Grafting of Poly[styrene-co-N-(4-vinylbenzyl)-N,N-diethylamine] Polymer Film onto the Surface of Silica Microspheres and Their Application as an Effective Sorbent for Lead Ions

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ABSTRACT: Amino containing polymer of poly[styrene-*co*-N-(4-vinylbenzyl)-*N,N*-diethylamine] (PS-*co*-PVEA) was successfully grafted onto the surface of silica microspheres via the seed dispersion polymerization of styrene and *N*-(4-vinylbenzyl)-*N,N*-diethylamine in the presence of divinylbenzene employing the 3-(methacryloxy)propyltrimethoxysilane activated silica microspheres as the seed. The polymerization led to thin chelating polymer films (30 nm) coated silica microspheres (silica@polymer) as determined by transmission electron microscopy. The synthesized silica@polymer composites were used as sorbents for lead ions (Pb^{2+}). The adsorption properties, such as the pH effect, the adsorption kinetic, adsorption isotherm as well as the reuse of the silica@polymer sorbent were evaluated. The results demonstrated that the optimized adsorption condition was under neutral and the silica@polymer sorbent was efficient since it showed higher adsorption amounts (8.0 mg/g) and shorter adsorption equilibrium time (8 h) than that of the PS-*co*-PVEA microspheres and the pristine silica microspheres. Moreover, the silica@polymer sorbent was reusable even after four cycles of adsorption. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2013**, *000*, 39973.

INTRODUCTION

Environmental contamination with heavy metal ions in the aqueous system is still a worldwide threat to human health because of their high tendency to accumulate in living organisms and toxicities in relatively low concentration.[1–4] Lead (Pb) is a major contaminant present in industrial effluents. The harms of Pb^{2+} ions for human body involve that it can cause severe damage to kidney, nervous system, reproductive system, liver, and brain and may even result in sickness or death.[5] Therefore, there is a continuous need for new separation techniques, by which Pb^{2+} ions can be extracted and removed from dilute waste waters and industrial process streams.[6–8] During the past few decades, many separation methods such as precipitation,[9] chemical reduction,[10] membrane separation,[11] adsorption,[12] and biological treatment[13] have been used to remove Pb^{2+} ions from waste water. Among these methods, adsorption is not only an effective and simple method, but also the solid adsorbent can be reused.[14–19]

Chelating resins with ligand such as amino,[20] carboxyl,[21] iminoacetate,[22] Schiffbase,[23] aminophosphonate,[24] 8-hydroxyquino-line,[25] amidoxime,[26] and so on, have been recognized as efficient adsorption sorbents for the removal of heavy metal ions from aqueous medium due to their high adsorption capacity and excellent selectivity. However, the relative low mechanical and thermal stability, acid/base corrosion and eventually the chelating group embedding inside the bulk resins greatly restrain their adsorption performance such as long adsorption equilibrium time and bad recycle ability.[27] In recent years, there is a clear tendency to synthesize inorganic support grafted chelating polymer composites for the application of removing heavy metal ions from aqueous medium, since these polymer/inorganic composite materials combine well the strong chelating property of the chelating polymer with the excellent properties of inorganic particles.[28–30] Moreover, the relatively thin polymer film grafted onto the surface of inorganic support instead of bulk particles leads to the good accessibility to the target species, and low mass-transfer resistance.[30]

Silica nanoparticles are considered as one of the most excellent support candidate due to their exceptional thermal stability, remarkable mechanical as well as large surface area.[31] Grafting

of chelating polymer film onto the surfaces of silica nanoparticles support would endow chelating polymer with large surface area. Additionally, the chelating sites in the outer layer of the composite adsorption materials would improve the accessibility of target ions and therefore reduce the binding time.[32] Generally, there are two methods for the grafting process called "grafting to" and "grafting from." Often in the "grafting to" technique, the living polymer chains are reacted with suitable termination groups on the inorganic particles surface. However, the formation of polymer layers on the surface by this technique is intrinsically limited due to kinetic hindrance, and therefore leads to low graft density.[33–35] In comparison, the "grafting from" method needs firstly functionalize the silica particles surface with an active group, which will take part in the polymerization process and subsequently the grafted polymer chains propagating from the surface via the grafting polymerization.[36] During the past few decades, a variety of polymer with functionalized groups has been successfully grafted onto the surface of silica microspheres via "grafting from" methods.[37–40] However, the application of chelating polymer grafted silica microspheres for heavy metal adsorption is relatively scarce. Panahi et al. reported the surface grafting of polymer containing a functional monomer for metal chelating, poly[1-(N,N-bis-carboxymethyl)amino-3-allylglycerol-co-dimethylacrylamide] onto silica gel modified by silylation with 3-mercaptopropyltrimethoxysilane.[32] Gao et al. have successfully grafted poly(glycidylmethacrylate) (PGMA) onto the surface of 3-(methacryloxy)propyltrimethoxysilane functionalized silica gel and the epoxy groups within the PGMA was subsequently reacted with iminodiacetic acid to obtain amino functionalized chelating polymer/silica composites.[20] Sun et al. have prepared chelating polymer/silica composites by grafting of PGMA onto the surface of silica microspheres and followed the modification of the epoxy groups by dimethylamine.[39] These as-prepared chelating polymer/silica composites were used as an effective adsorption material for heavy metal ions.

In this study, an alternative valid strategy was proposed to synthesize amino containing polymer grafted onto the surface of silica microspheres and their application as sorbents for Pb^{2+} ions was explored. Initially, monodispersed silica microspheres were synthesized by Stöber method and then activated by 3-(methacryloxy)propyltrimethoxysilane (MPS). The resultant MPS activated silica microspheres were coated with a thin layer of amino containing polymer of poly[styrene-co-N-(4-vinylbenzyl)-N,N-diethylamine] (PS-co-PVEA) by dispersion polymerization of styrene and N-(4-vinylbenzyl)-N,N-diethylamine in the presence of divinylbenzene and thus the polymer coated silica microspheres of silica@polymer composites were produced. The as-prepared silica@polymer composites were used as sorbents for Pb^{2+} ions. The adsorption properties, such as pH value effect, the adsorption kinetics, adsorption isotherm, as well as the reuse of the silica@polymer sorbent were discussed.

