Research Article

Tris(2-Aminoethyl)Amine-Functionalized Fe$_3$O$_4$ Magnetic Nanoparticles as a Selective Sorbent for Separation of Silver and Gold Ions in Different pHs

Hamid Reza Lotfi Zadeh Zhad, Forouzan Aboufazeli, Omid Sadeghi, Vahid Amani, Ezzatollah Najafi, and Najmeh Tavassoli

Department of Chemistry, Islamic Azad University Shahr-e-Rey Branch, P.O. Box 18735-334, Tehran, Iran

Correspondence should be addressed to Najmeh Tavassoli; h2o.group.chem@gmail.com

The usage of tris(2-aminoethyl)amine-functionalized Fe$_3$O$_4$ nanoparticles as a novel magnetic sorbent for rapid extraction, preconcentration, and determination of trace amounts of silver and gold ions was investigated. The optimum conditions for sample pH, eluent parameters (type, concentration and volume) were obtained. The effect of various cationic interferences on the adsorption of silver and gold was evaluated. The analytical efficiency values of both silver and gold ions were higher than 98.0% in the optimum conditions. The limits of detection (LOD) were less than 0.8 and 0.5 ng mL^{-1} for silver and gold, respectively. The linear ranges for silver and gold were 1.5–1000 ng mL^{-1} and 1.0–1000 ng mL^{-1} respectively. The maximum capacity of the modified magnetic nanoparticles was more than 97.3 mg g^{-1} and 167 mg g^{-1} for silver, and gold ions, respectively. The presented method was used to determine silver and gold ions in real samples. Finally, the method accuracy was confirmed by standard reference materials.

1. Introduction

Silver and gold have been known as precious metals for a long time. They are used to make jewelry, high-value tableware, utensils, and so forth. The silver compounds are extensively used in the processing of food, drugs, beverages, filters, and other equipments of water purification. These compounds also play an important role in electrical applications, photographic film production, and fungicides manufacturing [1, 2]. On the other hand, high levels of silver are toxic to human cells, which can decrease the rate of wound healing. Another problem caused by permanent exposure to silver compounds is argyria, which cause a permanent blue-gray discoloration of the skin [3]. Gold has been high demanded for using in coinage, jewelry, and so forth, since the beginning of the human history. For these reasons, extraction and determination of low levels of silver and gold are important. There have been lots of efforts for determining of these elements by researchers all over the world. Several techniques have been used to determine

silver or gold ions in real samples such as electrothermal atomic absorption spectrometry (ETAAS) [4, 5], inductively coupled plasma optical emission spectroscopy (ICP-OES) [6], inductively coupled plasma mass spectroscopy (ICP-MS) [7], and flame atomic absorption spectroscopy (FAAS) [8]. Nowadays, electrothermal atomic absorption spectrometry (ETAAS) is one of the most powerful and common analytical techniques for determination of low concentrations of heavy metals due to being costless and easy operation [9]. But there are many difficulties in determination of heavy metals in environmental samples by electrothermal atomic absorption spectrometry such as matrix interferences. However, this problem can be solved by preconcentration techniques due to the possibility of removing the sample matrix. Several methods have been developed and used for preconcentration and separation of elements in trace concentrations according to the nature of the samples, the concentrations of the analytes, and the measurement techniques. Some examples are ion exchange [10], coprecipitation [11], solvent extraction [12], and adsorption [13]. Among all these techniques, adsorption

is the most preferred technique because it is simple and does not consume high volumes of toxic solvents. Among variety of solid phases used for extraction of silver and gold such as activated carbon [14], pentathia-15-crown-5 [15], calix [4], arene [16], magnetic nanoparticles [17], modified silica [18], and polymer gels [19], magnetic nanoparticles have gained much importance due to their high surface areas, chemical and mechanical stability, simplicity of synthesis, and on the top possibility of easy separation. These magnetic nanoparticles could be easily functionalized with desired molecules using silane agents [20]. The silane group will be reacted with active hydroxyl groups on the surface of particles and cause formation of functionalized magnetic nanoparticles.

