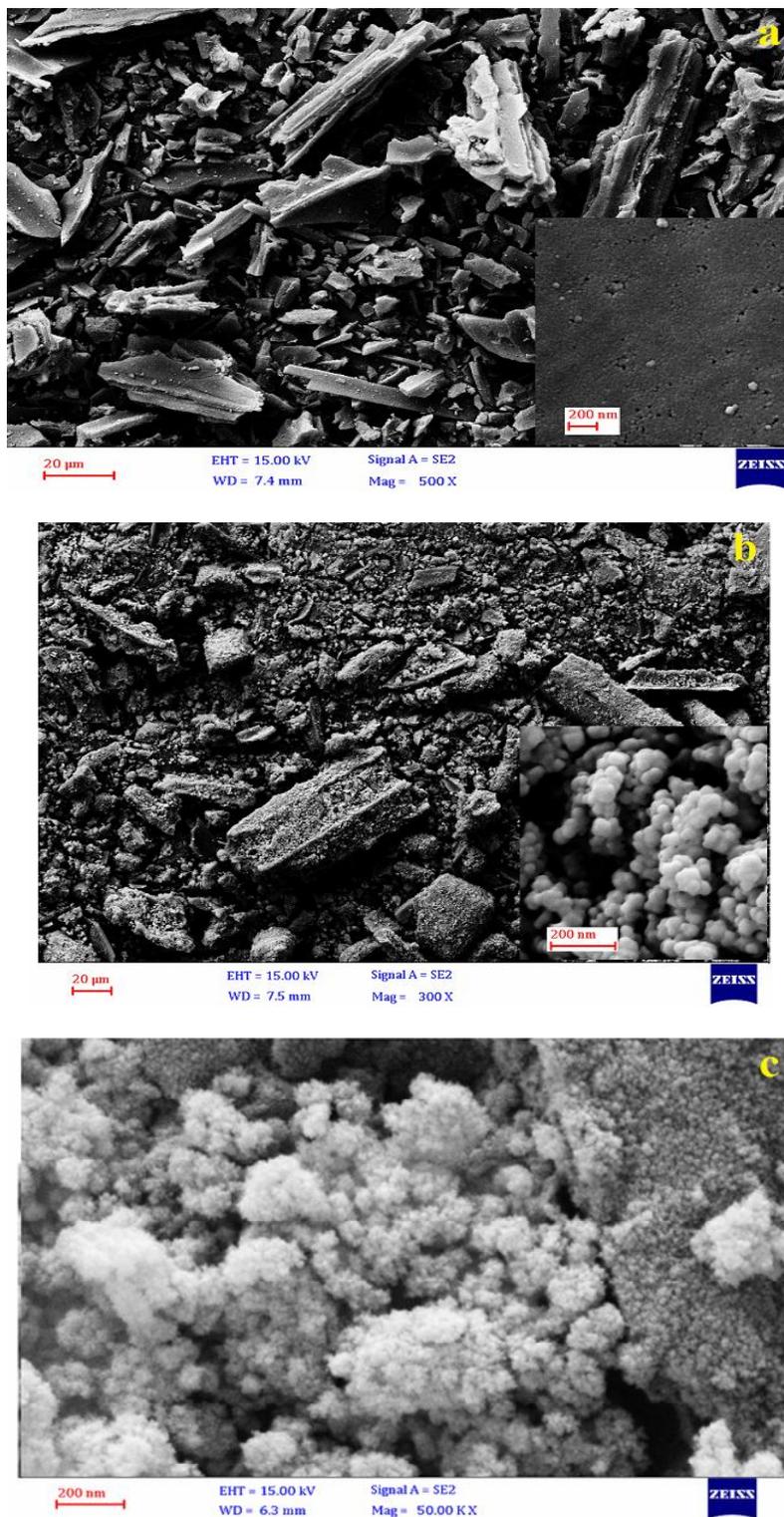


Fig. 4. FE-SEM images of (a) AC, (b) MAC and (c) MAC/TPPZ nanocomposite.

suggesting that the main structure of AC is amorphous. On the contrary, diffraction peaks at 2θ values of 30.56° , 35.94° , 43.60° , 53.95° , 57.64° and 63.19° can be indexed respectively to (220), (311), (400), (422), (511) and (440) planes. The presence of these peaks matched well with the JCPDS value (39-1346) of maghemite corroborates the presence of iron oxide nanoparticles on the AC surface.