EXPERIMENTAL
Materials
Azobisisobutyronitrile (AIBN, >99%, Tianjin Chemical Company Co.) was recrystallized from ethanol before being used.

The reagents including tetraethyl orthosilicate (TEOS, >98%, Tianjin DaMao Chemical Co.), ethylenediamine (>98%, Jiangsu FuChen Chemical Co.), chloromethylstyrene (CMS, >97%, Chengdu XiYa Chemical Co.), and 3-(methacryloxy)propyltrimethoxysilane (MPS, >97%, Shanghai YaoHua Chemical Co.) were used as received. Styrene (St, >98%, Tianjin Chemical Co.) and divinylbenzene (DVB, >98%, Tianjin Chemical Co.) were distilled under vacuum before being used. All the other chemical reagents were analytic grade and used as received.

Synthesis of N-(4-Vinylbenzyl)-N,N-diethylamine
The N-(4-vinylbenzyl)-N,N-diethylamine (VEA) was prepared by nucleophilic substitution reaction of chloromethylstyrene and ethylenediamine.[41] Typically, CMS (30.4 g, 0.20 mol), ethylenediamine (51.6 g, 0.40 mol), K_2CO_3 (48.8 g, 0.40 mol), and 200 mL of $CHCl_3$ were sequentially added into a 500 mL glass flask. The flask content was initially degassed by nitrogen purge and then heated at 50°C for 24 h with magnetic stirring. After completion of the reaction, the mixture was poured into 500 mL of water, and then the organic phase was collected. The collected organic phase was initially dried over anhydrous magnesium sulfate, and then the solvent was removed by rotary evaporation under vacuum at room temperature to obtain a crude product. The crude product was purified by firstly passed through a column of basic alumina to remove the inhibitor and then distilled under vacuum to acquire a colorless liquid of VEA. ^{1}H NMR (400MHz, $CDCl_3$, δ): 7.34 (d, $J = 8.2$ Hz, 2H), 7.29 (d, $J = 8.2$ Hz, 2H), 6.71 (dd, $J = 11.0$ and 17.8 Hz, 1H), 5.72 (dd, $J = 1.0$ and 16.6 Hz, 1H), 5.20 (dd, $J = 1.0$ and 11 Hz, 1H), 3.55 (s, 2H), 2.52(q, $J = 7.1$ Hz, 4H), 1.04 (t, $J = 7.1$ Hz, 6H). The ^{1}H NMR spectra as shown in Supporting Information Figure S1.

Synthesis of MPS Modified SiO2 Microspheres
The MPS modified SiO_2 microspheres were synthesized firstly by synthesis of SiO_2 microspheres through the Stöber method[42] and followed the modification of SiO_2 microspheres with MPS. In a typical procedure, 8.33 g (0.040 mol) of TEOS was added into 208 mL of the mixture of ethanol, water and 25 wt % ammonia aqueous solutions (180/20/8 by volume). The hydrolysis of TEOS was maintained at room temperature for 12 h with vigorous stirring. After that, 0.745 g MPS (3.0 mmol) was added into the reaction system and stirred another 12 h to accomplish the modification. Finally, the product was collected by centrifugation and purified through extraction with ethanol (30 mL × 3) for three times and then dispersed in 100 mL of ethanol for next use.

Synthesis of Poly[styrene-co-N-(4-vinylbenzyl)-N,N-diethylamine] Coated Silica Microspheres
A typical procedure for dispersion polymerization was as follows: into a 250 mL flask, 40 mL of MPS-modified silica microspheres suspension containing 0.8 g MPS-modified silica microspheres, 60 mL ethanol and PVP (0.2 g) were added and then the suspension was subjected to sonication for 20 min. Subsequently, the mixture of styrene (1.0 g, 10 mmol), VEA (1.0 g, 5.3 mmol) and DVB (40 mg, 0.31 mmol) was added dropwise with vigorous stirring. The flask content was purged with nitrogen at room temperature, and then AIBN (60 mg,

0.37 mmol) was added. The flask content was purged again, and polymerization was performed at 70°C for 24 h under nitrogen atmosphere with vigorous stirring. Finally, the product was initially purified by centrifugation, washed with ethanol, and then dried at 40°C under vacuum to obtain the silica@polymer composites.

Synthesis of Poly[styrene-co-N-(4-vinylbenzyl)-N,N-diethylamine] Microspheres

The PS-*co*-PVEA microspheres were synthesized via emulsifier-free emulsion polymerization. Into a glass flask, deionized water (500 mL) and PVP (0.30 g) were initially added at room temperature. Subsequently, the monomer mixture of St (2.5 g, 2.5 $\times 10^{-2}$ mol), VEA (2.5 g, 1.3 $\times 10^{-2}$ mol) was added dropwise with stirring. The mixture was vigorously stirred for 30 min at room temperature to form uniform oil-in-water droplets. The flask content was initially degassed under nitrogen purge to remove oxygen, then heated at 80°C, and followed addition of $K_2S_2O_8$ (0.15 g, 0.55 mmol). The polymerization was performed under nitrogen atmosphere with vigorous stirring for 20 h at 80°C. After completion of the polymerization, the product of the PS-*co*-PVEA microspheres was collected by centrifugation (12,000 r/min, 30 min), washed with ethanol (20 mL $\times$ 3), dried at 40°C under vacuum.

Adsorption Experiments

Certain amount of sorbents (25 mg) were contacted with 10 mL of $Pb(NO_3)_2$ aqueous solution with initial concentrations ranging from 5.0 to 80 mg·L^{-1}. The desired pH values of the suspensions were adjusted by adding negligible volumes of 0.01 mol L^{-1} HCl or NaOH solutions. The samples were placed in a constant temperature reciprocating shaker bath at 25°C. Samples were taken at regular time intervals during incubation in order to measure the time needed to reach equilibrium. Initial and final Pb^{2+} ion concentrations were determined by a Hitachi Z-8000 atomic absorption spectrophotometer. The adsorption amounts (Q) of Pb^{2+} ion were calculated according to the following equation:

$$Q = \frac{(C_o - C_e) \times V}{m} \qquad (1)$$

where C_o (mg/L) is the initial concentration of Pb^{2+} ion, C_e (mg/L) was the concentration of Pb^{2+} ion after adsorption, V (L) was the volume of the $Pb(NO_3)_2$ solution, and m (g) was the weight of the silica@polymer sorbent.

