



# Removal of transition metal ions from aqueous solutions by adsorption onto a novel silica gel matrix composite adsorbent

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## ABSTRACT

This paper presented the synthesis of a novel composite adsorbent silica gel microspheres encapsulated with 5-sulfosalicylic acid functionalized polystyrene (SG-PS-azo-SSA). It was characterized by titration method, FT-IR (Fourier transform infrared spectrometer), SEM (scanning electron microscope), EDXAS (energy dispersive X-ray analysis system), etc. SG-PS-azo-SSA has been used to investigate the adsorption of Mn(II), Fe(III), Co(II), Ni(II), Zn(II), Cd(II), Hg(II), Pd(II), Cu(II), Ag(I) and Au(III) from aqueous solutions. The research results revealed that SG-PS-azo-SSA has the better adsorption capacity for Cu(II), Ag(I) and Au(III). Langmuir and Freundlich isotherm models were applied to analyze the experimental data and the adsorption of Cu(II), Ag(I) and Au(III) on SG-PS-azo-SSA fitted well to the Langmuir isotherm equation. The obtained maximum adsorption capacity for Cu(II), Ag(I), and Au(III) is 0.472 mmol/g, 0.822 mmol/g and 0.810 mmol/g, respectively. Thus, silica gel encapsulated by 5-sulfosalicylic acid functionalized polystyrene (SG-PS-azo-SSA) is favorable and useful for the removal of Cu(II), Ag(I) and Au(III) metal ions.

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## 1. Introduction

Since polymer-coated inorganic oxide can offer very interesting and potential applications such as adsorbents, optics, and electronics, they have become paramount importance and received more and more attention recently [1]. Due to the excellent thermal and mechanical stability, unique large surface area and well-modified surface properties, silica gel was widely used as inorganic solid matrix [2,3]. Such kind of composite materials have been an increasing interest recently because of their excellent performance in the field of chromatography, adsorption, catalysis and so on [4,5]. Regarding to polystyrene/SiO<sub>2</sub>, Bourgeat-Lami and Lang conducted polymer encapsulation of silica particles by dispersion polymerization of styrene in aqueous ethanol medium in the presence of surface-functionalized silica particles using 3-(trimethoxysilyl) propyl methacrylate as the coupling agent [6,7]. Gu et al. [8] proposed the preparation of silica-polystyrene core-shell particles. In their work, silica particles were obtained through condensation and hydrolysis of tetraethyl orthosilicate in a water-ethanol-ammonia solution, and the silica particles were surface-modified with a coupling reagent, methacryloxypropyltrimethoxysilane. Sondi et al. reported stable dispersions of nanosilica coated with tert-butyl acrylate polymer by in situ polymerization of monomer

in 2-propanol [9]. Do et al. presented a novel synthesis of polystyrene/SiO<sub>2</sub> composite microparticles by dispersion polymerization in supercritical fluid [10].

On the other hand, water pollution due to toxic metals is a serious environmental and public health issue. The removal and recovery of heavy metal ions from industrial wastewater have been of importance in most industrial branches due to economic and environmental factors. Many treatment processes, such as chemical precipitation, electro dialysis, adsorption, are currently used. Among these methods, adsorption is highly effective and economical, and is a promising and widely applied method [11]. In the relative research work, people found that 5-sulfosalicylic acid had cation exchange groups, in addition, it could chelate with a variety of metal ions, and then it is often chosen in the field of adsorption. Cui et al. [12] made 5-sulfosalicylic acid anchored on nanometer SiO<sub>2</sub>, and found it had good adsorption and preconcentration of Fe(III) in aqueous solutions. If 5-sulfosalicylic acid group is grafted on the solid matrix, this kind of chemical modification can overcome the problems of its being soluble in water and being difficult to recover, and can enhance adsorption kinetics properties, then it can be used in adsorption of metal ions from aqueous solutions.

In the present work, we developed the coating of silica gel microspheres with 5-sulfosalicylic acid functionalized polystyrene (SG-PS-azo-SSA) in order to enhance removal of heavy metals from aqueous solutions. After its static adsorption process of Mn(II), Fe(III), Co(II), Ni(II), Zn(II), Cd(II), Hg(II), Pd(II), Cu(II), Ag(I) and Au(III) from aqueous solutions was studied, the results displayed

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that SG-PS-azo-SSA has the better adsorption capacities for Cu(II), Ag(I) and Au(III). In addition, the adsorption isotherms of the inorganic–organic hybrid adsorbent for Cu(II), Ag(I) and Au(III) ions were also investigated.