In this work, for the first time, the application of tris(2-aminoethyl)amine-functionalized Fe_3O_4 nanoparticles as a magnetic solid phase for separation and determination of silver and gold from aqueous solutions was investigated. The effects of type, concentration, and volume of eluent, sample pH, and interfering ions on method efficiency were studied. This method was applied to a numbers of industrial and natural samples. Moreover, the method accuracy was investigated by determination of gold and silver ions in different standard reference materials.

2. Experimental

2.1. Reagents and Materials.

All materials were of analytical grade and used without any further purification. Standard silver and gold ion solutions were prepared daily from stock solution of silver or gold solutions ($1000 \, \mu g \, L^{-1}$) which were purchased from Merck Company (Darmstadt, Germany). All reagents and solvents including sodium hydroxide, nitric acid, hydrochloric acid, thiourea, 3-chloropropyl triethoxysilane, tris(2-aminoethyl)amine, and triethylamine were purchased from Merck Company. All of the required solutions were prepared using deionized water, provided from a Milli-Q (Millipore, Bedford, Mass, USA) purification system. Fe_3O_4 nanoparticles with $305 \, m^2/g$ surface area were synthesized according to the previous report [21]. Tris(2-aminoethyl)amine-functionalized magnetic nanoparticles were prepared by reacting of activated Fe_3O_4 with silane agents.

For this approach, the surface of Fe_3O_4 was activated in a solution of $1 \, mol \, L^{-1}$ of NaOH and then they were suspended in 50 mL of toluene. Afterwards 1.0 g of 3-chloropropyltriethoxysilane was added to the mixture and was refluxed for 24 hours. The solid phase was separated by a magnet and was suspended again in 50 mL of triethylamine and toluene mixture (1 : 1 v/v), then 5 mL of tris(2-aminoethyl)amine was added and refluxed for 24 hours. These particles were washed with 10 mL ethanol and dried at room temperature. Functionalization by tris(2-aminoethyl)amine was confirmed by SEM photograph (Figure 1), IR spectroscopy, and elemental analysis. The average size of these nanoparticles calculated to be around 50 nm according to SEM photograph (Figure 1). A schematic model for synthesis of TREN-Fe_3O_4 is shown in Figure 2.
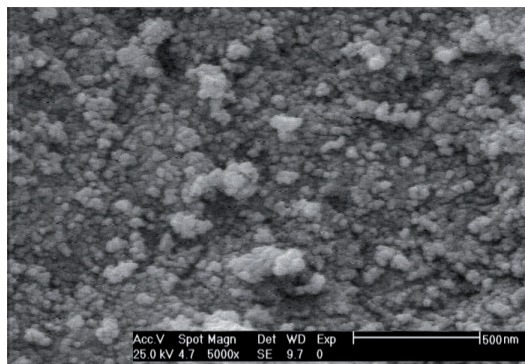

FIGURE 1: SEM micrograph of TREN-functionalized Fe_3O_4 nanoparticles.

IR spectroscopy confirmed the functionalization with following results (KBr, cm^{-1}): 3445 (NH), 2913 (CH, aliphatic), 1068 and 584 (Fe_3O_4). Elemental analysis of TREN-Fe_3O_4 sample gave a tris(2-aminoethyl)amine concentration of $0.92 \, mmol \, g^{-1}$ (C: 9.96, H: 2.13, N: 5.14%). As the Fe_3O_4 nanoparticles and Si atoms would not decompose in elemental analysis, so the burning part is this formula: $C_9H_{24}N_4$. Considering the results, the TREN loading is calculated to be $0.92 \, mmol \, g^{-1}$. The thermal stability of this sorbent has been investigated by TGA/DTA analysis. The results show that this sorbent is stable up to $300°C$ (Figure 3).

2.2. Apparatus.

A Shimadzu (Kyoto, Japan) Model AA-670G atomic absorption spectrometer equipped with a GFA-4A graphite furnace atomizer, an ASC-60G autosampler and a circulating cooling unit were employed. To correct the nonspecific absorbance, deuterium lamp background correction was used. The operating conditions of hollow cathode lamps and graphite furnace temperature programs for gold and silver are mentioned in Table 1. Pyrolytically coated graphite tubes were used. Argon 99.999% (Roham gas Co., Tehran, Iran), with a flow rate of $1.5 \, L \, min^{-1}$, was applied as a protective and purge gas. The measurements were performed in the peak height mode which was preferred over peak areas. A PreeKem WX-3000 microwave digestion system has been used for sample digestion. The specific surface area was measured using a Micrometritics ASAP 2010 analyzer. The thermal analysis was performed using a BAHR-Thermoanalyse GmbH (Germany) employing heating at rates of $10°C \, min^{-1}$ in air atmosphere.

