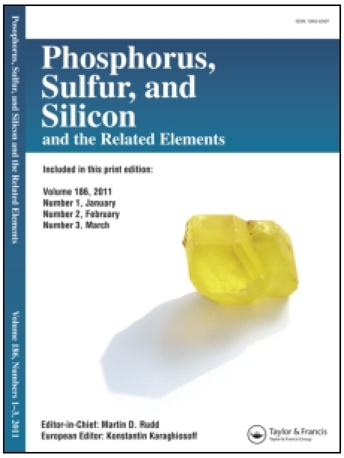

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Dynamic Adsorption and Desorption Behaviors of Cu(II), Ag(I), and Au(III) on Silica Gel Microspheres Encapsulated by Salicylic Acid-Functionalized Polystyrene

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DYNAMIC ADSORPTION AND DESORPTION BEHAVIORS OF Cu(II), Ag(I), AND Au(III) ON SILICA GEL MICROSPHERES ENCAPSULATED BY SALICYLIC ACID–FUNCTIONALIZED POLYSTYRENE

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Composite material silica gel microspheres encapsulated by salicylic acid functionalized polystyrene(SG—PS—azo—SA) have been synthesized, and the dynamic adsorption and desorption properties of this silica gel matrix inorganic–organic composite material for Cu(II), Ag(I), and Au(III) have been investigated. The results displayed that SG—PS—azo—SA had excellent adsorption for Cu(II), and the film diffusion dominated the adsorption process of SG—PS—azo—SA for Cu(II), Ag(I), and Au(III). These metal ions could be desorbed with the eluent solution of 2.5 mol/L HCl, 3% thiourea in 0.5 mol/L HCl, and 0.5% thiourea in 1 mol/L HCl, respectively. When the elution was carried out for 30 min, 30 min, and 132 min, the desorption ratio ω could reach 91.1%, 99.4%, and 60.84%, respectively. Thus, silica gel encapsulated by polystyrene coupled with salicylic acid (SG—PS—azo—SA) is favorable and useful for the removal of metal ions Cu(II), Ag(I), and Au(III), and the high adsorption capacity make it a promising candidate material for the metal ions removal.

Keywords Composite materials; dynamic adsorption; dynamic desorption; salicylic acid; silica gel

INTRODUCTION

Composite materials have been a significant concern because they are made from two or more constituent materials with significant physical or chemical properties, which work together to give the composite unique properties. Among them, polymer-encapsulated inorganic particles offer very interesting actual and potential applications, and may have prominent properties in areas such as adsorbents, optics, and electronics.[1] Due to the excellent thermal and mechanical stability, unique large surface area, and well-modified surface properties, silica gel has been widely used as an inorganic solid matrix in inorganic–organic composite materials.[2–3] Such composite materials have received a great deal of attention recently because of their excellent performance in the field of chromatography, adsorption, and

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catalysis.[4–5] Bourgeat-Lami and Lang conducted polymer encapsulation of silica particles using dispersion polymerization of styrene in aqueous ethanol medium, and investigated the effect of silica size and concentration on the morphology of composite particles.[6–7] Li et al.[8] reported that they obtained spherical hybrid silica particles from 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 divinylbene). The encapsulated packing was used as stationary phases in capillary electrochromatography, and displayed high column efficiencies.

The existence of oxygen atoms in the salicylic acid group makes the organic ligand coordinate with a variety of transition metal ions. If the salicylic group is grafted on a solid matrix such as a polymer matrix, this kind of chemical modification can overcome the problem of being soluble in water, and can be used in adsorption of metal ions from aqueous solutions. Boussetta et al.[9,10] made salicylic acid and derivatives anchored on poly (styrene-co-divinylbenzene) resin and membrane via a diazo bridge, and found that the adsorption capacities of these new materials for iron ions could reach 11.6 mg/g and 13.4 mg/g, respectively.

On the other hand, the removal and recovery of heavy metal ions from industrial wastewater has been a significant concern in most industrial branches due to economic and environmental factors. Many treatment processes, such as chemical precipitation, reverse osmosis, ion exchange, and adsorption, are currently used. Among these methods, adsorption is highly effective and economical, and is a promising and widely applied method.[11] Consequently, effective adsorbents with strong affinities and high loading capacity for targeted metal ions were subsequently prepared by functionalizing the surface of various substrates, such as chemical modification of silica gel.[12] 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 needs further improvement.