Characterization

Fourier-transform infrared (FT-IR) measurement was performed on a Nicolet 380 IR spectrometer (Thermo Fisher Scientific, MA) using KBr pellets. Thermogravimetric analysis (TGA) was carried out on a Q 50, TA instrument (TA Instrument, MA) under a flowing nitrogen atmosphere with a heating rate of 10°C/min. The differential scanning calorimeter (DSC) experiments were performed on a NETZSCH DSC 204 differential scanning calorimeter (NETZSCH-Geraetebau GmbH, Bavaria, Germany) in a dry nitrogen atmosphere with a heating rate of 10°C/min. The ^{1}H NMR spectrum was obtained on a Varian UNITY PLUS-400 NMR spectrometer (Varian, State of California) using CDCl$_3$ as solvent. The scanning electron microscopy (SEM) images and energy dispersive X-ray (EDX) spectra were

obtained with a Hitachi S-3000N microscope (Hitachi, Tokyo, Japan). Transmission electron microscopy (TEM) observation was performed using a Philips T20ST electron microscope (Philips, Eindhoven, Holland) at an acceleration of 200 kV, whereby a small drop of the aqueous dispersion of the synthesized microspheres was deposited onto a piece of copper grid and then dried at room temperature under vacuum. The concentration of Pb^{2+} ions was determined by Atomic Adsorption Spectrophotometer (AAS) on a Hitachi Z-2000 atomic absorption spectrometer (Hitachi, Tokyo, Japan) equipped with air–acetylene flame.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Polymer Coated Silica Microspheres

The synthesis of silica@polymer involves three steps: first, silica microspheres were synthesized by Stöber method; second, the silica microspheres were modified by MPS to anchor C=C bond on the surface of the silica microspheres; third, the dispersion polymerization of styrene and VEA in the presence of 2 wt % cross-linker of DVB employing the MPS modified silica microspheres as the seed and PVP as stabilizer, as illustrated in Scheme 1. During the polymerization, the generated active oligomer would deposit on the silica microspheres due to the hydrophobic surface of the MPS modified silica microspheres and copolymerized with the C=C bond to form polymer grafted silica microspheres of silica@polymer. The polymer layer was covalently bonding onto the surface of silica microspheres rather than simply physical adsorption. In the polymer layer, the PVEA segment containing amino group was used as ligand for the adsorption of Pb^{2+} ions while the PS segment was introduced to increase the thermal stability of the grafted polymer layer since the PVEA segment had a low glass transition temperature (T_g) of 35°C (Supporting Information Figure S2).

The FTIR was utilized to monitor the preparation process of silica@polymer, as shown in Figure 1. The spectrum of silica microspheres [Figure 1(a)] showed typical peaks of silica indicated by the sharpness peak of the Si–O–Si asymmetric stretching at 1087 and 1099 cm^{-1}. After the modification of silica microspheres by MPS, several new peaks were found [Figure 1(b)], i.e., methylene stretching vibration peaks at 2855 and 2920 cm^{-1}, the stretching vibrations of the vinyl groups and carbonyl groups at 1632 and 1715 cm^{-1}, respectively, indicating the successful introduction of MPS on the surface of silica microspheres. In the FTIR spectrum of the silica@polymer product [Figure 1(c)], besides the typical peak of silica, the characteristic bands at 1600, 1492, 1451, 757, and 699 cm^{-1} ascribed to the PS segment and the appearance of the C–N stretching vibration at 1000–1350 cm^{-1} and the methylene stretch at 2855 and 2920 cm^{-1} ascribed to the PVEA segment were clearly observed, confirming the formation of PS-*co*-PVEA polymer and silica composites.

To gain a more quantitative picture of the extent of silica microspheres grafting, the TGA was performed on the reaction product (Figure 2). The TGA plot of silica microspheres was also shown in Figure 2 [curve (a)], and indicated a gradual mass loss of 3.1 wt % as the temperature reached to 500°C
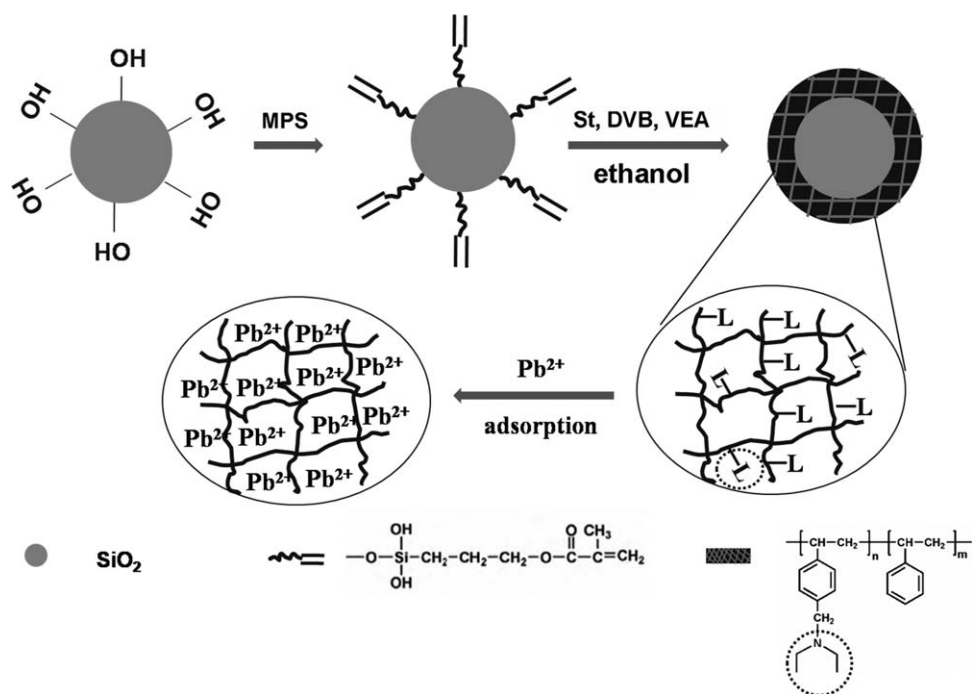
Scheme 1. Schematic grafting of poly[styrene-*co-N*-(4-vinylbenzyl)-*N,N*-diethylamine] polymer film onto the surface of silica microspheres and their application as an sorbent for Pb^{2+} ions.

which may attribute to the weight loss of hydroxyl group on the surface of silica microspheres. Chosen the mass loss of silica microspheres at 500°C as the reference, the mass loss of the MPS modified silica microspheres [Figure 2, curve (b)] at 500°C was about 8.3 wt % and the C=C band on the surface of silica microspheres was calculated to be 0.27 mmol/g. The TGA plot of the silica@polymer sample [Figure 2, curve (c)] showed that the weight loss of organic group on silica microspheres was about 67.2 wt % suggesting that the grafted polymer layer contents of 58.9 wt %.