The morphologies of the oxidized AC, MAC and the synthesized MAC/TPPZ adsorbent were obtained by FE-SEM (Fig. 4). As seen in the figure, the oxidized AC has a smoother surface compared to MAC nanocomposite. It is obvious that the surface of MAC is much rougher as a result of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticle deposition. The average size of the maghemite nanoparticles was about 35-75 nm as estimated from the FE-SEM. The combination of the oxidized AC with maghemite nanoparticle and then modification with TPPZ shows a nanocomposite with a rough surface.

The magnetization property of AC, MAC and

MAC/TPPZ was investigated at room temperature with an applied magnetic field of 10 kOe (Fig. 5). The saturation magnetization was found to be 24.1 emu g^{-1} for MAC/TPPZ, less than the MAC nanocomposite (29.2 emu g^{-1}). These results show that magnetic properties are hardly affected by the surface modification. The high saturated magnetization of MAC/TPPZ directly demonstrated the strong magnetic sensitivity of the magnetic nanocomposite. The results indicated that the magnetic susceptibility value is sufficient for this sorbent to be used in MSPE procedure.

Optimization of MSPE Parameters

Effect of pH. One of the most important parameters affecting the uptake of metal ions is the pH of the solution. To determine the optimal pH, the effect of pH on the adsorption of Rh(III) ions was studied over the range of 2.0-6.0 and the results are shown in Fig. 6. As can be seen, the sorption ability of Rh(III) ions by the as-prepared

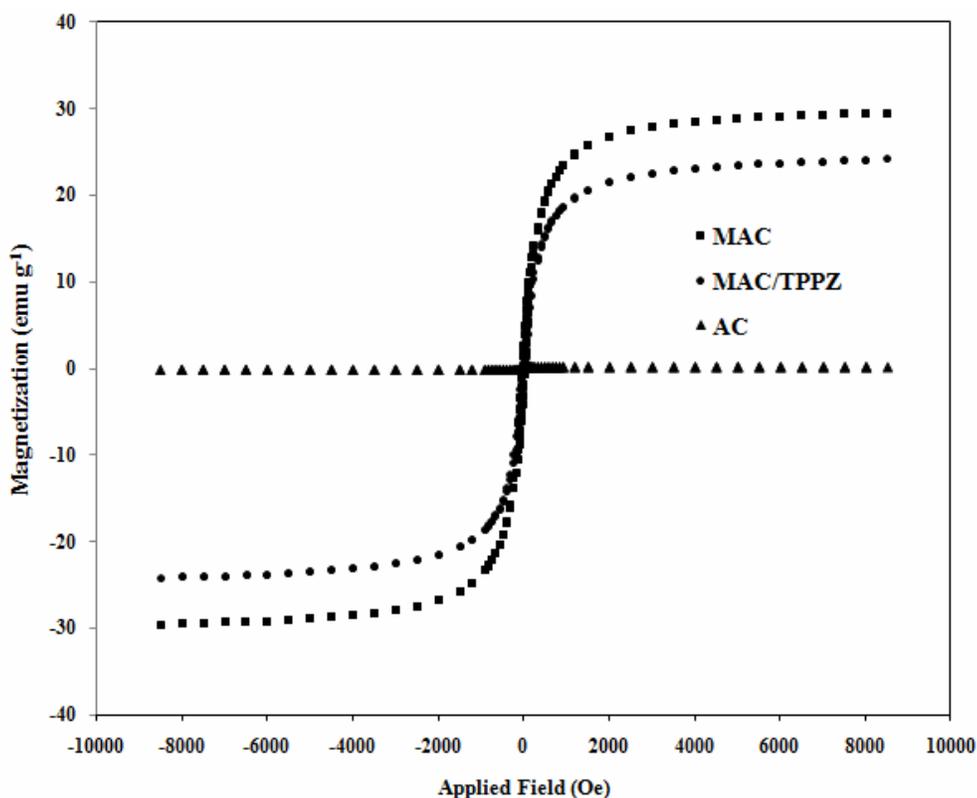


Fig. 5. Magnetic hysteresis curves of AC, MAC and MAC/TPPZ nanocomposite.