## 2. Experimental details

### 2.1. Materials 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 ( $10^{-2}$  to  $10^{-3}$  M) were prepared from metal salts.

The preparation steps of silica gel microspheres encapsulated by 5-sulfosalicylic acid functionalized polystyrene were as follow.

Silica gel spheres were activated with nitric acid ( $V_{\text{HNO}_3} : V_{\text{H}_2\text{O}} = 1 : 1$ ) 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  $\text{Cl}^-$ . Then they were dried in vacuum at  $120^\circ\text{C}$  for 48 h before use. 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 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  $50^\circ\text{C}$ , and it was referred to as SG-C=C. 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 alcohol were added to a 1000 mL flask. The mixture was stirred for 3 h, and then heated to  $70^\circ\text{C}$ . The alcohol solution of azobisisobutyronitrile (AIBN), which was recrystallized by 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 alcohol successively. The intermediate product silica gel encapsulated by polystyrene was dried under vacuum at  $50^\circ\text{C}$  and it was referred to as SG-PS.

10 g 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  $15^\circ\text{C}$ . After dropping, the reaction was conducted for 12 h at  $30^\circ\text{C}$ . 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  $80^\circ\text{C}$ , and it was referred to as SG-PS-NO<sub>2</sub>. 100 mL concentrated hydrochloric acid was put into a 250 mL flask, which was heated to  $60^\circ\text{C}$ . 20 g small Sn particles and 5.0 g SG-PS-NO<sub>2</sub> were added successively, and the reaction was carried out for 24 h at  $100^\circ\text{C}$ . 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 alcohol. The intermediate product silica gel encapsulated by polystyrene containing amino groups was dried under vacuum at  $36^\circ\text{C}$  for 10 h, and it was referred to as SG-PS-NH<sub>2</sub>.

3.0 g SG-PS-NH<sub>2</sub>, 60 mL water and 8.4 mL concentrated hydrochloric acid were added in a flask with ice water bath to cool to  $0\text{--}5^\circ\text{C}$ , and 20 mL solution containing 3.6 g NaNO<sub>2</sub> was added dropwise into the solution while stirring. Stirring was kept on for 6 h, and then the liquid in the flask was pumped out and washed by 1% (v/v) hydrochloric acid ( $0\text{--}5^\circ\text{C}$ ). Consequently, the diazonium salt SG-PS-N<sup>+</sup>=NCl<sup>-</sup> was obtained. 3.5 g 5-sulfosalicylic acid was dissolved in dilute sodium hydroxide solution, and the solution was kept under weak alkaline condition. The solution was

added then into the above-mentioned SG-PS-N<sup>+</sup>=NCl<sup>-</sup> solution. The reaction mixture was kept at  $0\text{--}5^\circ\text{C}$  for 10 h while stirring, and the temperature rose to  $40^\circ\text{C}$  with continuous stirring for 6 h. The product was washed with distilled water, soaked in hydrochloric acid solution, and then washed with distilled water until the filtrate became neutral. The final product silica gel encapsulated by polystyrene coupling with 5-sulfosalicylic acid was obtained, and it was referred to as SG-PS-azo-SSA.

### 2.2. Instruments

IR spectrum (KBr pellets) was recorded on a Magna-IR 550 (series II) Fourier transform spectrometer, Nicolet Co., USA. The morphology of the compounds was examined on JEOL JSM5600LV scanning electron microscope, JEOL Co., Japan. The EDXAS was performed on a NORAN LEVER-2 EDX analytical instrument. Thermogravimetric analysis (TG) was recorded on a Netzsch STA 409, Test conditions: type of crucible, DTA/TG crucible Al<sub>2</sub>O<sub>3</sub>; 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.