The EDX spectrum of the pristine silica microspheres and the silica@polymer were shown in Figure 3(A,B) and the element

contents were summarized in the table inserted. As shown, the pristine silica microspheres [Figure 3(A)] only contained Si, O while the silica@polymer [Figure 3(B)] revealed the presence of element N and C in addition to the Si, O. The mass contents of N and C in the silica@polymer were determined to be about 2.17 and 50.81%, respectively. These results suggested that the PS-*co*-PVEA polymer had been successfully grafted on the surface of silica microspheres and the weight ratio of PS and PVEA segment was closely to 1 : 1 which was equal to the feeding weight ratio. The morphological structure of the pristine silica microspheres and the silica@polymer were characterized by SEM, as depicted in Figure 4. As shown in the SEM images [Figure 4(A,B)], both the pristine silica microspheres and the
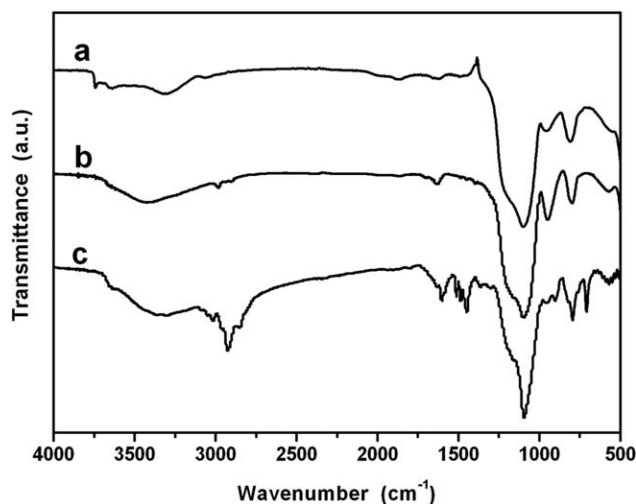

Figure 1. FTIR spectra of (a) silica microspheres, (b) MPS modified silica microspheres, and (c) silica@polymer composite.
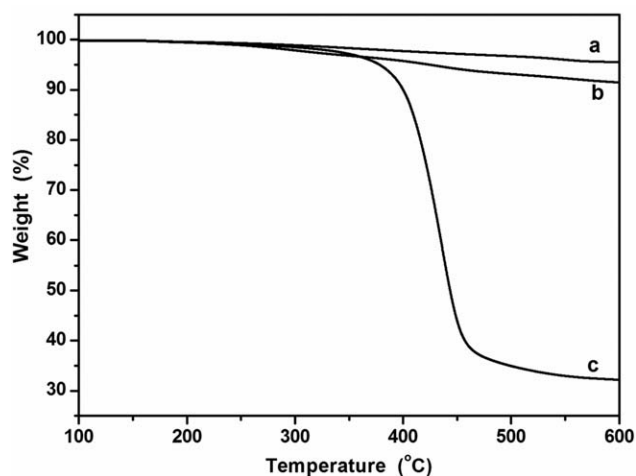

Figure 2. The TGA plots of the (a) silica microspheres, (b) MPS modified silica microspheres, and (c) silica@polymer composite.

Element	Wt(%)	At(%)
OK	67.56	78.52
SiK	32.44	21.48

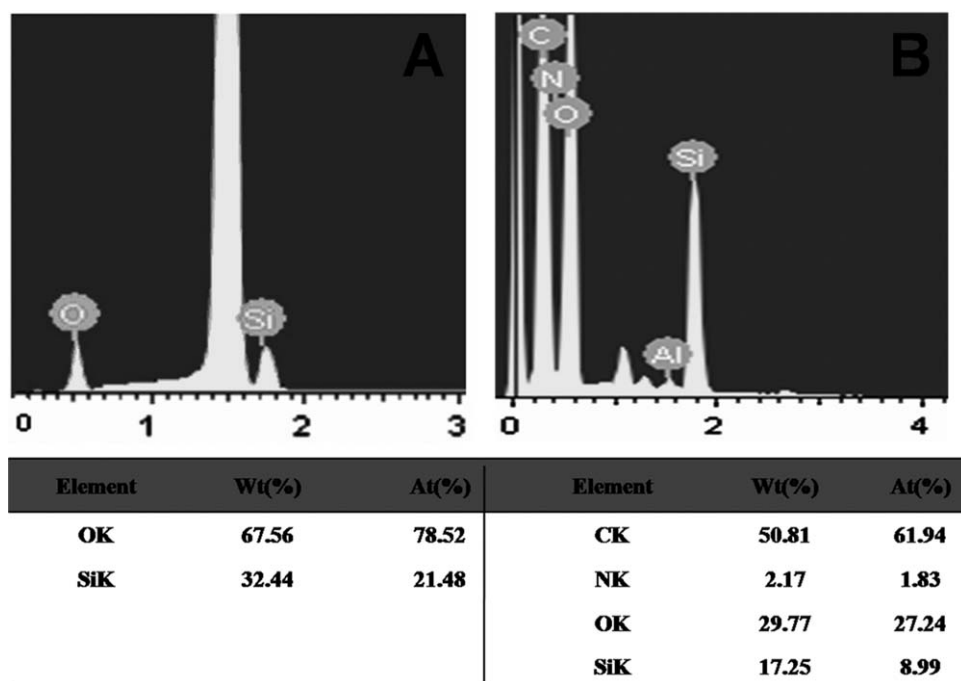| Element	Wt(%)	At(%)
CK	50.81	61.94
NK	2.17	1.83
OK	29.77	27.24
SiK	17.25	8.99

