

Adsorption Selectivity and Dynamic Adsorption Behaviors of Cu(II), Ag(I), and Au(III) on Silica Gel Encapsulated by Amino Functionalized Polystyrene

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Received 29 November 2008; accepted 11 February 2010

DOI 10.1002/app.32321

Published online 12 May 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Adsorption of precious metal ions from aqueous solutions has earned great concern recently due to environmental protection factor and the value of precious metals. In this article, a novel adsorbent silica gel microspheres encapsulated by amino functionalized polystyrene (SG-PS-NH₂) has been synthesized, and the adsorption selectivity and the dynamic adsorption properties of SG-PS-NH₂ for Cu(II), Ag(I), and Au(III) has been investigated. The results displayed that SG-PS-NH₂ had excellent adsorption for Au(III)/Ag(I) in binary ion systems, especially in the systems of Au(III)-Zn(II), Au(III)-Ni(II), and Ag(I)-Zn(II). The dynamic adsorption showed that the adsorption capacities of SG-PS-NH₂ for Cu(II), Ag(I), and Au(III) increased with the prolonging of contact time, and the affinity order of three metal ions adsorbed by SG-PS-NH₂ is Au(III) > Ag(I) > Cu(II), which is inversely correlated with

their electronegativities. The regeneration capacities of SG-PS-NH₂ were investigated by using the eluent solution of 0.5% thiourea in 1 mol/L HCl, and it is found that the changes of the adsorption capability are relatively small after several cycles of adsorption-desorption. Thus, silica gel encapsulated by polystyrene containing amino groups (SG-PS-NH₂) is favorable and useful for the removal of precious metal ions because it is eco-friendly and easier to reuse. The comparison of SG-PS-NH₂ with other adsorbents suggests that SG-PS-NH₂ have great potential applications in environmental protection and the recovery of precious metals. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 3645–3650, 2010

Key words: composites; core-shell polymer; adsorption; polymer-encapsulated inorganic materials; silica gel encapsulated by amino functionalized polystyrene

INTRODUCTION

Due to the specific physical and chemical properties of precious metals, they are widely used in the field of industry and medicine etc. It is very necessary to treat the waste aqueous solutions and try to recover them economically just because of the value and scarcity of precious metal such as gold and silver. Because of the reasons mentioned above and the increasing applications of precious metals, the relevant wastewater treatment has earned great concern recently. Many treatment processes, such as chemical precipitation, electro dialysis, reverse osmosis, ion

exchange, adsorption, are currently used. Among these methods, adsorption is highly effective and economical, and is a promising and widely applied method.^{1,2} Consequently, effective adsorbents with strong affinities and high loading capacity for the targeted precious metal ions were subsequently prepared by functionalizing the surface of various substrates, such as chemical modification of silica-gel, chitosan resin,^{3–6} etc. These adsorbents exhibited enhanced sorption toward heavy metals because of the specific affinity of heavy metals and complex groups on the adsorbent surfaces. However, the thermal and chemical stability of such hybrid adsorbents still needs further improvement.

Recently, polymer-encapsulated inorganic particles offer very interesting and potential applications, and may have prominent properties in areas such as adsorbents, optics, and electronics.⁷ Among the inorganic oxides, silica gel is widely used as inorganic solid matrix in inorganic-organic composite materials due to its excellent thermal and mechanical stability, unique large surface area and well-modified surface properties.^{8,9} The silica gel-polymer composite materials have received a great deal of attention recently because of their excellent performance in the field of chromatography, adsorption, catalysis.^{10,11} Li et al.¹² reported the spherical hybrid silica particles from

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Contract grant sponsor: Nature Science Foundation of Shandong Province; contract grant number: ZR2009FM075.

Contract grant sponsor: Promotional Foundation for the Excellent Middle-Aged and Young Scientists of Shandong Province of China; contract grant number: 2007BS08027.

Contract grant sponsor: Basic Project of Educational Bureau of Shandong Province of China; contract grant number: J07YA16.

Contract grant sponsor: Foundation of Innovation Team Building of Ludong University; contract grant number: 08-CXB001.