2.3. Procedure

2.3.1. Preconcentration Method.

In two separated 250 mL-stoppered-glass bottle, 100 mL of solutions containing $1 \, \mu g \, mL^{-1}$ of Au(III) or Ag(I) ions were prepared. The pHs were adjusted to 2 and 8 for Au(III) and Ag(I) ions, respectively. Then, 0.01 g of sorbent was added to each solution and the mixtures were shaken for 5 min. Subsequently, TREN-Fe_3O_4 NPs were isolated by placing
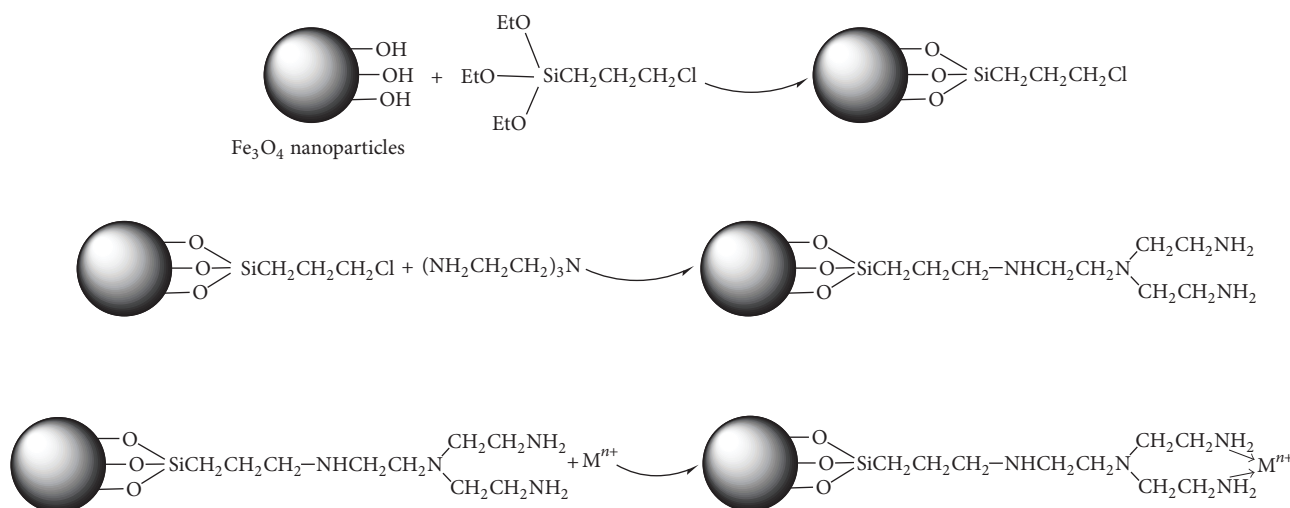
Figure 2: A schematic model for synthesis of TREN-functionalized Fe_3O_4 nano-particles.

Table 1: The operating conditions for silver and gold hollow cathode lamps and graphite furnace temperature program.

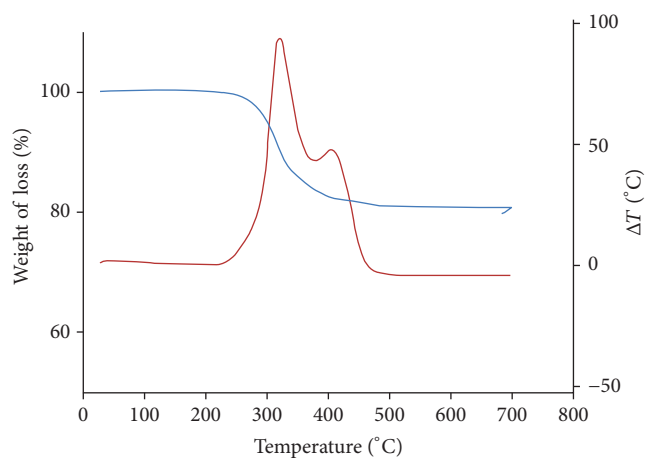| Stage	Temprature/°C		Time/s				Argon gass flow rate/L min^{-1}	
			Ramp		Hold			
	Ag	Au	Ag	Au	Ag	Au	Ag	Au
Drying	300	300	20	20	10	10	1.5	1.5
Atomization	1800	2400	0	0	4	6	0.0	0.0
Cleaning	2650	2650	1	1	3	3	1.5	1.5

