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Solid phase extraction of gold using nano-ZnO sorbent prior to its flame atomic absorption spectrometric determination

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ABSTRACT

A solid phase extraction procedure is presented for the separation and preconcentration of trace levels of Au (III) ions by using nano-ZnO. The experimental parameters such as sample pH, sorbent mass, contact time, sample volume, eluent volume, type of eluent, and interference of some ions on adsorption and recovery of Au(III) were investigated using batch procedure. The maximum adsorption capacity of the sorbent for Au(III) was found to be 584 mg g^{-1}. The sorption of Au (III) was quantitative in the pH range of 3.5-4.5 and quantitative desorption occurred with 5.0 mL of $Na_2S_2O_3$ and KSCN (1.0 mol L^{-1}). In the initial solution, the calibration curve was linear in the range of 1.3 - 200 $\mu g L^{-1}$ of Au(III) (r = 0.9994), the detection limit ($3\sigma_b$, n = 8) was 0.39 $\mu g\ L^{-1}$, relative standard deviation (R.S.D) of 15 $\mu g\ L^{-1}$ of Au(III) was 1.9 % (n = 8), and the preconcentration factor was 100. The proposed method has been successfully applied to separation and determination of gold(III) ions in water samples.

KEYWORDS

Determination;
Gold;
Solid phase extraction;
Zinc oxide.

INTRODUCTION

Gold is one of the most imporatnt nobel metals because it plays significant role in biology, environment and industry. Despite the important role of gold compound in biology and medicine, it is known to be very toxic for humans and living organisms, because of its disruptive effects on the activity of many enzymes[1]. Trace level determination of gold by flame atomic absorption spectrometry is often a difficult task because of its low concentration and complex matrices. Therefore, a separation and preconcentration step is often necessary for its determination[2].

Various techniques, such as liquid-liquid extraction[3-5], coprecipitation[6,7], cloud point extraction[8], electrodeposition[9], membrane disk[10], and solid phase extraction[11-20] have been used for separation and preconcentration of gold. Solid phase extraction, however, have attracted great attention as it offers several advantages such as simplicity, high enrichment factor, rapid phase separation, low consumption of organic solvents and low cost.

Among the many kinds of adsorbents, nano materials show a great potential for rapid and efficient extraction of metal ions owing to their unique physical and chemical properties[21-25]. A literature servy reveals that there is no report on the applcation of ZnO (especially nano sized-ZnO) as sorbent for analytical purpose. However, Mustafa et al utilized micro-sized ZnO for the removing of Co^{2+}, Zn^{2+} and Ni^{2+} from aqueous solutions[26]. The research was conducted, therefore, to assess the potential of nano-ZnO as sorbent for extraction of trace Au(III) ions from water samples. For this purpose, the nano-sized ZnO was prepared by precipitation method and examined as sorbent for separation and preconcentration of Au(III) ions.

EXPERIMENTAL

Apparatus

The prepared nano-ZnO was characterized by X-ray diffractometer (XRD; Philips, PW1800) using Cu-Kα radiation (λ = 0.15418 nm, 40 kV, 30 mA). The morphology and particle size of the prepared nano ZnO were studied by scanning electron microscopy (SEM) using a Philips XLS30 model. A Varian SpectrAA 220 atomic absorption spectrometer (Victoria, Australia) equipped with deuterium lamp background correction was used for determination of gold using an air/acetylene flame. The operating conditions were as follows: wavelength 248.2 nm, lamp current 4.0 mA and slit width 1.0 nm, air flow 3.5 L min^{-1} and acetylen flow 1.5 L min^{-1}. A digital pH meter, Metrohm model 827 Ion analyzer equipped with a combined pH glass electrode was used for the pH adjustment. A magnetic stirrer (Heidolph model MR 3001K) was used for mixing the adsorbent and aqueous solutions.

Materials and reagents

All reagents used in this study were of analytical grade and all solutions were prepared by using double distilled water. Stock solution of Au(III) at a concentration of 1000.0 μg mL^{-1} was prepared by dis-solving an appropriate amount of $HAuCl_4.4H_2O$ (Merck, Darmstadt, Germany) in HCl (0.001mol L^{-1}). Working reference solutions were prepared daily by stepwise dilution from stock solution. A solution of KSCN / $Na_2S_2O_3$ (1 mol L^{-1}) was prepared by dissolving their salts in double distilled water. The stock solutions of various metal ions were prepared from their nitrate or chloride salts (Darmstadt, Germany) and used to investigate the effects of interfering ions.