Journal of Applied Polymer Science, Vol. 117, 3645–3650 (2010)
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hydrolysis of tetraethoxysilane and vinyltriethoxysilane as the precursors using NH_4OH as catalyst, and the silica particles were subsequently encapsulated with a layer of PS-DVB, a polymeric mixture of styrene and divinylbenzene. The encapsulated packing was used as stationary phases in capillary electrochromatography, and displayed high column efficiencies. Bourgeat-Lami and Lang conducted polymer encapsulation of silica particles, using dispersion polymerization of styrene in aqueous ethanol medium, and investigated effect of silica size and concentration on the morphology of composite particles.^{13,14}

In this work, we explored the synthesis of silica gel microspheres encapsulated by amino functionalized polystyrene(SG-PS-NH₂) hybrid adsorbent for removal of Cu(II), Ag(I), and Au(III) from aqueous solutions. The adsorption selectivity, the dynamic adsorption properties and regeneration of this novel silica gel matrix inorganic-organic composite material SG-PS-NH₂ for Cu(II), Ag(I), and Au(III) has been investigated.

EXPERIMENTAL DETAILS

Materials, instruments, and preparation

Silica gel spheres (100–200 mesh) were obtained from Qingdao Marine Chemical Plant. All reagents were of analytical grade and used without further purification. Aqueous solutions containing various metal ions at a certain concentration (10^{-2} – 10^{-3} M) were prepared from metal salts, and the relative metal salts include manganese nitrate, nickel nitrate, zinc nitrate, lead nitrate, copper nitrate, silver nitrate, and chloroauric acid.

IR spectrum (KBr pellets) was recorded on a Magna-IR 550(series II) Fourier transform spectrometer, Nicolet. Thermogravimetric analysis (TG) was recorded on a Netzsch STA 409, Test conditions: type of crucible, DTA/TG crucible Al_2O_3 ; nitrogen atmosphere, flow rate 30 mL/min; heating rate: 10 K/min. A GBC-932 atomic adsorption spectrophotometer made in Australia was used, and all measurements were carried out in an air/acetylene flame.

The activation of silica-gel and the preparation of silica gel encapsulated by polystyrene containing amino (SG-PS-NH₂) are demonstrated in Refs. 15 and 16, the whole synthetic procedure includes activation of SG, syntheses of SG-C=C, SG-PS, SG-PS-NO₂, and SG-PS-NH₂.

Activation of silica-gel (SG)

Silica gel spheres were activated by refluxing with 50% v/v aqueous solution of nitric acid for 6 h followed by a 6 h reflux with 12M HCl, cooled and repeatedly washed using distilled water until there

were no Cl^- ions. Then the product was dried in vacuum at 120°C for 48 h before use.

Synthesis of SG-C=C

A suspension of 50.0 g of activated silica-gel and 50 mL vinyl triethoxysilane (VTES) were stirred at room temperature in 200 mL toluene solution for 12 h, first in an argon atmosphere for 30 min and then in ammonia atmosphere for the remaining time. The product was then filtered off, washed by ethyl alcohol several times, and transferred to a Soxhlet extraction apparatus for reflux-extraction in ethanol for 10 h. The solid product was dried in vacuum at 50°C, and it was referred to as SG-C=C.

Synthesis of SG-PS

Under argon atmosphere, a mixture of 50.0 g SG-C=C, 50 mL Styrene (St), 0.90 g polyvinyl pyrrolidone (PVP), 50 mL distilled water and 20 mL ethyl alcohol were added to a 1000 mL flask. The mixture was stirred for 3 h, and then heated to 70°C. The alcohol solution of azobisisobutyronitrile (AIBN), which was recrystallized by ethyl alcohol, was added into the flask dropwise within 90 min, and the reaction was conducted for 6 h. The solid product was repeatedly boiled with toluene, filtered whilst hot, and then extracted for 10 h by toluene and ethyl alcohol successively. The intermediate product silica gel encapsulated by polystyrene was dried under vacuum at 50°C and it was referred to as SG-PS.

Synthesis of SG-PS-NO₂

Ten gram of SG-PS and 80 mL concentrated nitric acid were added into a 250 mL flask, and concentrated sulfuric acid was slowly dropped with quick stirring at the temperature below 15°C. After dropping, the reaction was conducted for 12 h at 30°C. The solid intermediate product silica gel encapsulated by polystyrene containing nitro was washed with distilled water until pH value of the filtrate reached 7, dried at 80°C, and it was referred to as SG-PS-NO₂.