Figure 3: TG and DTA curves of TREN-functionalized Fe_3O_4 nanoparticles.

a strong magnet and the supernatant was separated. The silver and gold ions desorbed from Fe_3O_4 NPs by relative eluents (2 mol L^{-1} HCl and 0.1 mol L^{-1} thiourea in 1 mol L^{-1} H_2SO_4 for silver and gold ions, resp.) and the amounts of them in concentrated solution were determined by ETAAS.

2.3.2. Sample Preparation. Distilled water, tap water (Tehran, Iran) and river water (Babolrud River, Babol, Iran) were used as water samples. They were collected in cleaned polyethylene bottles and were filtered through a 0.45 μm pore size nylon filter (Millipore) just after sampling. The method was validated using three reference materials with a certified gold and silver content. The standard materials were digested with 6 mL of HCl (37%) and 2 mL of HNO_3 (65%) in a microwave digestion system. Digestions were carried out for 2 min at 250 W, 2 min at 0 W, 6 min at 250 W, 5 min at 400 W, 8 min at 550 W, and then venting for 8 min. The digestion residues were then diluted with deionized water. Finally, this method was applied to separate and preconcentrate silver and gold ions from the solution samples.

2.3.3. Kinetic Experiments. Kinetic studies were performed by shaking the 0.01 g of TREN-Fe_3O_4 into the solution containing 1 μg mL^{-1} of Au(III) or Ag(I) ions in pHs 2 and 8, respectively. Then, the sorbent was isolate from the solution at various time intervals and the silver or gold ions desorbed from Fe_3O_4 NPs by the relative eluents (2 mol L^{-1} HCl and 0.1 mol L^{-1} thiourea in 1 mol L^{-1} H_2SO_4 for silver and gold ions, resp.) and the their concentrations were determined by ETAAS.

3. Results and Discussion

In order to obtain quantitative recoveries of the silver and gold ions on TREN-Fe_3O_4, the others separation procedure was optimized for various analytical parameters such as pH, eluent type and volume, matrix effects, among others.
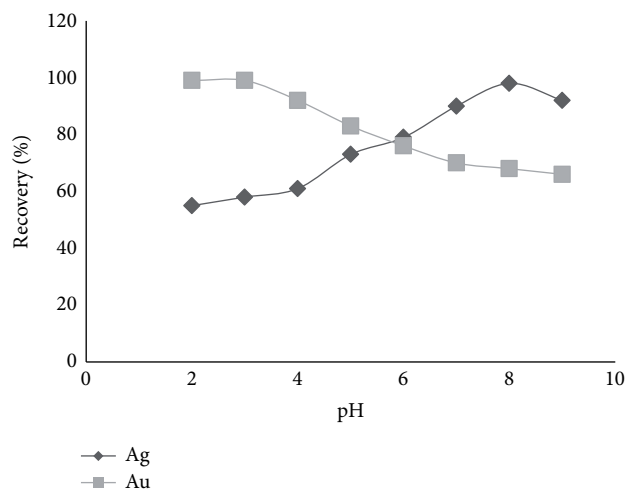
Figure 4: Effect of pH of sample solution on percent recovery of Ag(I) and Au(III) by TREN-Fe$_3$O$_4$. Conditions: Ag concentration, 1 mg L^{-1}; sample volume, 100 mL; eluent, 7 mL of HCl 2 mol L^{-1} solution. Au concentration, 1 μg mL^{-1}; sample volume, 100 mL; eluent, 8 mL of 0.1 mol L^{-1} thiourea in 1 mol L^{-1} H$_2$SO$_4$ solution.

The adsorbed ions on TREN-Fe$_3$O$_4$ nano-particles were calculated from the amounts of silver/gold ions in the starting sample and the amounts of silver/gold in the final solution.