The nano- ZnO was prepared by the procedure as described in Ref[27]. In a typical preparation, 2.4 g (30 mmol) of microsized ZnO powder was added into 6.0 mL NH_4HCO_3 aqueous solution (80% w/v) under vigorous stirring at 60 ^{0}C in two steps: (a) one third of the ZnO (0.8 g, 10 mmol) was added to the prepared NH_4HCO_3 solution until dissolving was completed, (b) the rest of ZnO (1.6 g, 20 mmol) and 0.2 g of $CS(NH_2)_2$ were added to the above solution and the mixture was stirred for another 2 h. Finally, the white precipitate was dried at 70 ^{0}C for 6 h, and calcinated at 400 ^{0}C for 1h to prepare the nano-ZnO. The prepared ZnO nanoparticles with average particles size of 10 nm were used as sorbent.

Preconcentration procedure

The general procedure for the extraction of Au(III) ions on nano-ZnO was performed as follows: an aliquot of gold(III) solution was transferred into a 100 mL beaker, the pH of solution was adjusted to desired value with HNO_3 or NaOH (0.10 mol L^{-1}) solution, and the final volume was diluted to 20 mL using double distilled water. Then, 0.01 g of nano-ZnO powder was added and the mixture was stirred vigorously for 30 min. After that, the solid mass was separated by centrifuging (6000 rm) and was washed with double-distilled water. In desorption experiments, 5.0 mL of $Na_2S_2O_3$/SCN (1 mol L^{-1}) solution was added to the adsorbent as eluent and the mixture was stirred vigorously for 10 min. Finally, the solid mass (adsorbent) was separated by centrifuging and the analyte in supernatant was determined by atomic absorption spectrometer. Also, a blank solution underwent the same conditions. All experiments were performed for three times and the mean value was used.

Sample preparation

Tap water samples were taken from drinking water (Qazvin, Iran) and well water was collected from city of Qazvin (Iran). The water samples were filtered through Whatman No.4 filter paper of 0.45μm pore size to remove any suspended particles. Then, 500 mL of sample was transferred to a beaker and the proposed procedure was applied to preconcentrate Au(III) ions.

RESULT AND DISCUSSION

Characterization of the nano-ZnO

The prepared nano-ZnO was characterized by

XRD and SEM techniques. Figure1 shows the XRD pattern of the prepared nano-ZnO. The diffraction peaks appeared at 2θ of 31.8^{0}, 34.4^{0}, 36.3^{0}, 47.6^{0}, 56.6^{0}, 62.8^{0}, 67.9^{0}, and 69.1^{0} can be perfectly indexed to the ZnO hexagonal wurtzite structure (JCPDS card 36-1451), indicating the resultant nanoparticles are pure. The average particle size of the prepared ZnO, calculated by the Scherrer equation was found to be about10 nm[28]. Figure 2 presents the SEM image of the prepared ZnO nanoparticles which exhibited a flower-like morphology.

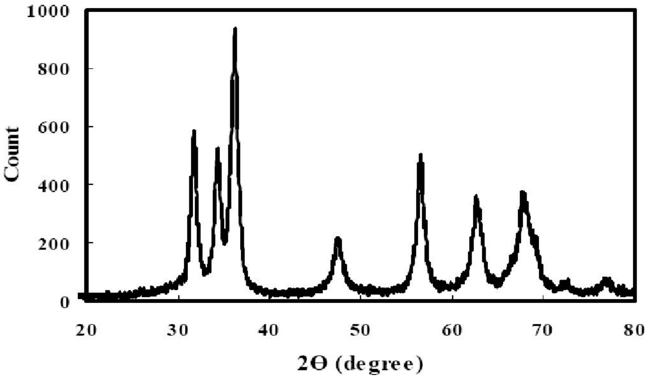

Figure 1: X-ray powder diffraction pattern of the nano-ZnO

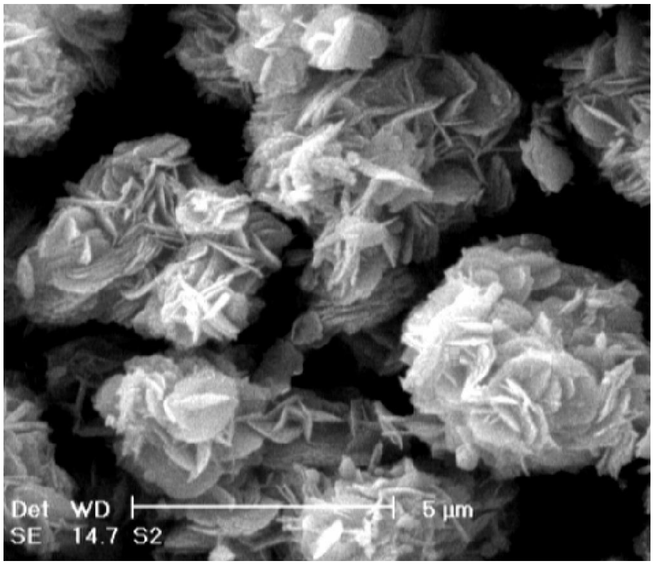

Figure 2 : SEM image of the nano-ZnO.