In the present article, we explore the synthesis of silica gel microspheres encapsulated by imidazole functionalized polystyrene (SG—PS—azo—SA) hybrid adsorbent for enhanced removal of Cu(II), Ag(I), and Au(III) from aqueous solutions. The dynamic adsorption and desorption properties of this novel silica gel matrix inorganic–organic composite material SG—PS—azo—SA for Cu(II), Ag(I), and Au(III) have been investigated.

RESULTS AND DISCUSSION

The synthetic route of SG—PS—azo—SA included the steps of activation of SG syntheses of SG—C=C, SG—PS, SG—PS—NO_2, SG—PS—NH_2, and the final product SG—PS—azo—SA, which is shown in Figure 1. The presence of amino groups in SG—PS—NH_2 is highly advantageous for conducting modification reactions, and we obtained silica gel encapsulated by polystyrene coupling with salicylic acid (SG—PS—azo—SA) by diazotization reaction and coupling reaction from SG—PS—NH_2. The C=C content of SG—C=C was detected by titration with $Na_2S_2O_3$ solution according to the method described in Ref [13], and the result was 1.82 mmol/g. The $–NH_2$ content of SGbond;PS—NH_2 was detected by back titration with NaOH solution according to the method described by Zhao,[13] and the result was 2.04 mmol/g. Similarly, the salicylic acid group was measured as 1.31 mmol/g. The infrared spectra of SG—PS—azo—SA displayed the presence of vibrational bands characteristic of a salicylic acid group, and the peak

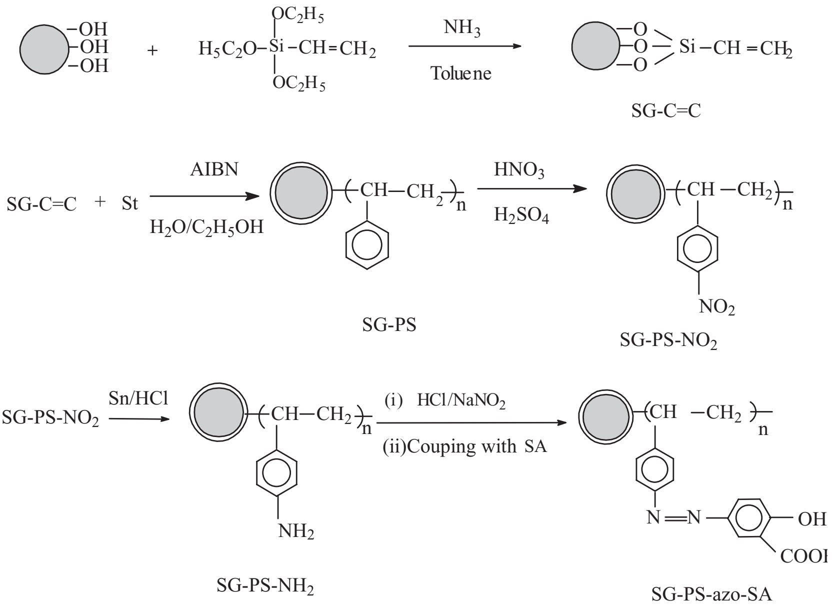

Figure 1 The synthetic route to SG—PS—azo—SA.

at 1600 cm^{-1} was caused by the stretching vibrations of C=N bonds. By comparison with the curve of SG—PS—NH$_2$, the bands at 1104 cm^{-1} almost disappeared, which was the characteristic peak of asymmetric stretching vibration of Si—O—Si, indicating that composite spheres form bonds with other substances, resulting in the relatively decrease of bands of silica gel. TGA of SG—PS—NH$_2$ and SG—PS—azo—SA displayed that the temperature of thermal decomposition of the organic layer in the final product SG—PS—azo—SA was about 336 °C, and the relative weight loss was 35.54%. Figure 2 shows all the diffraction peaks of SG and SG—PS—azo—SA at about 22°, which is the characteristic diffraction peak of amorphous silica gel. The results display that there was no an essential change occurred in SG—PS—azo—SA, implying that silica gel was stable enough to experience the relative reactions. Moreover, we found that the relative intensity of diffraction peak of SG—PS—azo—SA was stronger than that of SG, and that the introduction of grafted organic moieties led to the increase of diffraction peak, and this may be interpreted as the formation of strong hydrogen bond Si—O—H $\cdots$ N/O.