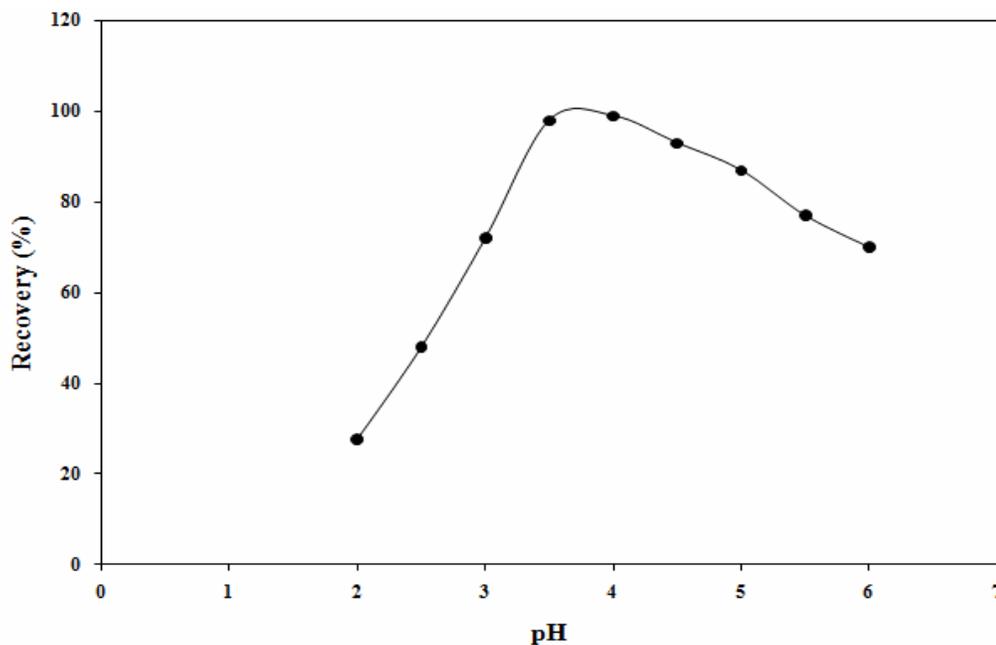


Fig. 6. The effect of sample solution pH. Other conditions: amount of sorbent = 0.03 g, [Rh(III)] = 50 $\mu\text{g l}^{-1}$, sample volume = 100 ml, extraction time = 2 min, eluent = 2.0 ml of 0.1 M thiourea/0.1 M HCl. Instrumental settings: wavelength = 343.5 nm, lamp current = 5.0 mA, slit width = 0.5 nm, acetylene flow = 1.5 l min^{-1} , air (as oxidant) flow = 3.5 l min^{-1} .