Figure 3. The EDX spectra of the (A) silica microspheres and (B) silica@polymer composite.

silica@polymer had a uniform size distribution, and the average diameter of the pristine silica microspheres and silica@polymer were about 120 and 180 nm, respectively. No polymer aggregates were found in the SEM images of the silica@polymer suggesting that the surface grafting polymerization was well-carried out and the unnecessary solution polymerization was avoid. To get a more clear observation of the morphological structure and determine the thickness of the grafted polymer layer, the pristine silica microspheres and the silica@polymer were characterized by TEM. From the TEM images it could be seen that the surface of the pristine silica microspheres was smooth [Figure 4(C)] while the silica@polymer exhibited an obviously core–shell structure and the average thickness of the polymer layer was measured to be 30 nm [Figure 4(D)].

Adsorption Properties of Silica@polymer

Compared with those chelating resin prepared by bulk or solution polymerization, the advantages of surface grafted chelating polymer lied in that the chelating groups were on the surface of sorbent and this would benefit to the accessibility of the target heavy metal ions.[32] Usually, for the amino containing chelating polymers the pH value of the solution affected the adsorption property of the sorbent.[43] Thus in the following discussion, the pH effect on the adsorption property of the silica@polymer sorbent was firstly explored. With the optimized pH value in hand, the adsorption dynamic, the adsorption isotherm as well as the reuse of the silica@polymer sorbent was studied.

In order to explore the pH effect on the adsorption property of the silica@polymer sorbent, adsorption experiments were performed with the initial concentration of Pb^{2+} ions at 30 mg/L, adsorption time of 24 h and the pH value of the $Pb(NO_3)_2$ aqueous solution ranging from 1 to 10 and the results were summarized in Figure 5. As shown in Figure 5, the adsorption

amounts (Q) of Pb^{2+} ion for the silica@polymer sorbent increased continuously with the decrease in the acidity and the adsorption amounts under neutral condition (pH = 7) showed the highest value of 8.1 mg/g. This may be because that under acid condition, the concentration of hydrion (H^+) in solution was relatively high and the surface of the silica@polymer sorbent was positively charged due to the ionization of the amino group in the polymer. On one hand, the H^+ would compete with Pb^{2+} to bind with the chelating polymer. On the other hand, positively charged surface of the silica@polymer sorbent greatly decreased the chelating opportunity of Pb^{2+} with chelating polymer. However, when the aqueous solution was basic, the adsorption amounts slowly decreased with the increasing of the pH value. The reason was ascribed to the decrease of the dispersibility and the swelling ratio of the silica@polymer sorbent under basic condition which would lead to the embedding of the chelating sites in the polymer and therefore a relatively low adsorption amounts.[39] These results suggest that the optimized adsorption pH value was 7 and all the subsequent adsorption experiments were performed under neutral condition if it was specially pointed out otherwise.

With the optimized pH value in hand, the adsorption kinetics of the Pb^{2+} ions on the silica@polymer, pure PS-*co*-PVEA microspheres synthesized by emulsion polymerization (Supporting Information Figure S3) and the pristine silica microspheres sorbents were evaluated under the condition pH = 7 and the initial concentration of Pb^{2+} ions at 30 mg/L. Here it should be pointed out that in the adsorption kinetic experiment the adding amounts of PS-*co*-PVEA microspheres sorbent was determined by keeping the molar mass of the amino group the same as the silica@polymer sorbent and the adding amounts of the pristine silica microsphere sorbents was the same as the silica@polymer sorbent. Figure 6(A) shows the adsorption amounts of
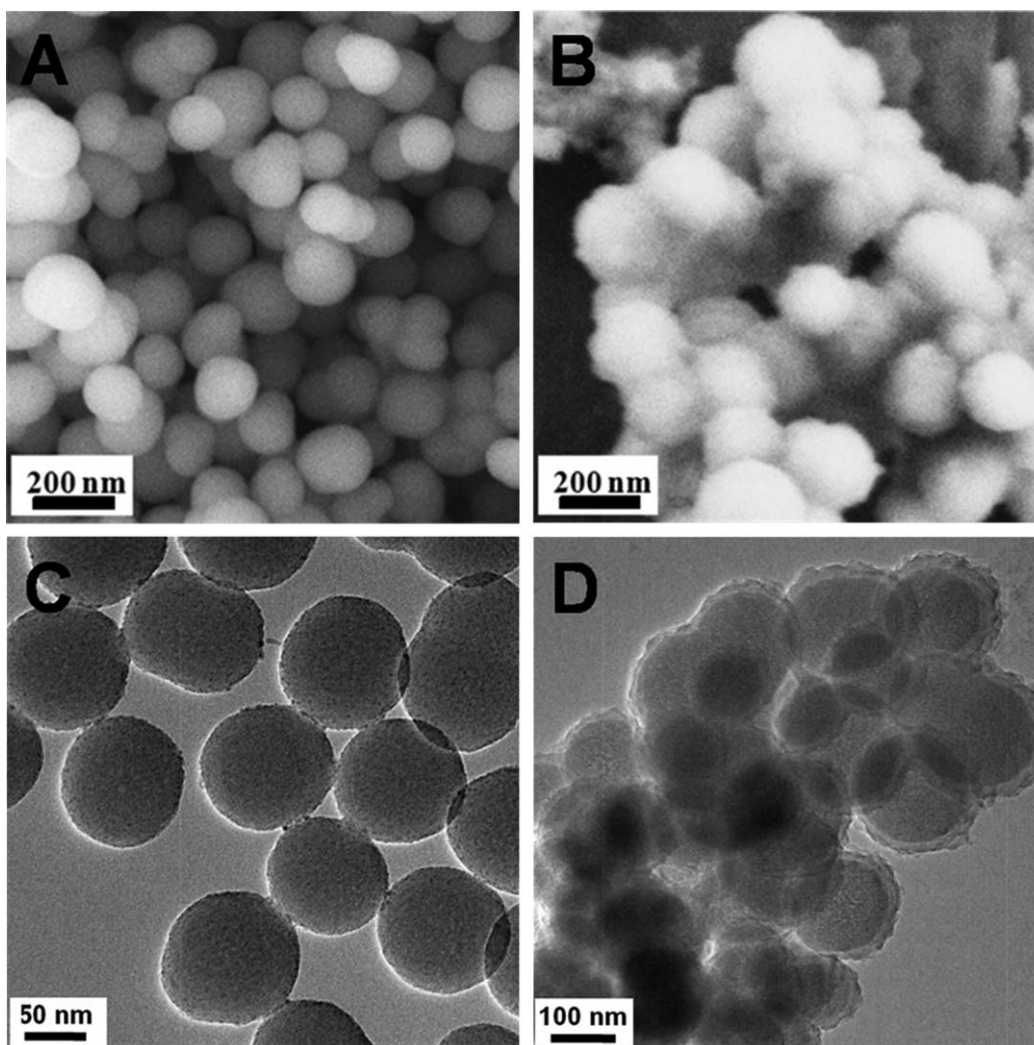
Figure 4. The SEM and TEM images of the (A,C) silica microspheres and (B,D) silica@polymer composite.