### 2.3. Adsorption procedure

Adsorption experiments were carried out using batch method in a thermostat-cum-shaking assembly. 0.02 g of the sample SG-PS-azo-SSA was shaken with 20 mL of solution containing metal ions with different concentrations for different hours. After the centrifugalization, 4 mL solution was taken out and put in 25 mL colorimetry-used 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 following equation:

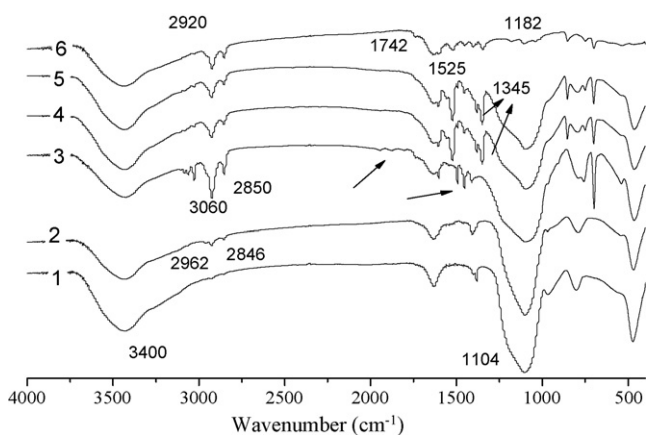
$$Q(\text{mmol/g}) = \frac{(C_0 - C)V}{W} \quad (1)$$

where  $C_0$  and  $C$  are the concentration of metal ions before and after sorption (mmol/L), respectively,  $V$  the volume of the solution used for sorption (L), and  $W$  is the weight of the sample SG-PS-azo-SSA (g).

## 3. Results and discussion

The synthetic route of SG-PS-azo-SSA included the steps of activation of SG, syntheses of SG-C=C, SG-PS, SG-PS-NO<sub>2</sub>, SG-PS-NH<sub>2</sub> and the final product SG-PS-azo-SSA. 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. The presence of amino groups in SG-PS-NH<sub>2</sub> is highly advantageous for conducting modification reactions, and we obtained silica gel encapsulated by polystyrene coupling with 5-sulfosalicylic acid (SG-PS-azo-SSA) through diazotization reaction and coupling reaction from SG-PS-NH<sub>2</sub>. The C=C content of SG-C=C was detected by titration with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution according to the method described in Ref. [13], and the result was 1.82 mmol/g. The -NH<sub>2</sub> content of SG-PS-NH<sub>2</sub> was detected by anti-titration with NaOH solution according to the method described in Ref. [13], and the result was 2.04 mmol/g. Moreover, 5-salicylic acid group was measured as 0.89 mmol/g through the EDXAS results. EDXAS showed the weight percentage of surface elements as: C: 46.07%; N: 16.18%; O: 32.95%; Si: 1.94%; S: 2.86%. Thus, the exist of sulfur element meant 5-salicylic acid group had been grafted successfully on the surface.

The infrared spectra of SG-PS-NH<sub>2</sub> and SG-PS-azo-SSA was shown in Fig. 1, and **1** displayed the presence of vibrational