3.1. Influences of pH.

Since pH of the sample is an important factor in solid phase extraction studies, the influence of pH of the analyte solutions on the recoveries of Ag(I)/Au(III) was investigated in the pH range 1.0–9.0. In this approach, the preconcentration method has been applied in different pHs and the recoveries were collected. As the results show, quantitative recovery (>98%) of silver and gold ions was observed in pH of 8.0–9.0 and 2.0–3.0, respectively (Figure 4.). It can be concluded that in acidic pHs, the amine groups will be protonated and the electrostatic interaction between H$^+$ and AuCl$_4^-$ cause gold adsorption. In contrast, Ag$^+$ ions could not be adsorbed in this pH. For silver adsorption, the mechanism is different as the amine group should coordinate to silver ions. By increasing the pH, the coordination ability of amine groups will increase and the recovery will be increase (up to 8.0). In high alkaline pHs, the silver hydroxide will be precipitate so the recovery will be reduced. So all the rest studies were carried out at pH 8.0 by using Na$_2$HPO$_4$/NaH$_2$PO$_4$ buffer solution for silver ions and at pH 2.0 by using a mixture of Na$_3$C$_3$H$_5$O(CO$_2$)$_3$/HCl (trisodium citrate/hydrochloric acid) solutions for gold ions.

3.2. Eluent Type and Volume.

Various eluent solutions were tested for desorption of silver or gold ions from TREN modified Fe$_3$O$_4$ nano-particles. For these studies, 0.01 g of sorbent was introduced to 100 mL of a solution containing 1 μg mL^{-1} of Au(III) or Ag(I) ions and shaken for 5 min. Subsequently, the sorbent was isolated by magnet and the silver or gold ions desorbed from Fe$_3$O$_4$ NPs by 10 mL of each eluents and the amounts of them in eluent were determined

Table 2: Effect of type of eluent on percent recovery of Ag(I) and Au(III) by TREN-Fe$_3$O$_4$.

Eluent	Ag recovery, %	Au recovery, %
H$_2$SO$_4$ 0.1 M	43.5	51.2
H$_2$SO$_4$ 0.5 M	48.7	59.7
H$_2$SO$_4$ 1 M	56.4	72.5
HCl 0.1 M	59.2	65.4
HCl 0.5 M	64.8	68.3
HCl 1 M	97.0	81.6
HCl 2 M	98.5	84.1
Thioacetamide 0.1 M + HCl 0.1 M	83.2	67.7
Thiourea 0.1 M + HCl 0.1 M	95.2	86.9
Thiourea 0.1 M + H$_2$SO$_4$ 0.1 M	95.3	97
Thiourea 0.1 M + H$_2$SO$_4$ 1 M	97.0	99.0

Conditions—Ag: 1 μg mL^{-1}; sample volume: 100 mL; pH: 8.
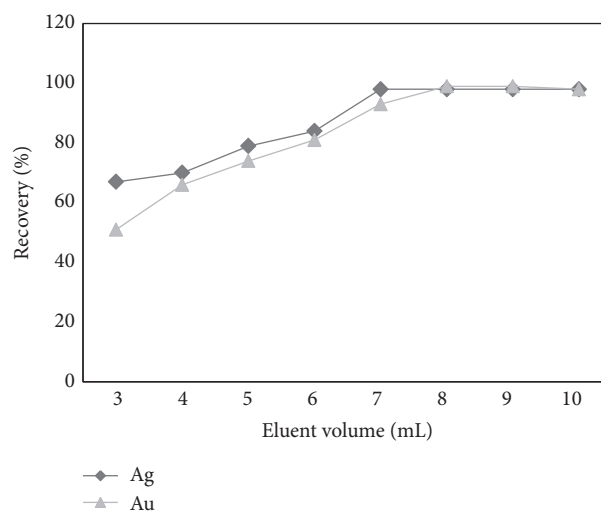Au: 1 μg mL^{-1} sample volume: 100 mL; pH: 2.