Effect of pH on Au(III) extraction

The effect of pH on the recovery of Au(III) was investigated in the pH range of 3.5–10 and the results were presented in Figure 3. No further studies were performed bellow pH 3 because of disoultion of ZnO in high acidic solution. As is seen (Figure 3), the recovery of gold was quantitative (>95%) in the pH range of 3.5 - 4.5, and it gradually decreased with the increase in pH. The results also demonstrated that the recovery was drastically declined above pH 9. This phenomenon can be explained by two pH dependent factors which affect the Au(III) adsorption efficiency: zero point charge of the adsorbent and the formation of Au chloroanionic species. As it was reported[29], the pH of zero point charge (pHzpc) for ZnO is 9, and hence at pHs <pHzpc, the surface of ZnO nanoparticles become positively charged owing to protonation of the hydroxyl groups[30]. At low pH, when solution acidity was controlled by HCl, the amount of chloride in the solution is high enough to favor the formation of Au choloroanioinic species such as $[AuCl4]^{-}$. Therefore, the sorption of Au(III) ions in acidic solutions can be attributed to electrostatic attractions between positively charged sites of sorbent and negatively charged Au(III) species. When pH value exceeds pHzpc, the surface sites of sorbent became deprotonated, causing decline in Au(III) adsorption, because of the repulsive electrostatic effects. Moreover, the decrease in adsorption of Au(III) with the increase in pH may be related to the presence of less-adsorbable Au(III) species which can stem from the lower availability of chloride anions. Given these results, the following experiments were carried out at pH 4. It is worthwhile to point out, high adsorption of Au(III) ions from acidic solutions is very promising for practical applications because strong acids are usually used to decompose materials consisting of gold.

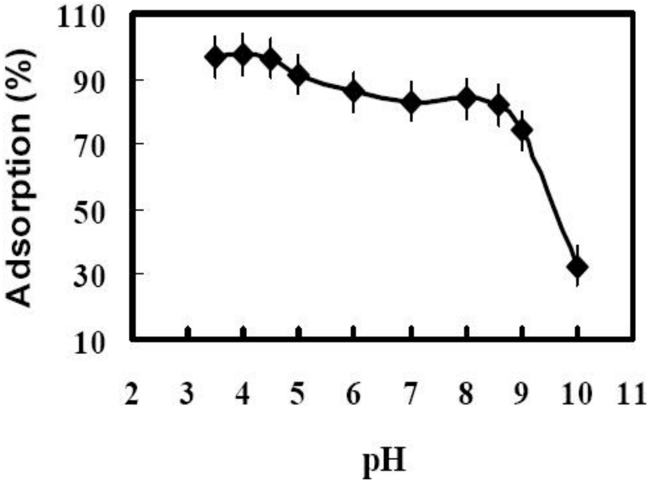

Figure 3 : Effect of pH on the adsorption of Au(III)) onto nano-ZnO (Au(III) : 20 µg mL^{-1}; sample volume: 25 mL; sorbent mass: 0.05 g ; contact time : 60 min).

Effect of contact time and amount of sorbent

The effect of contact time on the Au(III) sorption by nano-ZnO was investigated by mixing 25 mL of 20 μg mL^{-1} Au(III) solution with 0.05 g sorbent. As shown in Figure 4, the adsorption of Au(III) is over 96% during the first 5 min, indicating very fast adsorption process. The effect of nano-ZnO amount on the sorption of Au(III) ions was studied by mixing different amounts of sorbent (in the range of 0.1-0.15mg) with Au(III) solution for 10 min. It can be seen (Figure 4) that the amount of sorbent has no significant effect on adsorption percentages. Hence, the further experiments carried out by using of 0.01 g Nano-ZnO for 10 min.