Pb^{2+} ions versus the incubation time. Clearly, the silica@polymer required a shorter time (about 8 h) to reach adsorption equilibrium than that of the PS-*co*-PVEA microspheres (about 16 h) and the pristine silica microspheres (about 24 h) and the equilibrium adsorption amount of the three sorbents were in the order of silica@polymer (8.0 mg/g) > PS-*co*-PVEA microspheres (5.6 mg/g) > the pristine silica microspheres (1.7 mg/g). These comparative results suggested that the amino group played an important role in the adsorption of Pb^{2+} ions and the surface grafted polymer film of the silica@polymer sorbent benefited to the fast adsorption. For the purpose of investigation of the rate-controlling step in the adsorption mechanism, the kinetic data of silica@polymer sorbent against Pb^{2+} ions were dealt with pseudo-first order model. The pseudo-first order model was described in the following equation:

$$\ln(Q_e - Q_t) = \ln Q_e - kt \qquad (2)$$

where Q_t and Q_e (mg/g) represented the amount of metal ions adsorbed on the adsorbents at time t (h) and equilibrium, respectively. k (h^{-1}) was the rate constant of the pseudo-first order model. A linearized plot of $\ln(Q_e - Q_t)$ versus t was
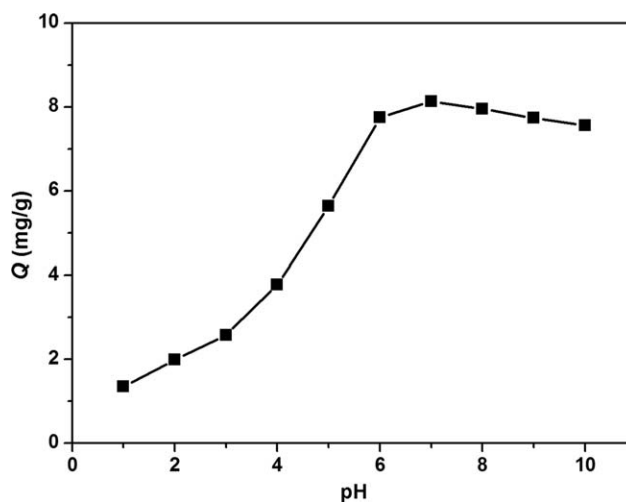

Figure 5. The pH effect on the adsorption property of the silica@polymer sorbent. Adsorption condition: amount of silica@polymer composite, 25 mg; initial concentration of Pb^{2+} ions, 30 mg/L; adsorption time, 24 h.
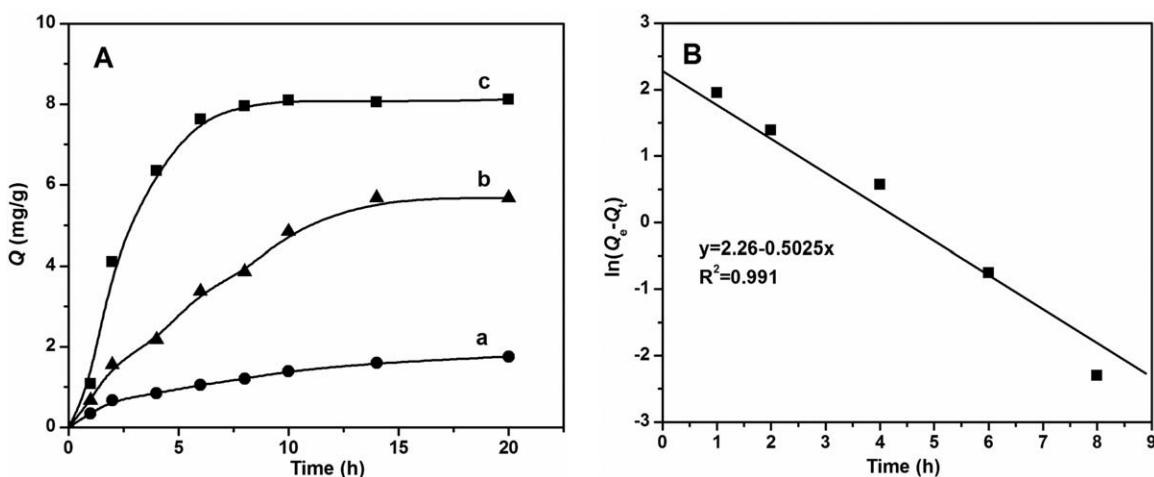
Figure 6. (A) Adsorption kinetic curves of Pb^{2+} ions on pure silica microspheres, PS-*co*-PVEA microspheres and silica@polymer sorbent, respectively, and (B) the pseudo-first order kinetic model plot for the adsorption of Pb^{2+} ions on silica@polymer sorbent. Adsorption condition: amount of sorbent: 25 mg; pH value: 7.0; initial concentration of Pb^{2+} ions: 30 mg/L.

obtained from the model, as shown in Figure 6(B). The correlation coefficient (R^2) value was 0.991 and the k value was measured to be 0.50 (h^{-1}). The theoretical calculated $Q_{e,cal}$ value obtained from the pseudo-first order model was close to the experimental one ($Q_{e,exp}$) (9.6 mg/g vs. 8.0 mg/g). These results suggest that the adsorption process satisfied the pseudo-first kinetic.