Figure 5: Effect of eluent volume on the percent recovery of Ag(I) and Au(III) by TREN-Fe$_3$O$_4$. Conditions: Ag concentration: 1 mg L^{-1}; sample volume, 100 mL; pH = 8; eluent, HCl solution (2 mol L^{-1}); Au concentration, 1 μg mL^{-1}; pH, 2; sample volume, 100 mL; eluent, Solution of 0.1 mol L^{-1} thiourea in 1 mol L^{-1} H$_2$SO$_4$.

by ETAAS. As the results show, quantitative recoveries for silver ions were obtained by 2 mol L^{-1} HCl, and the best eluent for gold ions was chosen to be 0.1 mol L^{-1} thiourea in 1 mol L^{-1} H$_2$SO$_4$ (Table 2).

The effect of eluent volume on the recoveries of the silver/gold ion extraction was also studied by using different volumes of selected eluents; as the results in Figure 5 show, the quantitative recoveries of silver and gold ions were obtained by 7.0 and 8.0 mL of eluent.

3.3. Effect of Shaking Time on Adsorption of Metal Ions.

In this order, 0.01 g of sorbent was introduced to 100 mL of a solution containing 1 μg mL^{-1} of Au(III) or Ag(I) ions, and it was shaken for different times interval. Then, the sorbent was isolated by magnet and the silver and gold ions were desorbed

TABLE 3: The tolerance limit of the diverse ions on the determination of silver and gold ions.

Interfering ions	Tolerable concentration for AgX/Ag	Recovery, %	Tolerable concentration for AuX/Au	Recovery, %
Na^+	2000	97.2	2000	98.3
K^+	1800	95.7	2000	98.7
Cs^+	1200	96.3	1500	98.9
Ca^{2+}	950	98.2	1200	98.1
Mg^{+2}	800	96.7	1000	98.6
Cd^{2+}	450	96.8	900	98.9
Ni^{+2}	50	97.2	100	97.8
Cu^{+2}	100	98.3	500	98.4
Cr^{+3}	125	98.4	400	96.8
Fe^{+2}	350	95.3	750	95.6
Pt^{2+}	10	93.5	5	95.1
Pd^{2+}	5	94.7	10	94.2
Zn^{+2}	100	98.1	200	96.7
Hg^{2+}	500	96.8	100	97.2

Conditions—Ag concentration, $1\,\mu g\,mL^{-1}$; pH: 8; sample volume: 100 mL; eluent: 7 mL of HCl $2\,mol\,L^{-1}$ solution.
Au concentration, $1\,\mu g\,mL^{-1}$; pH: 2; sample volume:100 mL; eluent: 8 mL of $0.1\,mol\,L^{-1}$ thiourea in $1\,mol\,L^{-1}$ H_2SO_4 solution.
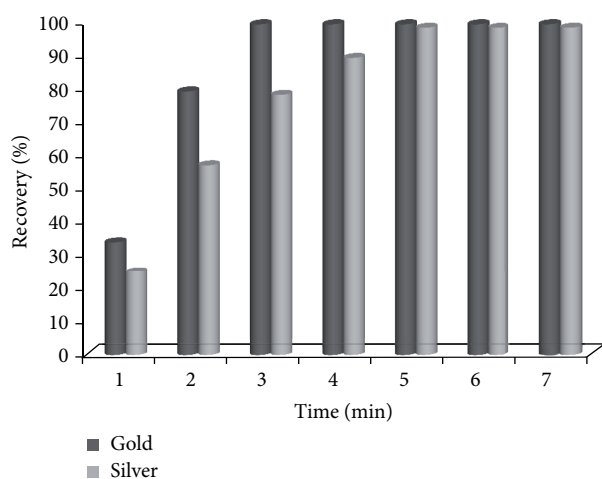

FIGURE 6: Effect of stirring time on the percent recovery of Ag(I) and Au(III) by TREN-Fe_3O_4. Conditions: Ag concentration: $1\,mg\,L^{-1}$; sample volume, 100 mL; pH = 8; eluent, 7 mL of HCl $2\,mol\,L^{-1}$ solution; Au concentration, $1\,\mu g\,mL^{-1}$; pH, 2; sample volume, 100 mL; eluent, 8 mL Solution of $0.1\,mol\,L^{-1}$ thiourea in $1\,mol\,L^{-1}$ H_2SO_4.

from Fe_3O_4 NPs by relative eluents and the amounts of them in concentrated solution were determined by ETAAS. The results show that the recoveries of gold and silver ions had no obvious increase after 3 and 5 min, respectively (Figure 6). Thus, 5 min were chosen as the time of the preconcentration of silver and gold ions in subsequent experiments.