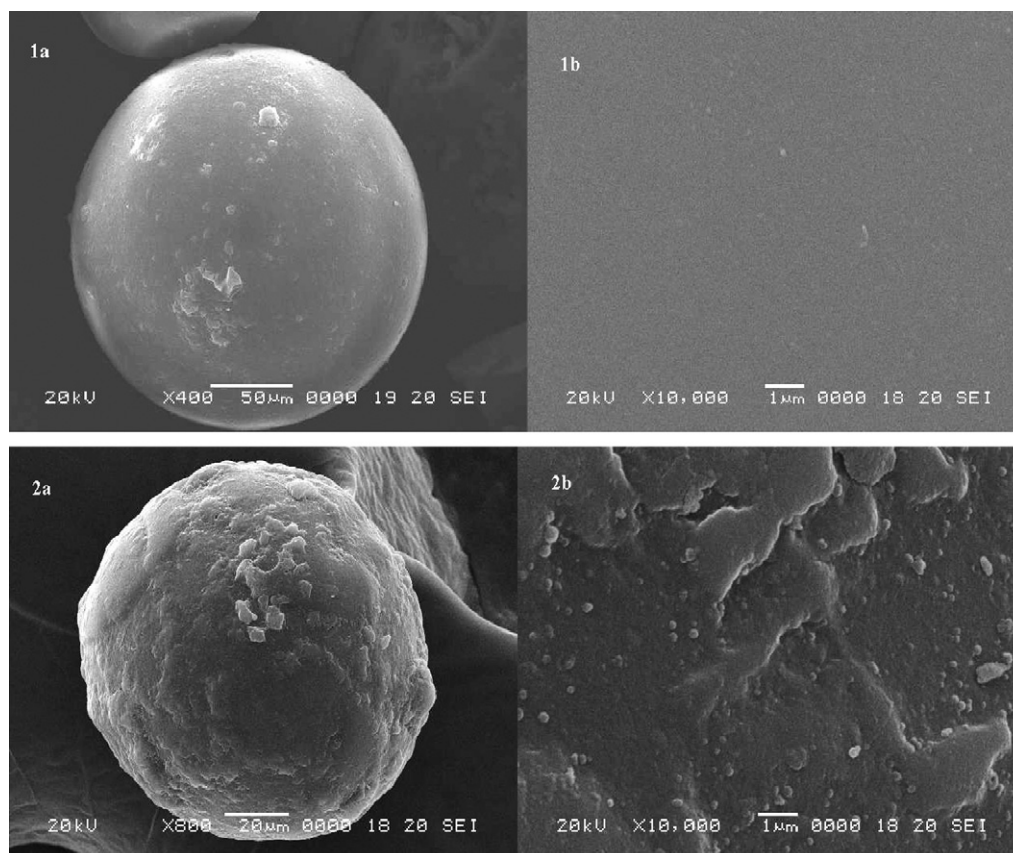
**Fig. 1.** FT-IR spectra of the intermediates and the composite SG-PS-azo-SSA. (1: SG; 2: SG-C=C; 3: SG-PS; 4: SG-PS-NO<sub>2</sub>; 5: SG-PS-NH<sub>2</sub>; 6: SG-PS-azo-SSA).

band characteristic of silanol groups at 3400 cm<sup>-1</sup> and asymmetric stretching vibration of Si-O-Si at 1104 cm<sup>-1</sup>; **2**: symmetric and asymmetric vibrations of saturated C-H bond at 2850 cm<sup>-1</sup> and 2920 cm<sup>-1</sup> suggested that silane agent had been bonded on the surface of silica gel; **3**: the stretching vibrations of C-H in benzene ring were at 3100–3000 cm<sup>-1</sup>, and the peaks of benzene skeleton vibration at 1494 cm<sup>-1</sup> and 1454 cm<sup>-1</sup> meant that polystyrene had been bonded on the surface of modified silica gel successfully; **4**: symmetric and asymmetric vibrations of C-N in Ar-NO<sub>2</sub> were at 1520 cm<sup>-1</sup> and 1350 cm<sup>-1</sup>, respectively, and the bending vibration of C-N bond was at 860 cm<sup>-1</sup>, which suggested that benzene rings had been connected to the nitro groups; **5**: the stretching vibrations (1677 cm<sup>-1</sup>) and the in-plane bending vibration (1640–1560 cm<sup>-1</sup>)

of the N-H bonds relatively widen the peak at 1623 cm<sup>-1</sup>. By comparison with the curve of SG-PS-NO<sub>2</sub>, the bands at 1520 cm<sup>-1</sup> and 1350 cm<sup>-1</sup> almost disappeared, indicating that the nitro groups decreased, and were changed to the amino groups. **6**: it displayed the presence of vibrational bands characteristic of 5-sulfosalicylic acid group, the peak at 1742 cm<sup>-1</sup> was caused by the stretching vibrations of C=O bonds, the peak at 1180 cm<sup>-1</sup> the symmetric stretching vibrations of S=O and the bending vibrations of ArO-H, and the peak at 1041 cm<sup>-1</sup> the stretching vibrations of ArO-H. By comparison with the curve of SG-PS-NH<sub>2</sub>, the bands at 1104 cm<sup>-1</sup> almost disappeared, which was the characteristic peak of asymmetric stretching vibrations of Si-O-Si, indicating that composite spheres form bonds with other substances resulting in the relatively decrease of bands of silica gel.