Synthesis of SG-PS-NH₂

Concentrated hydrochloric acid (100 mL) was put into a 250 mL flask, which was heated to 60°C. 20 g small Sn particles and 5.0 g SG-PS-NO₂ were added successively, and the reaction was carried out for 24 h at 100°C. The solid product was washed with distilled water, 10% (m/V) NaOH solution, distilled water successively until the liquid washed down reach neutral, then washed with ethyl alcohol. The intermediate product silica gel encapsulated by polystyrene containing amino groups was dried under

vacuum at 36°C for 10 h, and the final product was referred to as SG-PS-NH₂.

Adsorption selectivity of Au(III) and Ag(I) in binary ion systems

Adsorption experiments were carried out using batch method in a thermostat-cum-shaking assembly. Only binary ion systems of Au(III) and Ag(I) were studied for adsorption on SG-PS-NH₂ as it has higher adsorption capacities for these ions than Cu(II). To investigate the competitive adsorption of Au(III), Ag(I), Zn (II), Ni(II), Mn(II), and Pb (II) by SG-PS-NH₂, 0.050 g of the adsorbent was shaken with 20 mL of solution containing metal ions with the concentration of 2.0 mmol/L for 5 h [binary ion systems include: Au(III)-Zn(II), Au(III)-Ni(II), Au(III)-Pb(II), Au(III)-Cu(II) at pH: 2.8 for Au(III)-containing system; Ag(I)-Cu(II), Ag(I)-Zn(II), Ag(I)-Pb(II), Ag(I)-Mn(II) at pH: 5.0 for Ag(I)-containing system]. Then, after centrifugalization, 4 mL solution was taken out and put in 25 mL tube, and the distilled water was put in until the whole volume was 25 mL, and the concentrations of metal ion solution were determined on a GBC-932 atomic adsorption spectrophotometer. Adsorption amount (*Q*) was calculated according to the eq. (1),

$$Q(\text{mmol/g}) = (C_0 - C)V/W \quad (1)$$

where *C*₀ and *C* are the concentration of metal ions before and after sorption (mmol/L), respectively; *V* is the volume of the solution used for sorption (L); and *W* is the weight of the sample SG-PS-NH₂ (g).

Dynamic adsorption of SG-PS-NH₂ for Cu(II), Ag(I) and Au(III)

Column method was employed on the Flow Injection Analysis Processor to determine the dynamic adsorption behaviors of SG-PS-NH₂ for Cu(II), Ag(I), and Au(III). 0.05 g SG-PS-NH₂ was packed in a glass microcolumn by slurry method. 4.54 μg/mL Cu(II) containing solution, 5.35 μg/mL Ag(I) containing solution and 8.02 μg/mL Au(III) containing solution was passed through the microcolumn with a constant flow rate of 1.25 mL/min, respectively. The effluent fraction was collected every 1–5 min and its concentration was determined by atomic adsorption spectrophotometer. Equilibrium was reached when the concentration of the effluent fraction was equal to the initial concentration. The amounts of Cu(II), Ag(I), Au(III) adsorbed *Q* (mmol/g) were calculated according to the equation (2),

$$Q = \sum_{i=1}^n \left(\frac{(C_0 - C_i)vt}{Mm} \right) \quad (2)$$

where *C*₀ is the initial concentration (μg/mL), *C*_{*i*} is the concentration of metal ion in the effluent (μg/mL); *v* is the flow rate of solution passing through the column (mL/min); *t* is the time of collecting the effluent (min); *M* is the molar mass of the metal ion (g/mol); *m* is the mass of SG-PS-NH₂ (mg).

Regeneration of SG-PS-NH₂

The solution of 0.5% thiourea in 1 mol/L HCl was employed as the desorption medium, and the desorption of metal ions was investigated by the following procedure: the metal ions loaded SG-PS-NH₂ was soaked in the solution of 0.5% thiourea in 1 mol/L HCl for 12 h, and washed until the filtrate became neutral. The sample was then soaked in hydrochloric acid for 5 h, and washed until the filtrate became neutral. After it was soaked in sodium hydroxide for 5 h, it was washed with distilled water and dried. The treated sample was used to adsorb metal ions, and detected the metal ion adsorption capacity.