Figure 3 shows the dynamic adsorption kinetics of SG—PS—azo—SA for Cu(II), Ag(I), and Au (III) at room temperature. As is shown in Figure 3, the adsorption capacities of SG—PS—azo—SA for Cu(II) increased contact time was prolonged. It increased quickly in the first 120 min and then slowly, and reached the equilibrium at 220 min with the adsorption capacity being 0.17 mmol/g. As for Ag(I), it increased drastically within 40 min and then slowly. At 220 min, its adsorption capacity reached 0.063 mmol/g. Similarly, after 50 min of quick increase, the Au(III) adsorption capacity slowed to 0.051 mmol/g at 220 min. At the same time, it was clear that the affinity order of three metal ions adsorbed by of SG—PS—azo—SA was Au(III) < Ag(I) < Cu(II), which was correlated with their electronegativity. Through the —N=N— groups and salicylic acid groups, SG—PS—azo—SA can form stable chelating compounds with many transition metal ions

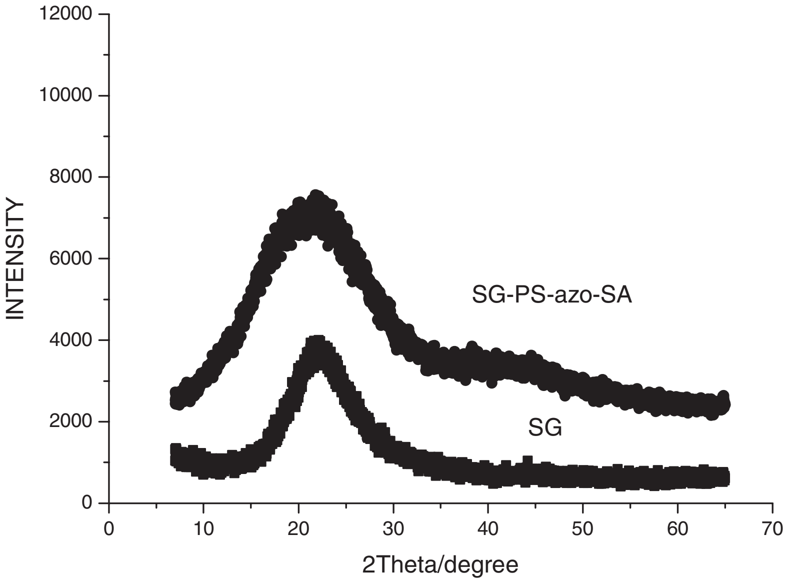

Figure 2 XRD patterns of SG and SG—PS—azo—SA.

such as Cu(II), etc. 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 electronegative donor atoms. As we compared the adsorption capacity of different types of adsorbents used for Cu(II), Ag(I), and Au (III) adsorption, it was obvious that the