It is well known that the concentration of the metal ions is a key parameter on the adsorption experiment. Herein, the adsorption isotherms of the silica@polymer sorbent for Pb^{2+} ions under the condition pH = 7, adsorption time of 8 h and the concentration of Pb^{2+} ions ranging from 5.0 to 80 mg/L was studied. As shown in Figure 7(A), the adsorption amounts of Pb^{2+} ions dramatically increased from 1.7 to 8.3 mg/g with the initial Pb^{2+} ions concentration increased from 5.0 to 30 mg/L and the adsorption amounts slowly increased with the initial Pb^{2+} ions concentration above 30 mg/L. In order to understand how the adsorbates interact with the silica@polymer adsorbents, Langmuir isotherm based on the assumption that

all the adsorption sites were energetically identical and adsorption occurred on a structurally homogenous adsorbent was drawn according to the Freundlich equations:

$$\frac{C_e}{Q} = \frac{1}{Q_{max}\,b} + \frac{C_e}{Q_{max}} \tag{3}$$

where Q (mg/g) was the equilibrium adsorption capacity, Q_{max} (mg/g) was the maximum amount of metal ion per unit weight of the cell to form a complete monolayer coverage on the surface bound at high equilibrium metal ion concentration C_e (mg/L) and b (L/mg) was Langmuir constant related to the binding sites affinity. Q_{max} represented the practical limiting adsorption capacity when the surface was fully covered with metal ions, assisting the comparison of adsorption performance, and b indicated the bond energy of adsorption reaction between metal and material. A linearized plot of C_e/Q versus C_e was obtained from the model, as shown in Figure 7(B), demonstrating that the adsorption isotherms fit the Langmuir model. Based on the slope and interception of the linearized plot, the Q_{max} and b were calculated to be 9.1 mg/g and 0.58 L/mg, respectively.
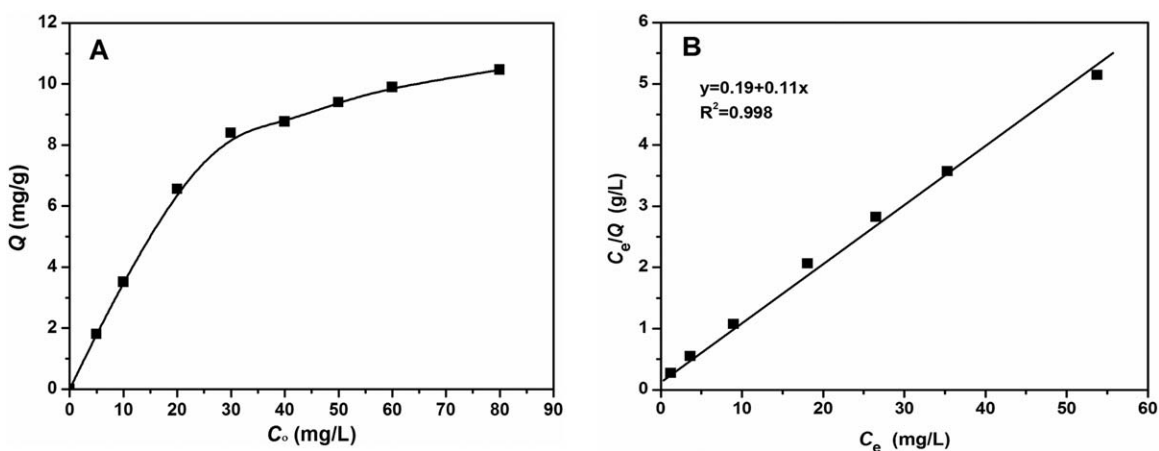

Figure 7. (A) Adsorption isotherm and (B) Langmuir isotherm of Pb^{2+} ions on silica@polymer sorbent. Adsorption condition: amount of silica@polymer composite: 25 mg; pH value: 7.0; adsorption time: 8 h.
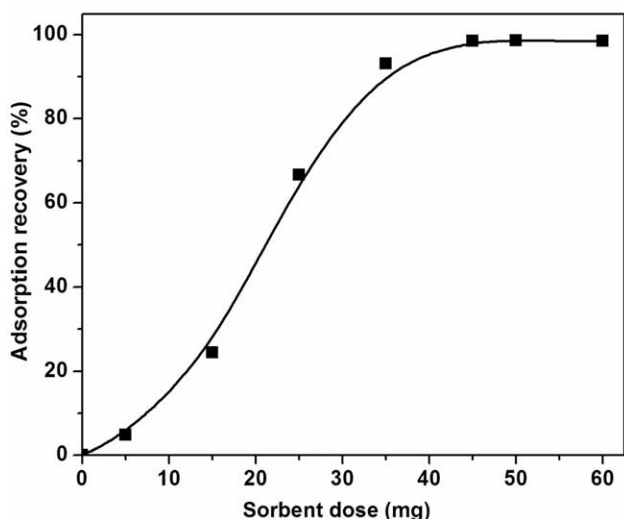
Figure 8. The effect of sorbent dose on adsorption recovery. Adsorption condition: initial concentration of Pb^{2+} ions: 30 mg/L; adsorption time: 8 h; pH value: 7.0.

Figure 9. The reuse of silica@polymer sorbent. Adsorption condition: amount of silica@polymer sorbent: 45 mg; initial concentration of Pb^{2+} ions: 30 mg/L; adsorption time: 8 h; pH value: 7.0.

As one of the artificial heavy metal receipted materials, the adsorption recovery was also a crucial parameter of sorbents. The adsorption recovery was directly correlation with the adding amounts of sorbents. Therefore, the effect of the sorbent dose on the adsorption recovery was evaluated under the condition pH = 7, adsorption time of 8 h and the concentration of Pb^{2+} ions at 30 mg/L with different adding amounts of the silica@polymer sorbents. As shown in Figure 8, the adsorption recovery increased greatly from 5.6% to 92.1% as the sorbent dose increase from 5 mg to 35 mg, and then reached a plateau of 98.7% with the sorbent dose increasing from 45 to 60 mg. These observations can be illustrated by that the increase of the sorbent dose may multiply the number of available adsorption sites, hence leading to the raise of the removal efficiency. However, when nearly all the heavy metals in the aqueous solutions were adsorbed by the adsorbents, the number of unoccupied active adsorption sites grew, which would no longer contributed to the removal percentage, and thus resulted in a constant of adsorption recovery.