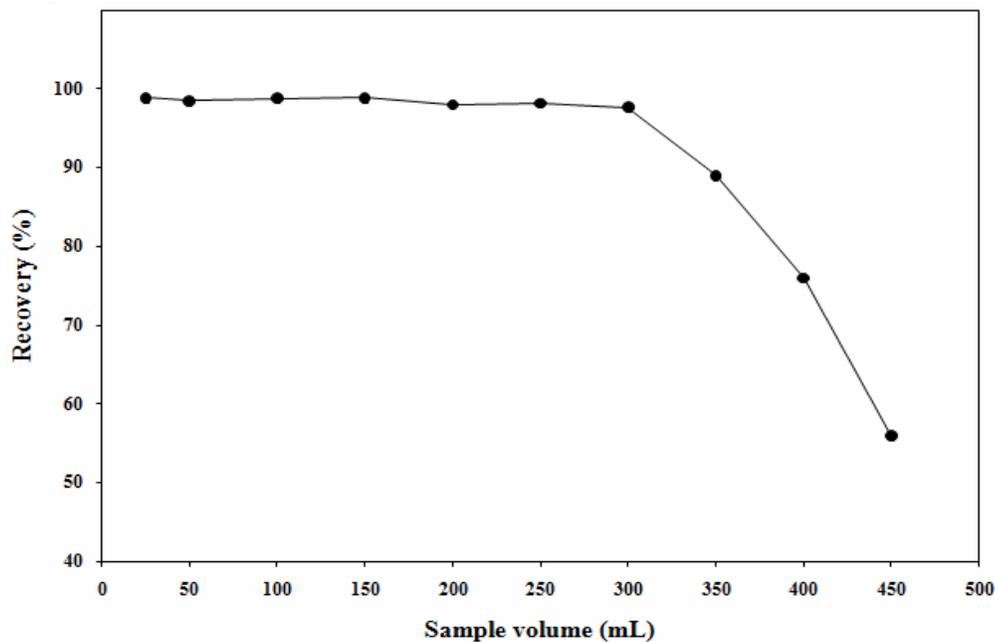


Fig. 7. Effect of sample volume on the recovery of Rh(III). Other conditions: amount of sorbent = 0.03 g, amount of Rh(II) = 5 μg , pH 4.0, extraction time = 3 min, eluent = 2.0 ml of 0.1 M thiourea/0.1 M HCl.

nanocomposites significantly dependent on the pH value of the aqueous solution. The extraction efficiency for Rh(III) increased with pH from 2.0 to 3.5, with full quantitative extraction observed within the pH range of 3.5-4.0. The progressive decrease in the extraction of the analyte at low pH is due to competition between hydrogen ion with rhodium for reaction with the chelating agent. In subsequent studies, the pH was maintained at approximately 4.0 with acetate buffer.

Effect of type and concentration of eluent. The influence of various acids such as HCl, H₃PO₄ and HNO₃ in different concentrations and also their mixture with thiourea as an auxiliary ligand were explored for the recovery of Rh(III) by MAC/TPPZ nanocomposite. The experimental results indicated that the retained rhodium ions were quantitatively eluted with a solution containing 0.1 M of HCl and 0.1 M of thiourea.

Effect of sample volume. The sample volume is an important parameter to obtain a high enrichment factor. Due to the magnetically assisted separation of the adsorbent (MAC/TPPZ), it is possible to collect the adsorbent from

larger volumes of the sample solution. To study the effect of sample volume on the extraction of rhodium ions, sample volumes of 25-450 ml containing fixed amounts of rhodium were used. The recovery values at different volumes are shown in Fig. 7. It was observed that recovery of Rh(III) ions were almost constant up to 300 ml of the aqueous phase. Hence, the theoretical preconcentration factor was 150, while in an experimental state, enrichment factor was found to be 136.

Effect of extraction and desorption time. In this work, for both extraction and desorption, ultrasonic treatment times in the range 1-8 min were investigated. The experimental results indicated that 3 min was sufficient for achieving quantitative recovery of rhodium ions for adsorption and desorption. Meanwhile, due to the super paramagnetic property of the MAC/TPPZ nanocomposite, the sorbent could be separated rapidly (less than 4 min) from the sample solution using a strong magnet instead of filtration or centrifugation. In a word, analysis time is shortened greatly compared with the traditional column-passing SPE.