The SEM images of SG and SG-PS-azo-SSA were shown in Fig. 2, and the scanning electron microscopy analysis revealed that the sphere appearance and size of the two samples were similar, demonstrating that the microspheres of silica gel have good mechanical stability and they have not been destroyed during the whole reaction. There appeared more layered-folds on the surface of the sample SG-PS-azo-SSA comparing with those of SG, which relatively increased its specific surface area and was conducive to rapid adsorption. TGA of SG-PS-NH<sub>2</sub> and SG-PS-azo-SSA was shown in Fig. 3, and the results showed that the temperature of thermal decomposition of the organic lay in the final product SG-PS-azo-SSA was about 338 °C, and the relative weight loss was 36.56%.

The introduction of the 5-sulfosalicylic acid groups and -N=N- groups onto the coatings can make this composite material form the stable chelating compounds with many transition metal ions. The aim of encapsulating functionalized polystyrene onto silica gel is to make the most of the excellent coordination properties with metal ions of the composite material to obtain novel adsorbent with high



**Fig. 2.** SEM images of the particles: 1a, 1b, the silica gel; 2a, 2b, SG-PS-azo-SSA.

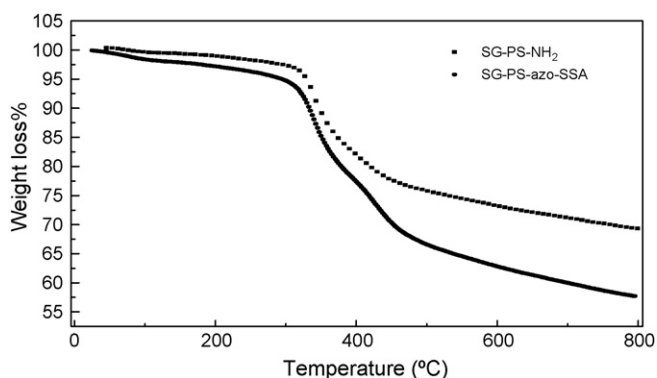


Fig. 3. TGA of SG-PS-NH<sub>2</sub> and SG-PS-azo-SSA.

loading of metal ions. Saturated adsorption capacities for metal ions are generally considered as one of the most critical parameters for judging adsorbents. Mn(II), Fe(III), Co(II), Ni(II), Zn(II), Cd(II), Hg(II), Pd(II), Cu(II), Ag(I) and Au(III) metal ions were chosen as representatives to investigate the loading properties of SG-PS-azo-SSA through static adsorption process, and the results were shown in Fig. 4. The research results revealed that SG-PS-azo-SSA has the better adsorption capacity for Cu(II), Ag(I) and Au(III). 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. The maximum adsorption capacity for Cu(II), Ag(I) and Au(III) was 0.26 mmol/g, 0.43 mmol/g, and 0.61 mmol/g, respectively, with the metal initial concentration was 2.0 mmol/L and pH 5.0 (except pH 2.7 for Au(III) and pH 2.2 for Fe(III)).

The effect of different concentrations of Cu(II), Ag(I) and Au(III) on the adsorption has been investigated at room temperature, Cu(II), Ag(I) and Au(III) adsorption capacities of SG-PS-azo-SSA were give as a function of the equilibrium concentration in Fig. 5. It is clear that the Cu(II), Ag(I) and Au(III) adsorption capacities of SG-PS-azo-SSA rise with the increase of the equilibrium concentration, especially between 0.0 and 8.0 mmol/L range. The adsorption isotherms were studied and the data were analyzed with Langmuir (2) and Freundlich (3) equations [14], respectively (fitting result please see Figs. 6 and 7).

$$\frac{C}{Q} = \frac{1}{bQ_0} + \frac{C}{Q_0} \quad (2)$$

$$\ln Q = \ln K_F + \frac{\ln C}{n} \quad (3)$$

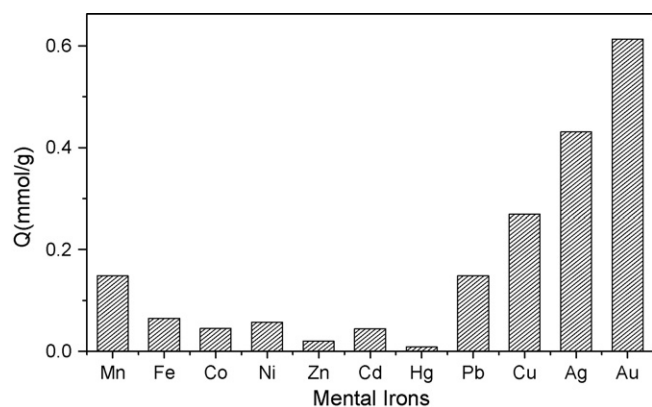


Fig. 4. The saturated adsorption capacities of SG-PS-azo-SSA for metal ions with all the initial concentration of metal ions at 2.0 mmol/L.