RESULTS AND DISCUSSION

The synthetic route of SG-PS-NH₂ was shown in Figure 1, and it included the steps of activation of SG, syntheses of SG-C=C, SG-PS, SG-PS-NO₂, and the final product SG-PS-NH₂. In this synthesis, silanol groups on the silica surface were mainly “initiator site,” which readily react with silane coupling agent to introduce surface functional groups. Therefore, in the process of activation of silica gel, nitric acid, and hydrochloric acid treatment before use are very necessary because the acidification process could increase obviously the content of silanol groups on the surface of SG. The C=C content of SG-C=C was detected by titration with Na₂S₂O₃ solution according to the method described in Ref. 15, and the

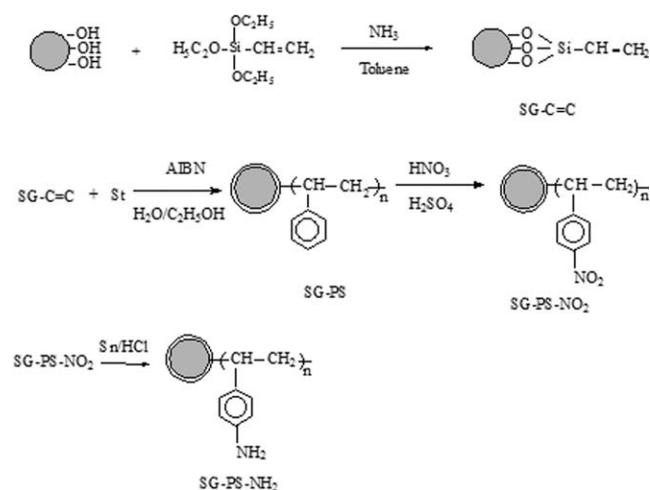


Figure 1 The synthetic route of SG-PS-NH₂.

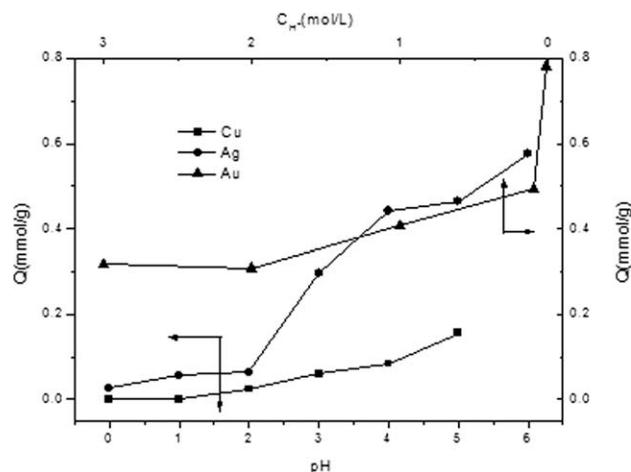


Figure 2 The effect of acid concentration on the adsorption of SG-PS-NH₂ for Cu(II), Ag(I), and Au(III).

result was 1.82 mmol/g. The $-NH_2$ content of SG-PS-NH₂ was detected by back titration with NaOH solution according to the method described in Ref. 15, and the result was 2.04 mmol/g. The Infrared spectra of SG-PS-NH₂ displays the presence of vibrational bands characteristic of amino group, the stretching vibrations (1677 cm^{-1}) and the in-plane bending vibration ($1640\text{--}1560\text{ cm}^{-1}$) of the N—H bonds relatively widen the peak at 1623 cm^{-1} . By comparison with the curve of SG-PS-NO₂, the bands at 1520 cm^{-1} and 1350 cm^{-1} almost disappeared, indicating that the nitro groups decreased, and were changed to the amino groups. TGA of SG-PS-NH₂ showed that the temperature of thermal decomposition of the organic lay in the final product SG-PS-NH₂ was about 341°C , and the relative weight loss was 25.01%.

The introduction of the amino groups onto the composite material can make this composite material form the stable chelating compounds with many transition metal ions. The aim of encapsulation of functionalized polystyrene is to make a composite material having excellent coordination properties with metal ions and to obtain novel adsorbent with high loading of metal ions. Through the amino groups, SG-PS-NH₂ can form the stable chelating compounds with many transition metal ions, especially with Au(III) and Ag(I). According to the theory of hard and soft acids and bases (HSAB) defined by Pearson, metal ions will have a preference for complexing with ligands that have more or less same electronegative donor atoms. Chelating agents with N groups are highly efficient for the selective sorption of precious metal ions.