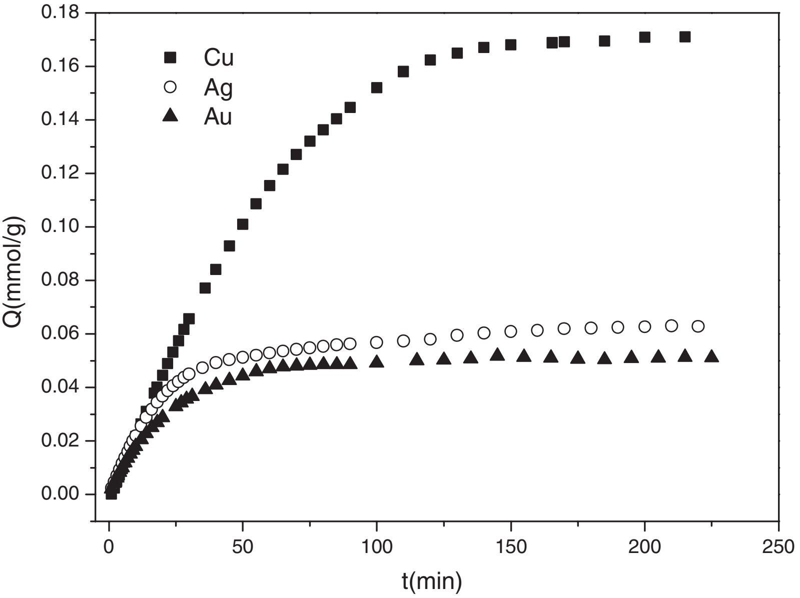

Figure 3 The dynamic adsorption of SG—PS—azo—SA for Cu(II), Ag(I), Au(III) at room temperature.

adsorption capacity of SG—PS—azo—SA was relatively high when compared to several other adsorbents such as L-lysine-modified crosslinked chitosan resin, thiol cotton fiber, alfalfa biomass, and poly(vinylbenzylchloride-acrylonitryle-divinylbenzene) modified with tris(2-aminoethyl)amine.[14–18] The differences of metal ion uptake on various adsorbents are due to the differences in the properties of the adsorbents, such as their function groups, surface area, and particle size.

Following Boyd et al.,[19] the adsorption procedure of adsorbents for metal ions was considered to take place through the mechanism of film diffusion. The Boyd equation is as follows:

$$\ln(1 - Q_t/Q_0) = kt \tag{1}$$

where Q_t is the amount of adsorbate taken up at time t, and Q_0 is the maximum eqilibrium uptake, k is adsorption rate (min^{-1}), and t is adsorption time. Film diffusion was rate-controlling when the adsorbent was exposed to the low metal ion concentration, and if the adsorption process was governed by the film diffusion, variations in the flow velocity of the solution should have significant effect on dynamic adsorption rate. Otherwise, the high solution concentration and temperature tended to promote particle diffusion. As seen in Figure 4 and Table I, the dynamic adsorption data was fitted to the Boyd equation by least squares fit, the regression coefficient R^2 obtained was 0.9869, 0.9925, and 0.9988, and the adsorption rate k was 0.0165 min^{-1}, 0.0417 min^{-1}, and 0.0408 min^{-1}, for Cu(II), Ag(I), and Au(II), respectively, which suggested that the film diffusion dominated the adsorption process of SG—PS—azo—SA for Cu(II), Ag(I), and Au (III).

The regeneration capacities of SG—PS—azo—SA were investigated by using a solution of 2.5 mol/L HCl, 3% thiourea in 0.5 mol/L HCl, and 0.5% thiourea in 1 mol/L HCl as the eluents for Cu(II), Ag(I), and Au(III), respectively. The dynamic desorption

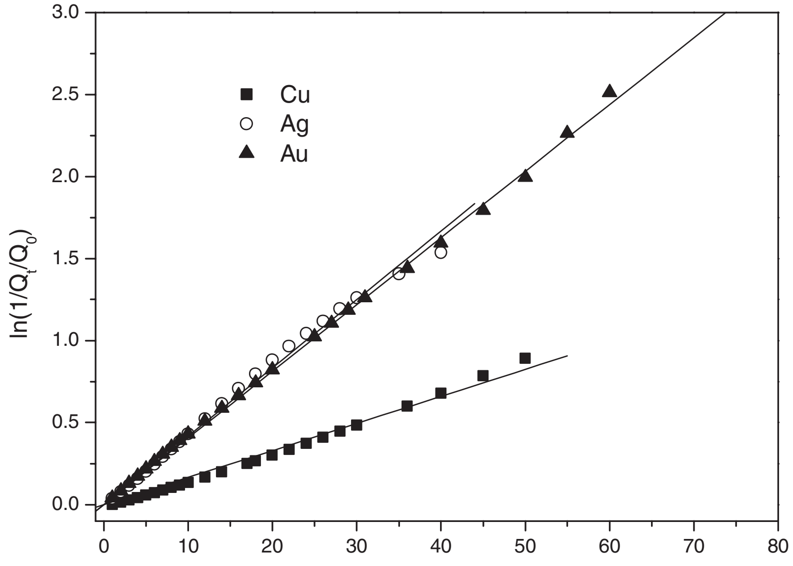

Figure 4 Linear fit of the Boyd equation was determined by least squares fit.