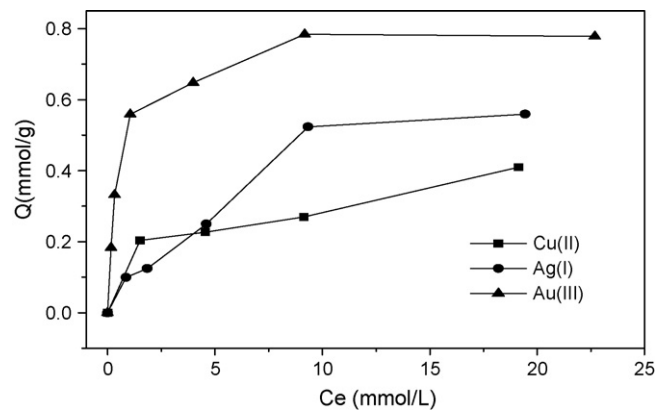


Fig. 5. The isothermal adsorption of SG-PS-azo-SSA for Cu(II), Ag(I), Au(III).

where  $Q$  is the adsorption capacity (mmol/g),  $C$  the equilibrium concentration of Au(III) ions (mmol/ml),  $Q_0$  the saturated adsorption capacity (mmol/g),  $b$  an empirical parameter,  $n$  the Freundlich constant, and  $K_F$  is the binding energy constant reflecting the affinity of the adsorbent to metal ions. It is well known that the Langmuir equation is applicable to homogeneous adsorption, where the adsorption of each adsorbate molecule onto the surface had equal adsorption activation energy. On the other hand, the Freundlich equation is used to describe heterogeneous systems and reversible adsorption, and it is not restricted to the formation of monolayer.

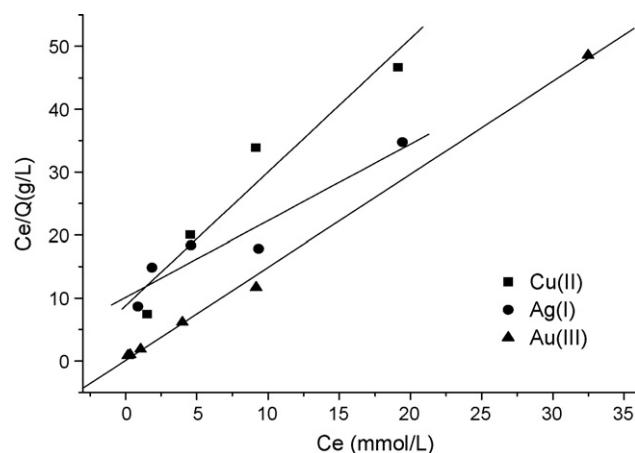


Fig. 6. The Langmuir isotherms of the sample SG-PS-azo-SSA for Cu(II), Ag(I) and Au(III).

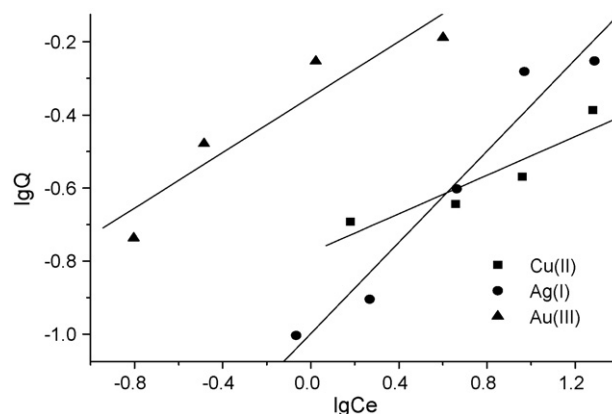


Fig. 7. The Freundlich isotherms of the sample SG-PS-azo-SSA for Cu(II), Ag(I) and Au(III).