The pH affects to the adsorption capacity of the absorbent was shown in Figure 2, and it showed the effect of solution acidity on the adsorption of SG-PS-NH₂ for Cu(II), Ag(I) and Au(III) metal ions. Obvi-

ously, the adsorption capacity showed a growing trend with the decrease of acidity in the range of pH = 0.0–6.0 when nitric acid was used as medium. It may be attributed to the protonation of N of SG-PS-NH₂ under strong acidic conditions resulting thereby decrease in its coordination capacity and hence decrease in its adsorption capacity.

The competitive adsorption of Au(III)-Zn(II), Au(III)-Ni(II), Au(III)-Pb(II), Au(III)-Cu(II), Ag(I)-Cu(II), Ag(I)-Zn(II), Ag(I)-Pb(II), and Ag(I)-Mn(II) binary systems on SG-PS-NH₂ were studied. The initial gold/silver concentration as well as other divalent ions such as Zn(II), Ni(II), Pb(II), Mn(II), and Cu(II) was 2.0 mmol/L. The obtained results for gold/silver adsorption at room temperature are presented in Table I. It is clear that SG-PS-NH₂ has excellent adsorption for Au(III), especially in the systems of Au(III)-Zn(II) and Au(III)-Ni(II). In these two binary ion systems, the selectivity coefficient is 42.2 and 20.6, respectively. In four binary ion systems of Ag(I)-Cu(II), Ag(I)-Zn(II), Ag(I)-Pb(II), and Ag(I)-Mn(II), the sample has a certain adsorption selectivity for Ag(I). In particular, the selectivity coefficient of Ag(I)-Zn(II) is 54.0. Thus, this novel composite material with core-shell structure (silica gel encapsulated by polystyrene containing amino groups, SG-PS-NH₂) has good adsorption properties and high capacity for Au(III) and Ag(I) and can be applied for the preconcentration and purification of these precious elements from aqueous solutions. Kavakli et al. reported the synthesis of a novel adsorbent 1,5,9,13-tetrathiacyclohexadecane-3,11-diol anchored poly(*p*-CMS-DVB), and they found that selectivity of the modified microbeads followed the order Au(III) > Ag(I) > Pd(II) > Pt(II) below pH = 2.¹⁷

TABLE I
The Adsorption Selectivity of SG-PS-NH₂ for Au(III) and Ag(I) in Binary Ion Systems

System	Metal ions	Adsorption capacity (mmol/g)	Selective coefficient
Au(III)-Zn(II)	Au(III)	0.211	42.2
	Zn(II)	0.005	
Au(III)-Ni(II)	Au(III)	0.103	20.6
	Ni(II)	0.005	
Au(III)-Pb(II)	Au(III)	0.214	2.46
	Pb(II)	0.087	
Au(III)-Cu(II)	Au(III)	0.115	12.8
	Cu(II)	0.009	
Ag(I)-Cu(II)	Ag(I)	0.184	3.29
	Cu(II)	0.056	
Ag(I)-Zn(II)	Ag(I)	0.214	54.0
	Zn(II)	0.004	
Ag(I)-Pb(II)	Ag(I)	0.219	4.47
	Pb(II)	0.049	
Ag(I)-Mn(II)	Ag(I)	0.258	2.66
	Mn(II)	0.097	

As we compared the adsorption capacity of different types of adsorbents using for Au(III)/Ag(I) adsorption, it was clear that the adsorption capacity of SG-PS-NH₂ was relatively high when compared to several other adsorbents such as L-lysine modified crosslinked chitosan resin, thiol cotton fiber, Alfalfa biomass, poly(vinylbenzylchloride-acrylonitrile-divinylbenzene) modified with tris(2-aminoethyl)-amine. For example, the maximum adsorption capacity was found to be 70.34 mg/g for Au(III) by L-lysine modified crosslinked chitosan resin and 0.396 mmol/g for Ag(I) by waste biomass, respectively. However, the relative values of SG-PS-NH₂ were 0.939 mmol/g for Au(III) and 0.582 mmol/g for Ag(I).^{4-6,15,18-21} The differences of precious metal Au(III)/Ag(I) ion uptake on various adsorbents are because of the differences in the properties (function groups, surface area, particle size, etc.) of the adsorbents. The aforementioned research results mean that silica gel encapsulated by polystyrene containing amino groups (SG-PS-NH₂) is favorable and useful for the removal of precious metal ions, and the high adsorption capacity make it a good promising candidate material for Au(III)/Ag(I) uptake.