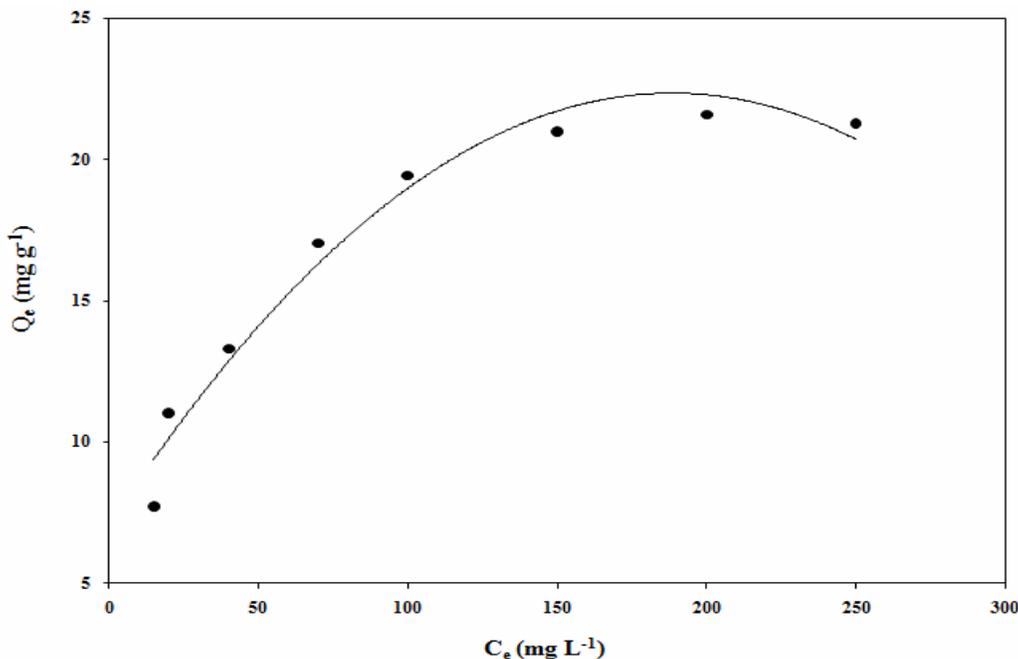


Fig. 8. Rh(III) adsorption capacity for MAC/TPPZ nanocomposite. Other conditions: amount of sorbent = 0.03 g, pH 4.0, extraction time = 3 min.

Adsorption capability. The capacity of the MAC/TPPZ adsorbent is an important factor because it determines how much adsorbent is required to remove quantitatively a specific amount of metal ions from the solutions [32]. The adsorption capacity of the sorbent was determined using the batch technique. 100 ml of sample solutions containing 15, 20, 40, 70, 100, 150, 200 and 250 $\mu\text{g l}^{-1}$ Rh(III) were adjusted to pH 4.0 and added to an Erlenmeyer flask containing 30 mg of the sorbent. After equilibration and separation using an external magnet, the concentrations of the analytes remaining in solution were measured by FAAS. The equilibrium binding amount of TPPZ immobilized MAC nanocomposite towards rhodium ions were calculated according to the following equation:

$$q_e = (C_i - C_e) VW^{-1} \quad (1)$$

where q_e is the adsorption capacity (mg g^{-1}), C_i and C_e are initial and equilibrium concentrations (mg l^{-1}) of rhodium ions in aqueous solutions respectively, W (g) and V (l) are the weight of the sorbent and volume of aqueous solution respectively.

The results are given in Fig. 8. The amount of Rh(III) adsorbed per unit mass of adsorbent increased with increasing the initial concentration of Rh(III) and reaches to a constant value at higher concentration region. The maximum adsorption capacity of the MAC/TPPZ towards rhodium, as evaluated from the plateau region of Fig. 8 was 21.6 mg g^{-1} .

Table 1. Effects of Coexisting Ions on the Preconcentration and Detection of $50 \mu\text{g l}^{-1}$ of Rh(III) Ions

Foreign ion	Foreign ion/Rh ratio	Recovery (%)
Na ⁺	2000	98.1 ± 2.8
K ⁺	2000	97.9 ± 2.2
Ca ²⁺	1500	98.3 ± 1.5
Mg ²⁺	1000	98.2 ± 2.6
Pd ²⁺	350	98.3 ± 1.9
Cu ²⁺	300	98.2 ± 2.2
Cd ²⁺	300	97.9 ± 1.4
Mn ²⁺	500	99.2 ± 3.2
Ni ²⁺	500	100.1 ± 2.9
Zn ²⁺	450	98.7 ± 3.3
Hg ²⁺	200	98.4 ± 3.2
Al ³⁺	650	96.8 ± 2.9
Cr ³⁺	250	98.0 ± 2.7
Fe ³⁺	300	97.4 ± 3.2
Ru ³⁺	200	97.1 ± 3.0
CO ₃ ²⁻	1500	98.8 ± 1.7
SO ₄ ⁻	1000	99.6 ± 2.0
HCO ₃ ⁻	2000	96.8 ± 2.3

Table 2. Determination of Rhodium in Real Samples

Sample	Added ($\mu\text{g l}^{-1}$)	Found ($\mu\text{g l}^{-1}$) ^a	Recovery (%)
Aqueduct water	-	N.D. ^b	-
	10.0	9.8 ± 0.5	98.0
	25.0	24.6 ± 0.4	98.4
Well water	-	N.D.	-
	10.0	10.3 ± 0.4	103.0
	25.0	24.4 ± 0.3	97.6
Synthetic sample	-	19.3 ± 0.6	96.5
Platinum-iridium alloy ^c	-	6.73 ± 0.1	96.1

^aMean \pm standard deviation, (n = 3). ^bNot detected. ^cCertified value (7.0%).