**Table 1**  
Freundlich and Langmuir constants of SG-PS-azo-SSA for Cu(II), Ag(I), Au(III).

Metal ions	Freundlich parameters			Langmuir parameters		
	$K_F$	$n$	$R_F^2$	$Q_0$	$B (\times 10^{-3})$	$R_L^2$
Cu(II)	0.1675	3.789	0.8540	0.472	0.241	0.9267
Ag(I)	0.1003	1.602	0.9523	0.822	0.120	0.9096
Au(III)	0.4105	3.621	0.8610	0.810	1.778	0.9992

Table 1 displayed the Langmuir and Freundlich isotherms for the studied system, and it can be seen that the regression coefficient  $R^2$  obtained from Langmuir model is much higher than that from Freundlich model, suggesting the Langmuir model is better than Freundlich model, and could well interpret the studied adsorption procedure. It is well known that the Langmuir equation is applicable to homogeneous adsorption, where the adsorption of each adsorbate molecule onto the surface had equal adsorption activation energy. The maximum adsorption capacity of SG-PS-azo-SSA for Cu(II), Ag(I) and Au(III) obtained from Langmuir model is 0.472 mmol/g, 0.822 mmol/g and 0.810 mmol/g, respectively. As we compared the adsorption capacity of different types of adsorbents using for Cu(II), Ag(I) and Au(III) adsorption, it was clear that the adsorption capacity of SG-PS-azo-SSA was relatively high when compared to several other adsorbents such as L-lysine modified crosslinked chitosan resin, thiol cotton fiber, biomass, poly(vinylbenzylchloride-acrylonitrile-divinylbenzene) modified with tris(2-aminoethyl)amine, functionalized SBA-16 mesoporous silica and chemically modified melamine resins [15–21]. The above-mentioned research results show that the novel composite material silica gel encapsulated by polystyrene coupling with 5-sulfosalicylic acid (SG-PS-azo-SSA) is favorable and useful for the removal of Cu(II), Ag(I) and Au(III) metal ions, and the high adsorption capacity make it a good promising candidate material for uptake of these metal ions.

#### 4. Conclusions

Synthesis of novel hybrid adsorbent silica gel microspheres encapsulated with 5-sulfosalicylic acid functionalized polystyrene (SG-PS-azo-SSA) has been developed, and the nature of the sample was characterized by titration, FT-IR, SEM, TG techniques. The results of the adsorption of various metal ions Mn(II), Fe(III), Co(II), Ni(II), Zn(II), Cd(II), Hg(II), Pd(II), Cu(II), Ag(I) and Au(III) from aqueous solution on the as-synthesized SG-PS-azo-SSA showed that this high efficient inorganic–organic hybrid adsorbent had good adsorption capacity for Cu(II), Ag(I), and Au(III). It was concluded that this material silica gel encapsulated by functionalized polystyrene had a significant potential for enrichment of trace Cu(II), Ag(I), and Au(III) and removing these metal ions from wastewater using adsorption method.