Figure 3 shows the dynamic adsorption kinetics of SG-PS-NH₂ for Cu(II), Ag(I), and Au(III) at room temperature. As is shown in Figure 3, the adsorption capacities of SG-PS-NH₂ for Cu(II), Ag(I), and Au(III) increased with the prolonging of contact time. It increased quickly within the first 6 min for Cu(II), the relative adsorption capacity could reach 0.018 mmol/g at 175 min. As for Ag(I) adsorption, it increased rapidly within the first 12 min, the adsorption capacity reached 0.050 mmol/g at 250 min. Similar with Cu(II) and Ag(I) systems, Au(III) adsorption was quick in the first 60 min, and did not reach the equilibrium at 125 min with the adsorption

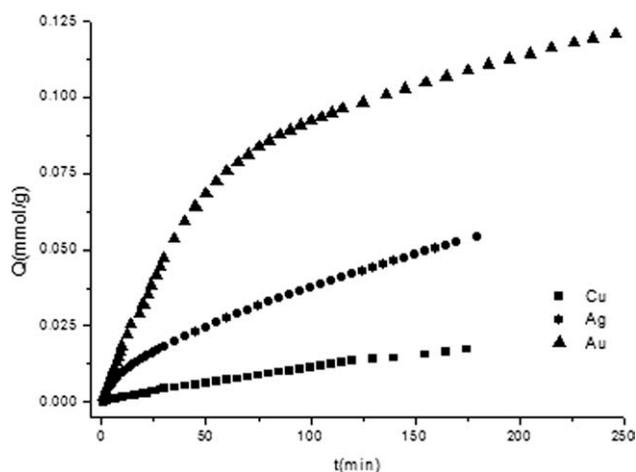


Figure 3 The dynamic adsorption of SG-PS-NH₂ for Cu(II), Ag(I), and Au(III).

TABLE II
The Regeneration Properties of SG-PS-NH₂ for Cu(II), Ag(I), Au(III)

Regeneration time	Q(mmol/g)		
	Cu(II)	Ag(I)	Au(III)
1	0.17	0.47	0.59
2	0.15	0.45	0.56
3	0.14	0.42	0.53

capacity being 0.120 mmol/g. So, it was clear that the affinity order of three metal ions adsorbed by of SG-PS-NH₂ was Au(III) > Ag(I) > Cu(II), which is inversely correlated with their electronegative nature.

The reusability is an important factor for an advanced adsorbent material. Therefore, if an adsorbent with higher adsorption capability and better desorption property will significantly reduce the overall cost for adsorbent. The regeneration capacities of SG-PS-NH₂ were investigated by using the solution of 0.5% thiourea in 1 mol/L HCl as the eluent. The regeneration results of SG-PS-NH₂ for Cu(II), Ag(I), and Au(III) is shown in Table II, and it is apparent that the adsorption properties of silica gel encapsulated by amino functionalized polystyrene (SG-PS-NH₂) decrease a little after three cycles of adsorption-desorption. However, in general, the changes of the adsorption capability are relatively small. For example, the adsorption capacity of SG-PS-NH₂ for Au(III) was 0.59 mmol/g for the first time, that value changes to 0.53 mmol/g for the third regeneration time. Thus, SG-PS-NH₂ can be employed repeatedly in precious metal adsorption, it has excellent separation and adsorption properties for Au(III)/Ag(I), and it is a promising material used in the removal of these metal ions from wastewater.

CONCLUSIONS

Synthesis of silica gel encapsulated by amino functionalized polystyrene (SG-PS-NH₂) with core-shell structure has been developed, and the nature of the sample was characterized by titration, FTIR, TG. The results showed that this high efficient inorganic-organic hybrid adsorbent had excellent adsorption for Au(III)/Ag(I) in eight binary ion systems. The dynamic adsorption of SG-PS-NH₂ for Cu(II), Ag(I), and Au(III) have been investigated, and Cu(II), Ag(I), and Au(III) ions could be easily desorbed from SG-PS-NH₂ with the eluent solution of 0.5% thiourea in 1 mol/L HCl, and the adsorbent could be used several cycles. Based on these results, it was concluded that functional groups were distributed on its surface, and it made adsorption, desorption

and regeneration easy. Thus, this composite material has a significant potential for removing Au(III)/Ag(I) from wastewater using adsorption method.

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