3.4. Influence of Matrix Ions.
The influence of different cationic matrix ions found in real samples was studied on adsorption of silver and gold ions. For this purpose, different concentrations of Na^+, K^+, Cs^+, Ca^{2+}, Mg^{2+}, Cd^{2+}, Ni^{2+}, Cu^{2+}, Fe^{2+}, Pt^{2+}, Pd^{2+}, Zn^{2+}, Hg^{2+}, and Cr^{+3} were dissolved

in 100 mL solution containing $0.001\,mg\,L^{-1}$ of silver(I) or gold(III) ions. The pHs were adjusted to 2 and 8 for Au(III) and Ag(I) ions, respectively. Then, 0.01 g of sorbent was added to each solution and shaken for 5 min. Then, the sorbent was isolated by magnet and the silver and gold ions desorbed from sorbent by relative eluents. Then, the amounts of them in eluent were determined by ETAAS and the results are listed in Table 3. As the results show, this sorbent is selective for gold adsorption in pH = 2 and selective toward silver ions in pH = 8. This phenomenon could be explained by hard and soft acid and base (HSAB) theory and also the pH adsorption mechanism which mentioned before. By changing the pH, the amine groups become soft or hard which have different affinity for gold or silver ions. Moreover, in acidic pHs, amine group will be protonated which make an ion pair with gold ions which exist in $AuCl_4^-$ forms.

3.5. Maximum Adsorption Capacity.
In order to obtain the maximum adsorption capacity, 100 mg of TREN-Fe_3O_4 was added to 500 mL aqueous solution containing 100 mg of silver or gold ions. After 5 min, the sorbent was separated, washed with distilled water and the ions were eluted with relative eluents and their concentrations were determined using ETAAS. The maximum capacities of TREN-Fe_3O_4 nano-particles, obtained in three parallel works, were found to be $97.3\,mg\,g^{-1}$ and $167\,mg\,g^{-1}$ for silver and gold solutions, respectively.

3.6. Figures of Merit.
In order to determine the detection limit of this method, 0.01 g of TERN-Fe_3O_4 was introduced to 500 mL of a blank solution ($n = 10$) under the optimum experimental conditions. The LOD values for silver and gold ions on TERN-Fe_3O_4 nanoparticles are $0.8\,ng\,mL^{-1}$ and $0.5\,ng\,mL^{-1}$, respectively. The results are obtained from $C_{LOD} = K_b S_b / m$ where $k_b = 3$ [22]. The LOD values for solid materials were evaluated by digestion of

TABLE 4: The optimum conditions for extraction of gold and silver ions.

Analyte	Adsorption pH	Eluent type and concentration	Elunet volume (mL)	Adsorption time (min)
Silver	8.0	$2 \, mol \, L^{-1}$ HCl	7.0	5.0
Gold	2.0	$0.1 \, mol \, L^{-1}$ thiourea in $1 \, mol \, L^{-1}$ H_2SO_4	8.0	3.0

TABLE 5: A comparison between the analytical performance of this method with similar methods.

Solid-phase	Ion	PF	LOD ($ng \, mL^{-1}$)	Reference
2-mercaptobenzothiazole-silica gel	Ag	300	NR	[23]
diethyldithiocarbamate PTFE	Ag	110	20	[24]
TREN-Fe_3O_4	Ag	142	0.8	This work
Dowex M-4195 chelating resin	Au	31	1.61	[25]
Amberlite XAD-2000/DDTC	Au	200	16.6	[26]
pentathia-15-crown-5 modified Octadecyl silica	Au	200	1.0	[15]
TREN-Fe_3O_4	Au	125	0.5	This work

TABLE 6: Data of real sample analysis for Ag and Au on TREN-Fe_3O_4.