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#### References

- [1] Y. Haga, S. Inoue, T. Sato, R. Yosomiya, Photoconductivity properties of zinc oxide encapsulated in polymers, *Angew. Makromol. Chem.* 139 (1986) 49–61.
- [2] D. Perez-Quintanilla, I.D. Hierro, M. Fajardo, I. Sierra, 2-Mercaptothiazoline modified mesoporous silica for mercury removal from aqueous media, *J. Hazard. Mater.* 134 (2006) 245–256.
- [3] Y. Jiang, Q. Gao, H. Yu, Y. Chen, F. Deng, Intensively competitive adsorption for heavy metal ions by PAMAM-SBA-15 and EDTA-PAMAM-SBA-15 inorganic–organic hybrid materials, *Micropor. Mesopor. Mater.* 103 (2007) 316–324.
- [4] P. Liu, Z. Su, Thermal stabilities of polystyrene/silica hybrid nanocomposites via microwave-assisted in situ polymerization, *Mater. Chem. Phys.* 94 (2005) 412–416.
- [5] Y.M. Zuo, B.R. Zhu, M.D. Gui, Polymer encapsulated packing material for reversed phase liquid chromatography, *Chromatographia* 38 (1994) 756–761.
- [6] E. Bourgeat-Lami, J. Lang, Encapsulation of inorganic particles by dispersion polymerization in polar media: 1. Silica nanoparticles encapsulated by polystyrene, *J. Colloid Interf. Sci.* 197 (1998) 293–308.
- [7] E. Bourgeat-Lami, J. Lang, Encapsulation of inorganic particles by dispersion polymerization in polar media: 2. Effect of silica size and concentration on the morphology of silica–polystyrene composite particles, *J. Colloid Interf. Sci.* 210 (1999) 281–289.
- [8] S. Gu, T. Kondo, M. Konno, Preparation of silica–polystyrene core–shell particles up to micron sizes, *J. Colloid Interf. Sci.* 272 (2004) 314–320.
- [9] I. Sondi, T.H. Fedynshyn, R. Sinta, E. Matijevic, Encapsulation of nanosized silica by in situ polymerization of t-butyl acrylate, *Langmuir* 16 (2000) 9031–9034.
- [10] K.M. Do, H. Yuvaraj, M.H. Woo, H.G. Kim, E.D. Jeong, K.P. Johnson, K.T. Lim, Synthesis of polystyrene/SiO<sub>2</sub> composite microparticles by dispersion polymerization in supercritical fluid, *Colloid Polym. Sci.* 286 (2008) 1343–1348.
- [11] Y. Li, Z. Di, J. Ding, D. Wu, Z. Luan, Y. Zhu, Adsorption thermodynamic, kinetic and desorption studies of Pb<sup>2+</sup> on carbon nanotubes, *Water Res.* 39 (2005) 605–609.
- [12] Y. Cui, X. Chang, X. Zhu, N. Jiang, Z. Hu, N. Lian, Nanometer SiO<sub>2</sub> modified with 5-sulfosalicylic acid as selective solid-phase extractant for Fe(III) determination by ICP-AES from biological and natural water samples, *Microchem. J.* 86 (2007) 23–28.
- [13] G. Zhao, Preparation and Adsorption Properties of Silica Gel Composite Microspheres Encapsulated by Functionalized Polystyrene, Master's thesis, Ludong University, Yantai, 2008, pp. 25–26.
- [14] Z.-G. Zhao, The Application Principle of Adsorption, Chemical Industry Press, Beijing, 2005, pp. 173–313.
- [15] K. Fujiwara, A. Ramesh, T. Maki, H. Hasegawa, K. Ueda, Adsorption of platinum (IV), palladium (II) and gold (III) from aqueous solutions onto L-lysine modified crosslinked chitosan resin, *J. Hazard. Mater.* 146 (2007) 39–50.
- [16] M. Yu, D. Sun, W. Tian, G. Wang, W. Shen, N. Xu, Systematic studies on adsorption of trace elements Pt, Pd, Au, Se, Te, As, Hg, Sb on thiol cotton fiber, *Anal. Chim. Acta* 456 (2002) 147–155.
- [17] G. Gamez, J.L. Gardea-Torresdey, K.J. Tiemann, J. Parsons, K. Dokken, M.J. Yacamán, Recovery of gold (III) from multi-elemental solutions by alfalfa biomass, *Adv. Environ. Res.* 7 (2003) 563–571.
- [18] D. Jermakowicz-Bartkowiak, B.N. Kolarz, A. Serwin, Sorption of precious metals from acid solutions by functionalised vinylbenzyl chloride-acrylonitrile-divinylbenzene copolymers bearing amino and guanidine ligands, *React. Funct. Polym.* 65 (2005) 135–142.
- [19] M.A. Abd El-Ghaffar, Z.H. Abdel-Wahab, K.Z. Elwakeel, Extraction and separation studies of silver (I) and copper (II) from their aqueous solution using chemically modified melamine resins, *Hydrometallurgy* (2008), doi:10.1016/j.hydromet.2008.07.008.
- [20] X. Xue, F. Li, Removal of Cu(II) from aqueous solution by adsorption onto functionalized SBA-16 mesoporous silica, *Micropor. Mesopor. Mater.* 116 (2008) 116–122.
- [21] C. Chen, J. Wang, Removal of Pb<sup>2+</sup>, Ag<sup>+</sup>, Cs<sup>+</sup> and Sr<sup>2+</sup> from aqueous solution by brewery's waste biomass, *J. Hazard. Mater.* 151 (2008) 65–70.