Table I Adsorption rate constants *k* and regression coefficients R^2

Metal ions	*k*	R^2
Cu(II)	0.0165	0.9869
Ag(I)	0.0417	0.9925
Au(III)	0.0408	0.9988

SG—PS—azo—SA for these three kinds of metal ions is shown in Figure 5, and the results clearly displayed that the elution of Cu(II) was the fastest. When the elution was carried out within 2 min, the desorption ratio *ω* was 89.71%, and when the elution time was 30 min, *ω* could reach 91.10%. As for Ag(I), the desorption ratio *ω* was about 50% within the first 3 min, and *ω* could reach 99.41% when the elution time was 30 min. In general, the elution of Au(III) was less effective, and the total desorption ratio *ω* only reached 60.84% at 132 min. The effective and quick elution of Cu(II) and Ag(I) made it possible to pre-concentrate them on-line.

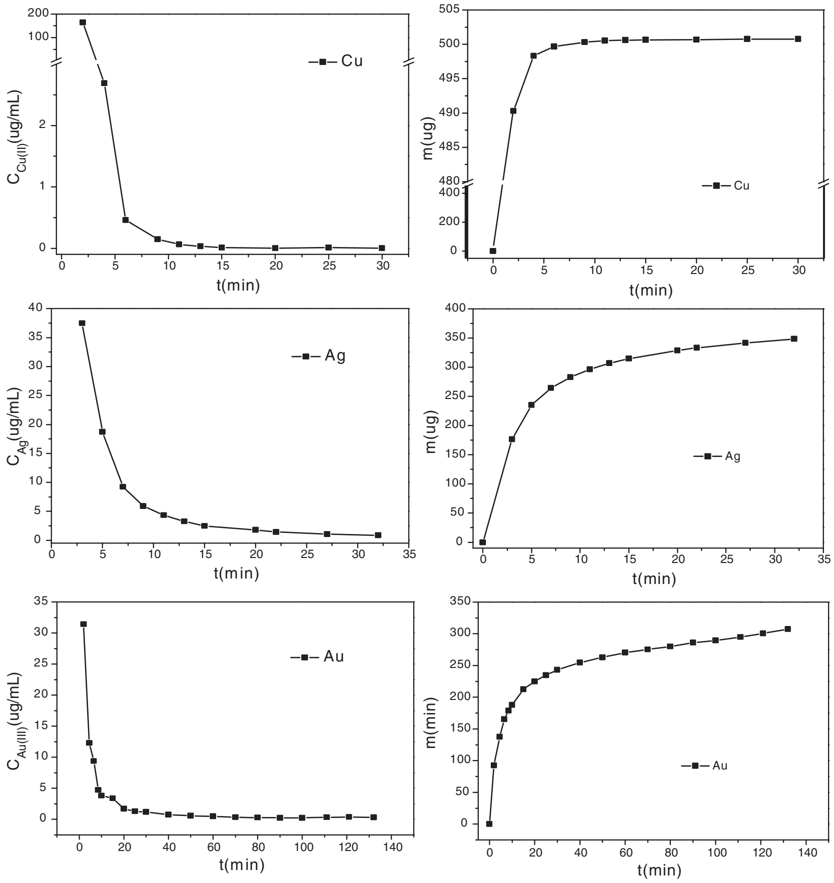

Figure 5 The curve of the dynamic desorption of SG—PS—azo—SA for Cu(II), Ag(I), and Au(III).

The above-mentioned research results mean that silica gel encapsulated by polystyrene containing salicyclic acid groups (SG—PS—azo—SA) is favorable and useful for the removal of precious metal ions, and the high adsorption capacity makes it a promising candidate material for transition metal ions uptake, especially for Cu(II).

CONCLUSIONS

Synthesis of silica gel encapsulated by polystyrene coupling with salicylic acid (SG—PS—azo—SA) with core-shell structure has been developed, and the dynamic adsorption and desorption properties of the sample for Cu(II), Ag(I), and Au(III) were studied. The results showed that this highly efficient inorganic–organic hybrid adsorbent had excellent adsorption for Cu(II), and Boyd equation fitting displayed the film diffusion dominated the adsorption process of SG—PS—azo—SA for Cu(II), Ag(I), and Au(III). Moreover, these metal ions can be easily desorbed with the relative eluent solution, and almost all of Cu(II) and Ag(I) could be desorbed within 30 min. Based on these results, it was concluded that there was small swelling for this material, functional groups were distributed on its surface, and it made adsorption, desorption, and regeneration easy. Thus, this composite material had a significant potential for removing Cu(II) from wastewater using the adsorption method.