	Unit	Real sample		Added		Found		Recovery, %	
		Ag	Au	Ag	Au	Ag	Au	Ag	Au
Distilled water	$ng \, mL^{-1}$	ND	ND	50.0	50.0	49.3	48.3	98.6	96.6
Tap water	$ng \, mL^{-1}$	ND	ND	50.0	50.0	50.8	49.3	101.6	98.6
Sea water	$ng \, mL^{-1}$	ND	ND	50.0	50.0	50.9	50.1	101.8	100.2
River water	$ng \, mL^{-1}$	ND	ND	50.0	50.0	48.9	50.8	97.8	101.6
SRM 2711	$\mu g \, mg^{-1}$	4.70	0.13	0.00	0.00	4.50	0.12	95.7	92.3
SRM 2781	$\mu g \, mg^{-1}$	94.20	0.070	0.00	0.00	91.8	0.064	97.4	91.4
NCS DC 73323	$\mu g \, mg^{-1}$	4.40	0.260	0.00	0.00	4.46	0.254	101.4	97.7

ND: not detected.

blank solid materials ($n = 10$). The LOD values for silver and gold ions on TERN-Fe_3O_4 nano-particles are $2.1 \, ng \, g^{-1}$ and $1.3 \, ng \, g^{-1}$, respectively. The linear range for silver and gold were $1.5–1000 \, ng \, mL^{-1}$ and $1.0–1000 \, ng \, mL^{-1}$ respectively.

The precision of the method under the optimum conditions was determined by performing ten replicates. The recoveries were found to be $98.5 \pm 1.0\%$ and $99.0 \pm 1.5\%$ for Ag and Au ions on TERN-Fe_3O_4 nano-particles, respectively. Also, as the breakthrough volume is 1000 mL, the preconcentration factors were found to be 142 and 125 for silver and gold ions, respectively.

The optimum conditions for the extraction are listed in Table 4. A comparison between the analytical performances of this method with similar methods is presented in Table 5. Although in some cases the sorbent has less preconcentration factor which is its weakness, but possibility of easy separation and lower detection limits is the advantages of this work.

3.7. Validation of the Method. Three certified reference materials SRM 2711, SRM 2781, and NCS DC 73323 were used to validate this method. As it can be seen in Table 6, good correlations were obtained between the estimated contents and certified content using this method. Therefore, TREN-Fe_3O_4 nano-particles could be used as a promising solid phase for extraction and determination of silver and gold ions in aqueous samples. Moreover, the results indicate that the proposed method for Ag and Au ions determination is not affected by matrix elements of the analyzed samples.

3.8. Sorbent Reusability. The reusability of this magnetic sorbent was investigated by subsequent sorption and elution cycles for gold ions. In this approach, 0.01 g of sorbent was introduced to 100 mL of a solution containing $1 \, \mu g \, mL^{-1}$ of Au(III) in pH = 2. After shaking for 5 min, the sorbent was isolated by magnet and the gold ions was eluted from Fe_3O_4 NPs by 8 mL of $0.1 \, mol \, L^{-1}$ thiourea in $1 \, mol \, L^{-1}$ H_2SO_4 and the gold concentrations were determined by ETAAS. The results show that there is no significant decrease in gold ions recovery (less than 10%) after 8 adsorption-desorption cycle.
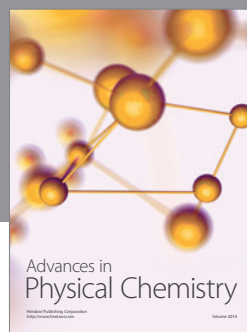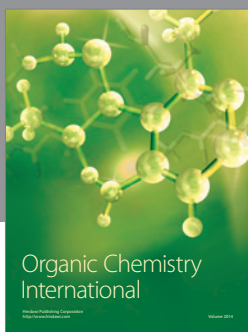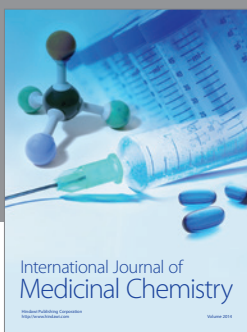
4. Conclusion

High selectivity and accuracy of the proposed method have made it a suitable and selective method for extraction and preconcentration of silver and gold ions from aqueous solutions by changing pH. The simplicity of Fe_3O_4 modification with the TREN ligand group, easy separation, and the high capacity factor improves the application of this compound as special unique solid phase for magnetic solid phase for gold and silver extraction. Comparing to the reported

procedures, this method has lower detection limit and is more conventional (easy sorbent separation by magnet), however, its preconcentration factor is lower than some methods.

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