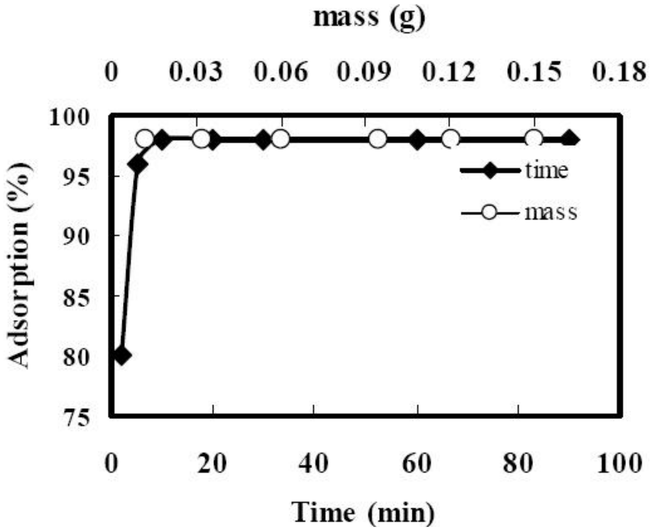

Figure 4 : Effect of sorbent amount and contact time on the adsorption of Au(III) by nano-ZnO (Au(III) : 20 μg mL^{-1}; sample volume: 25 mL; pH: 4.0)

Choice of eluent

In order to choose a proper eluent for desorption of the retained analyte, various eluents including H_2SO_4/ NH_3, $Na_2S_2O_3$/KSCN, $Na_2S_2O_3$, NH_3, and thiourea were examined for the desorption of the retained Au from nano-ZnO sorbent. As can be seen from TABLE 1, the best recovery was obtained with 5 mL $Na_2S_2O_3$ /KSCN solution (1 mol L^{-1}). Thus five mililiters of $Na_2S_2O_3$/KSCN (1 mol L^{-1}) was used as proper eluent for the further experiments.

Effect of sample volume

To determine the maximum applicable sample volume, various volumes of sample solutions (50,100, 200, 300, 400, 500, 600, 800 and 1000 mL) containing 20 μg of Au(III) ions were treated according to the proposed procedure. The results showed that the recovery of gold is quantitative (> 95%) up to 500 mL, and at greater volume the percent of recovery is decreased. With respect to elution volume of 5 mL, a preconcentration factor of 100 was obtained for gold extraction.

TABLE 1: Effect of eluent on the desorption of Au(III) from Nano-ZnO

Type of eluent	Recovery (%)
10 mL H_2SO_4 / NH_3 (4 mol L^{-1})	18.2
10 mL H_2SO_4 (2 mol L^{-1}) / NH_3 (4 mol L^{-1})	23.8
10 mL $Na_2S_2O_3$ (1 mol L^{-1})	57.8
10 mL NH_3 (2 mol L^{-1})	14.5
10 mL thiourea (0.5 mol L^{-1})	7.5
10 mL KSCN / $Na_2S_2O_3$ (0.5 mol L^{-1})	63.6
10 mL KSCN / $Na_2S_2O_3$ (1 mol L^{-1})	92.5
5 mL KSCN / $Na_2S_2O_3$ (1 mol L^{-1})	101

Interference studies

Interference effect of common coexisting ions on the adsorption of Au(III) ions by nano-ZnO was investigated. For this purpose, various amounts of interfering ions (in the form of their nitrate or chloride salts) were added individually to a solution containing 40 μg Au(III) and the recommended procedure was applied. The tolerance limits of coexisting ions, defined as the maximum concentration making the recovery of Au less than 95%, were given in TABLE 2. The results revealed that the presence of major cations and anions has no

TABLE 2 : Tolerance limits of the diverse ions on the adsorption of 2 μg mL^{-1} Au (III).

Diverse ion	Tolerance limit (μg mL^{-1})
Na^+	2000
K^+	1500
Cu^{2+} , Zn^{2+}	400
Mg^{2+}	1000
Ca^{2+}	1500
Al^{3+}	200
Fe^{3+}	200
Cl^-	3000
SO_4^{2-}	1500
PO_4^{3-}	200
NO_3^-	2400

obvious influence on extraction of trace amount of Au (III) ions in water samples under the selected conditions.

Adsorption capacity

The adsorption capacity is an important characteristic which determines the amount of the sorbent required for quantitative extraction of the analyte from a given solution. To evaluate the adsorption capacity of the nano-ZnO, increasing amounts of Au(III) ions were added to a 10 mg nano-ZnO sorbent for saturation and the adsorption procedure was followed under optimum conditions at room temperature. Then, the amount of Au(III) ions adsorbed per unit mass of sorbent at each concentration level was determined. The results revealed that adsorption capacity of the sorbent was increased with increase in the concentration of Au(III) and reaches the plateau which determines the adsorption capacity values . From the experimental data, the maximum adsorption capacity (Q_{max}) of the nano-ZnO for Au(III) ions was found to be 584 mg g^{-1}.