The reuse of the silica@polymer sorbents was further studied. After the adsorption recovery reaches to 98.7% was just com-
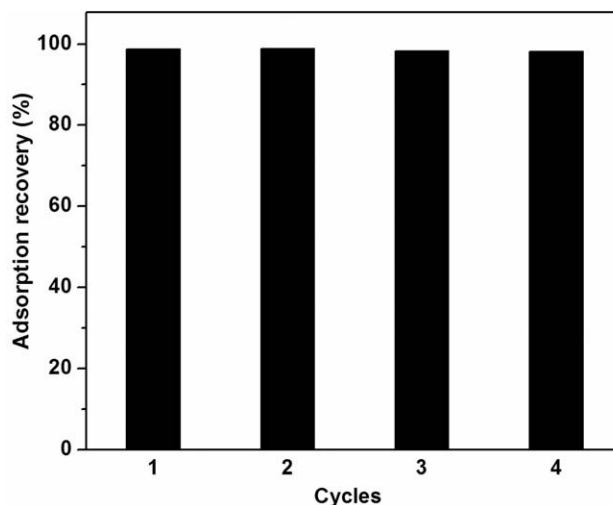
pleted in 8 h, the silica@polymer sorbents was centrifugated, washed several times with dilute nitric acid (5 wt %) to remove the adsorbed Pb^{2+} ions. It was found that after three times of nitric acid treating there was no Pb^{2+} ions in the aqueous solution detected by AAS analysis (detection limit was 0.03 ppm) indicating the complete desorption of Pb^{2+} on the silica@polymer sorbents. The sorbents were then neutralized by sodium hydrate (5 wt %) and finally washed with water until the aqueous solution was neutral (pH = 7). The separated sorbents was reused in the next run. The results showed that the adsorption recovery of the Pb^{2+} ions kept more or less the same (~95%) even after four cycles of adsorption (Figure 9). The recycled sorbents was further characterized by TEM. As shown in Supporting Information Figure S4, the morphology of the silica@polymer sorbents after recycling remained similar to the fresh one, indicating the stability and reusability of the silica@polymer sorbents in the present condition.

Comparison of Other Sorbents

Comparative information from the studies on Pb^{2+} ions adsorption by other polymer/silica sorbents was presented in Table I. As shown in Table I, the adsorption capacity of the

Table I. Comparison of Adsorption Capacity and Adsorption Equilibrium Time with Some Literatures

Matrix	Adsorption property		References
	Capacity (mg/g)	Equilibrium time (h)	
Support: silica microsphere			
Silica@polymer	8.0	8	Our sorbent
EDTA-modified chitosan/SiO_2/Fe_3O_4 adsorbent	9.3	3	[44]
Support: silica gel			
IDAA-PGMA/silica gel	240	20	[20]
Poly(AGE/IDA-co-DMAA)-grafted-silica gel	15.0	4	[32]

silica@polymer sorbents are comparable with some of sorbents reported in the literature such as poly(AGE/IDA-*co*-DMAA)-*grafted*-silica gel[32] and EDTA-modified chitosan/SiO$_2$/Fe$_3$O$_4$ adsorbents.[44] While the adsorption equilibrium time for silica@-polymer sorbents was shorter than that of IDAA-PGMA/silica gel sorbent.[20] This might ascribed to that the present silica@polymer sorbent possessed the well-defined structure and the relatively thin chelating polymer film which endowed the chelating polymer/silica composites with large surface area and easy accessibility for Pb^{2+} ions. The feasibility of the repeated use of the present silica@polymer was an additional advantage since the silica microspheres had exceptional thermal stability, remarkable mechanical. Moreover, the cheating polymers were synthesized just by the copolymerization of styrene and a functional monomer of *N*-(4-vinylbenzyl)-*N*,*N*-diethylamine, get rid of the tedious post-functionalization process such as the preparation of IDAA-PGMA/silica gel,[20] poly(AGE/IDA-*co*-DMAA)-*grafted*-silica gel,[32] and PVA/silica gel sorbent.[40] This offered the easy control of the chemical component and the thickness of grafted polymer film on silica microspheres. We believe that a silica@polymer sorbent with high adsorption capacity and even shorter adsorption equilibrium time can be prepared by carefully controlling the synthetic condition. The effect of chemical component, the degree of cross-linking, thickness of grafted polymer film on adsorption property of silica@polymer sorbent will be discussed in the future work.

CONCLUSIONS

Synthesis of amino containing polymer grafted onto the surface of silica microspheres (silica@polymer) via the seed dispersion polymerization of styrene and *N*-(4-vinylbenzyl)-*N*,*N*-diethylamine in the presence of divinylbenzene employing the 3-(methacryloxy)propyltrimethoxysilane activated silica microspheres as the seed and their application as an effective sorbent for lead ions (Pb^{2+}) was reported. The advantages of the silica@polymer sorbent lied in: (1) the synthesis was relatively easy without the post modification process; (2) the grafted thin polymer film (about 30 nm) made the chelating group of amino distribute on the surface of silica microspheres which led to the easy accessibility for Pb^{2+}; (3) the composites of polymer and silica combined well the chelating ability of the polymer and the mechanical stability of silica microspheres. Adsorption experiments demonstrated that the optimized adsorption pH value was 7, the adsorption equilibrium time of silica@polymer sorbent was 8 h which was shorter than that of the PS-*co*-PVEA microspheres and the pristine silica microspheres, and the maximum adsorption amounts was about 8.0 mg/g. The kinetic study demonstrated that the adsorption process of silica@polymer against Pb^{2+} satisfied the pseudo-first kinetic. The adsorption isotherms fit the Langmuir model. Moreover, the silica@polymer sorbent was reusable even after four cycles of adsorption. This kind of sorbent was expected to have practical application in wastewater treatment.

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