EXPERIMENTAL

Materials, Instruments, and Preparation

Silica gel spheres (100–200 mesh) were obtained from Qingdao Marine Chemical Plant. All reagents were analytical-grade chemical products and used without further purification, and distilled water was used for all dilutions. Aqueous solutions containing various metal ions at a certain concentration (10^{-2}–10^{-3} M) were prepared from metal salts.

IR spectrum (KBr pellets) was recorded on a Magna-IR 550 (series II) Fourier transform spectrometer, Nicolet Co., USA. 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.

Silica-gel spheres were activated with 7.5 M nitric acid at refluxing temperature for 6 h, with 12 M hydrochloric acid at refluxing temperature for 6 h, allowed to cool, and repeatedly washed using distilled water until there was no Cl^- (as revealed by testing with $AgNO_3$ solution and HNO_3 solution). Then they were dried in vacuum at 120°C for 48 h prior to use. The preparation of silica gel microspheres encapsulated by imidazole functionalized polystyrene (SG—PS—azo—SA) hybrid adsorbent is demonstrated by Zhao.[13]

Dynamic Adsorption of SG—PS—azo—SA for Cu(II), Ag(I), and Au(III)

The column method was employed on the flow injection analysis processor to determine the dynamic adsorption behaviors of SG—PS—azo—SA for Cu(II), Ag(I), and Au(III). 0.05 g of SG—PS—azo—SA was packed in a glass microcolumn by the slurry method. 3.40 μg/mL Cu(II) containing solution, 5.43 μg/mL Ag(I) containing solution, and 9.60 μg/mL Au(III) containing solution were passed through the microcolumn with a constant flow rate of 2.28 mL/min, respectively. The effluent fraction was collected every 2–5 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), and Au(III) adsorbed Q (mmol/g) were calculated according to the Equation (1),

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

where C_0 is the initial concentration (μg/mL), C_i is the concentration of metal ion in the effluent (μg/mL), ν 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), and m is the mass of SG—PS—azo—SA (mg).

Dynamic Desorption of Cu(II), Ag(I), and Au(III)

Dynamic desorption experiments were conducted to assess the reusability of SG—PS—azo—SA. The solution of 2.5 mol/L HCl, 3% thiourea in 0.5 mol/L HCl, and 0.5% thiourea in 1 mol/L HCl were employed as the desorption medium for Cu(II), Ag(I), and Au(III), respectively. The dynamic desorption of Cu(II), Ag(I), and Au (III) was investigated by the following procedure. The metal ion–loaded SG—PS—azo—SA in the microcolumn was eluted by the relative desorption medium at a flow rate of 1.5 mL/min until equilibrium was reached. The effluent fraction was collected every 2–5 min, and the concentration of metal ions in each sample was determined by atomic adsorption spectrophotometer. When no metal ion was detected in the effluent, the equilibrium was reached. The amounts of Cu(II), Ag(I), Au(III) desorbed Q (mmol/g) were calculated according to the Equation (2),

$$Q = \sum_{i=1}^{n} \left(\frac{C_i vt}{Mm} \right) \tag{3}$$

where C_t is the concentration of metal ion in the effluent (μg/mL), ν is the elution rate (mL/min), t is the time of collecting the effluent (min), M is the molar mass of the metal ion (g/mol), and m is the mass of SG—PS—azo—SA (mg).

The desorption ratio ω was calculated according to the amount of Cu(II), Ag(I), Au(III) absorbed on SG—PS—azo—SA and that desorbed in the eluent [Equation (4)]:

$$\omega = \frac{Q_{desorption}}{Q_{adsorptin}} \times 100\% \tag{4}$$

where $Q_{desorption}$ is the amount of metal ions desorbed on SG—PS—azo—SA and $Q_{adsorption}$ is the amount of metal ions absorbed on SG—PS—azo—SA.

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