ANALYTICAL PERFORMANCE

Under the optimal experimental conditions, the calibration curve for Au(III) was found to be linear in the range of 1.3 - 200 µg L^{-1} of Au(III) in the initial solution. The linear regression equation was $A = 0.0313C + 0.0048$ with correlation coefficient of $r = 0.9994$ (n=8), where A and C are the absorbance and concentration of Au(III) in µg L^{-1}, respectively. The limit of detection (LOD) was calculated as three times the standard deviation of eight replicate measurements of blank solution using the preconcentration method was found to be 0.39 µg L^{-1}. The relative standard deviation (RSD) for eight replicate measurments of 50 mL of 15 µg L^{-1} Au(III) solution was 1.9 %, indicating good precision of the method. The accuracy and applicability of the proposed method for determination of Au(III) in water samples were tested by spiking experiments. For this aim, various amounts of Au (III) were spiked into water samples including tap water and well water and the

TABLE 3 : Determination of Au(III) in water samples.

Samples	Added (µg L^{-1})	[a]Found (µg L^{-1})	Recovery (%)
Tap water	0	[b]nd	-
	15	15.5 ± 0.2	103
	25	24.4 ± 0.3	97.6
Well water	0	nd	-
	15	14.3 ± 0.4	95
	25	24.1 ± 0.3	96

[a] Mean ± standard deviation (n=4); [b] nd: Not detected

TABLE 4 : Comparative data from some recent studies on solid phase extraction of Au(III).

Sorbent	Eluent	Q_{max} (mg g^{-1})	PF	LOD (µg L^{-1})	R.S.D (%)	Reference
Nano-ZnO	$Na_2S_2O_3$/KSCN (1 mol L^{-1})	584	100	0.39	1.9	This work
Nanometer TiO_2 immobilized on silica gel	0.1 mol L^{-1} HNO_3	3.56	50	0.21	1.8	21
Modified activated carbon	2% thiourea in 1mol L^{-1} HCl	32	200	0.26	3.1	14
Amidinothioureido- silica gel	5 % thiourea	54.5	-	13	1.2	19
Alumina /3-(8-quinolinylazo)-4-hydroxybenzoicacid	1 mol L^{-1} HNO3 and 3% thiourea	17.7	10	0.27	4.5	24
Dowex M-4195 Chelating resin	2 molL^{-1} H_2SO_4 + 4molL^{-1} NH_3	8.1	31	1.61	< 5	17
Amberlite XAD-2000	0.07 mol L^{-1} NH_3	-	30	2	3.2	16
Modified activated carbon	4% thiourea in 1mol L^{-1} HCl	302	125	5	<3	18
Amberlite XAD-2000/DDTC	1 mol L^{-1} HNO_3 in acetone	12.3	200	16.6	<6	15
DWCNTs	1 mol L^{-1} HNO3 in acetone	10.0	150	1.5	-	22
MWCNTs	3% thiourea in 1 mol L^{-1} HCl	14.8	75	0.15	3.1	23

proposed procedure was followed. The results indicate (TABLE 3) that the proposed procedure is suitable for preconcenration of trace level of Au(III) ions and has potential for application in separation/determination of gold from water samples.

COMPARISON OF THE NANO-ZnO WITH OTHER SOLID PHASE EXTRACTANTS

A comparison of the proposed method with some other preconcentration procedures for solid phase extraction of Au(III) is given in TABLE 4. As it is obvious, the maximum adsorption capacity of the present nano-ZnO is surprisingly higher than that of other sorbents. In addition, the present method has comparatively low detection limit, high enrichment factor and good precision. Moreover, unlike the majority of adsorbents used (TABLE 4), the present nano-ZnO could provide a superior adsorption capacity and high analytical performance without the need for additional treatment such as surface modification or using chelating reagents.

CONCLUSION

A simple procedure was proposed for solid phase extraction of trace level of Au(III) using nano-ZnO as sorbent. Compared to many other adsorbents, the present nano-ZnO exhibited a superior adsorption capacity (584 mg g^{-1}) towards Au(III) ions. It also could provide high enrichment factor, low detection limit and good precision for separation and preconcentration of Au(III) in aqueous solutions. Moreover, the present sorbent can be prepared by a simple procedure and low cost materials. Considering the above-mentioned merits, the nano-ZnO is a potentially promising sorbent for solid phase extraction of gold. However, more studies are required to develop the method to determine gold in real samples with complex matrices.

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