Table 3. Comparison of Analytical Parameters of the Proposed Method with other Reported Methods for Determination of Rh(III)

Method	Linear range ($\mu\text{g l}^{-1}$)	LOD ($\mu\text{g l}^{-1}$)	Enrichment factor	Ref.
IEM ^a -ETAAS ^b	0.9-50	0.3	20	[33]
SPE-FIA ^c /FAAS	-	3	-	[34]
SPE-Spectrophotometry	40-7500	20	40	[35]
SPE-DPP ^d	250-7500	60	-	[36]
MSPE-FAAS	0.8-650	0.1	150	This work

^aIEM: ion exchange microcolumn. ^bETAAS: Electrothermal atomic absorption spectrometry. ^cFIA: Flow injection. ^dDPP: Differential pulse polarography.

Effects of coexisting ions. Under optimized conditions, the interference of coexisting ions on the recovery of Rh(III) ions was investigated. For doing so, a solution of $50 \mu\text{g l}^{-1}$ of rhodium containing the corresponding interfering ions was prepared and operated according to the recommended procedure. The criterion for the interference of each species was set at $\pm 5.0\%$ in the analytical signal obtained for a solution containing Rh(III). Table 1 shows the substances studied and their maximum tolerable amounts. The recovery of Rh(III) was not less than those in the absence of

coexisting ions, indicating that MAC/TPPZ had a high selectivity towards Rh(III) and presented a potential to apply in real samples analysis.

Analytical Figure of Merit

By employing the optimum experimental conditions, the calibration graph was found to be linear with the correlation coefficient of 0.9967 in the range of $0.8-650 \mu\text{g l}^{-1}$. The detection limit based on $3S_b/m$ (where S_b is the standard deviation of the blank signals and m is the slope of the

calibration curve after extraction) and relative standard deviation (RSD) for eight replicate measurements at 50 $\mu\text{g l}^{-1}$ of Rh(III) were found to be 0.1 $\mu\text{g l}^{-1}$ and $\pm 3.6\%$, respectively. The enrichment factor of 150 was calculated as the ratio of the initial volume to the final. Also, under the optimized conditions, the adsorbents could be reused at least 5 times without decreasing extraction efficiency. These results clearly show the merits of MSPE using the prepared MAC/TPPZ as the adsorbent and indicate that the developed method has high efficiency and sensitivity, and can be used for trace rhodium determination.

Analytical Applications

The proposed procedure was applied to the determination of the trace amount of rhodium ions in water and synthetic samples with diverse matrix ion concentrations. The analytical results are given in Table 2 and satisfactory recoveries were obtained for spiked analyte ion. The recoveries were higher than 95%, confirming the accuracy of the presented procedure. Moreover, according to the F-test (95% confidence level), there was no significant difference in the precision of the results obtained for spiked water samples with those obtained for ultra-pure water spiked.

To verify the validity of the procedure, the proposed method was also applied to the determination of rhodium in a platinum-iridium alloy. The results (Table 2) indicate the effectiveness and accuracy of the MSPE method. Table 3 compares the characteristic data of the current method with other methods [9,33-36] for determination of Rh in diverse samples. As can be seen, from several points of view, the comparison is favorable to the procedure discussed here.

CONCLUSIONS

In this study, a novel modified magnetic sorbent (MAC/TPPZ) was successfully synthesized and applied to separate and preconcentration of trace amounts of rhodium prior to the determination by FAAS. The synthesized adsorbent was characterized by XRD patterns, FE-SEM images, FT-IR and VSM analyses. The simple and rapid determination of rhodium with high sensitivity and reproducibility are the advantages of modified nanocomposite. This methodology gives low limits of

detection, good accuracy, excellent precision and high kinetic sorption on the target analyte. Also, the combination of MSPE by the as-prepared nanocomposite with FAAS offers significant analytical performance.

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