Preparation of organically functionalized silica gel as adsorbent for copper ion adsorption

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Received 26 December 2008; revised 17 April 2009; accepted 21 April 2009

Abstract

A novel adsorbent (AMPS-silica) was synthesized by bounding AMPS (2-acrylamido-2-methylpropanesulfonic acid) onto silica surface, which functioned with γ-methacryloyloxypropylmethoxysilane reagent. The adsorbent was characterized by nitrogen adsorption/desorption measurement, thermogravimetric analysis (TGA) and potentiometric titration analysis. The TGA result indicated that the surface modification reactions introduced some organic functional groups onto the surface of silica. The surface area of AMPS-silica was 389.7 m²/g. The adsorbent was examined for copper ion removal in series of batch adsorption experiments. Results showed that the adsorption of Cu²⁺ onto AMPS-silica was pH dependent, and the adsorption capacity increased with increasing pH from 2 to 6. The adsorption kinetics showed that Cu²⁺ adsorption was fast and the data fitted well with a pseudo second-order kinetic model. The adsorption of Cu²⁺ onto AMPS-silica obeyed both Freundlich and Langmuir isotherms, with \( r^2 = 0.993 \) and \( r^2 = 0.984 \), respectively. The maximum Cu²⁺ adsorption capacity was 19.9 mg/g. The involved mechanism might be the adsorption through metal binding with organic functional groups such as carboxyl, amino, and sulfonic groups. Cu²⁺ loaded on AMPS-silica could be desorbed in HNO₃ solution, and the adsorption properties remain stable after three adsorption-desorption cycles.

Key words: organically functionalized silica gel; 2-acrylamido-2-methylpropanesulfonic acid (AMPS); adsorption

DOI: 10.1016/S1001-0742(08)62442-0

Introduction

Copper is extensively used in the electrical and semiconductor industries, and in the manufacture of fungicides and antifouling paints. As a result, waste streams containing low-to-medium level of Cu²⁺ are often encountered in industries. Copper contamination is of great concern due to its high toxicity and non-biodegradability. Recent studies also showed that copper might be a human carcinogen (Liu et al., 2006). Hence, it is of great practical interest to develop effective technologies to remove Cu²⁺. Many methods, such as chemical precipitation, ion exchange, reverse osmosis, and adsorption, have been employed to remove Cu²⁺ from solutions (Kim et al., 2008; Liu et al., 2006; Özcan et al., 2005). Among these methods, adsorption, being combined with appropriate desorption step, is an effective and versatile method and can avoid the disposal of large scale sludge. Several low-cost adsorbents, such as activated carbon, rice husk, montmorillonite, and natural bentonite, have been proposed to remove Cu²⁺ (Bhattacharyya and Gupta, 2007; Wong et al., 2003).

In recent years, the modification of adsorbents with organic functional groups has received great attention due to its high adsorption capacity, high selectivity, and easy regenerability (Chakraborty and Tare, 2006; Kumar et al., 2007; Xue et al., 2008). The functional groups on the surfaces of the adsorbents play important roles in the adsorption performance. The amine (–NH₂) group has been reported to be one of the most efficient functional groups to remove heavy metal ions, owing to the coordination between metal ions and amine groups (Ghoul et al., 2003; Gupta et al., 2004; Zhang et al., 2007). Various adsorbents containing –NH₂ groups in its backbone or from the synthetic polymers which are subsequently immobilized with –NH₂ groups, have been developed from natural biopolymers (e.g., chitosan) (Deng et al., 2003; Juang and Shao, 2002). Although adsorbents from natural biopolymers may be cost effective and have good adsorption performance, they are generally suffer from inherent problems such as mechanical and thermal instability.

Synthetic adsorbents with immobilized amine open a broad spectrum of prospects for tailor-made applications in the removal of different types of heavy metal ions, in the selective adsorption of individual types of heavy metal ions for recovery. To facilitate metal ions removal, different amine-containing compounds have been reported to immobilize onto various substrates such as polyacrylonitrile fiber (Deng et al., 2003), activated carbon (Yantasee et al., 2004), or cellulose (Torres et al., 2006). Besides amine
group, there are also other functional groups, such as iminodiacetic, thiol, carboxyl and sulfonic groups, which can bind heavy metal ions. Therefore, some new adsorbents which containing above functional groups had been prepared and used in heavy metal removal from aqueous solution (Chen and Yang, 2006; Gad, 2008; Liu et al., 2008; Yetimoğlu et al., 2007).

In this study, a novel AMPS-silica adsorbent was prepared by grafting AMPS (2-acrylamido-2-methylpropanesulfonic acid) on silica gel to obtain an adsorbent with carboxyl, sulfonic and amide groups. Silica gel was used as carrier because of its large surface area and easy modification surface. AMPS was chosen as a functional monomer because it has amide, sulfonic, and carbonyl groups that could bind heavy metal ions. To our best knowledge, the grafting of AMPS on silica gel for heavy metals removal has not been reported. As an evaluation, the AMPS-silica adsorbent was examined for their performance in Cu²⁺ removal.

1 Materials and methods

1.1 Materials

The toluene, γ-methacryloxypropyltrimethoxysilane, (Dow Corning Z-6030 Silane, USA), silica gel, ammonium persulphate, and AMPS (Aldrich, USA) were used to prepare the adsorbent. Copper solutions were prepared from copper nitrate trihydrate (A.R.).

1.2 Adsorbent preparation

The method for functionalization of silica gel is illustrated in Scheme 1. The first stage in the preparation was the reaction between the silylating agent (γ-methacryloxypropyltrimethoxysilane) and the silanol groups on the silica surface. After dried at 120°C for 4 h, 10 g silica gels were dispersed in 250 mL of toluene before adding 1.0 g of γ-methacryloxypropyltrimethoxysilane. The mixture was stirred and refluxed for 12 h under nitrogen atmosphere at 50°C. The resulting product A (Scheme 1) was filtered and washed 2 times with toluene (50 mL), 4 times with ether (200 mL) and 8 times with ethanol (400 mL), and then was dried at 105°C for 4 h.

The second stage of the preparation procedure is as following: AMPS (1.0 g) and ammonium persulphate (0.02 g) were dissolved in 20 mL and 10 mL of deionized water, respectively. Ten grams of product A were immersed in 200 mL of deionized water and the mixture was heated to 90°C. Under vigorous magnetic-stirring, the AMPS solution and ammonium persulphate solution were added into the mixture drop by drop. Then, the formed suspension was continuously stirred for 8 h at 90°C. The final product (AMPS-silica) was filtrated and washed repeatedly with deionized water, and was dried at 105°C for 4 h.

1.3 Characterization

The thermal stability of the modified silica gel and silica gel was investigated by thermogravimetric analysis (TGA) (Q50, Thermal Analysis Co., USA). Nitrogen adsorption/desorption isotherms of the materials were determined by an ASAP 2000 surface analyzer (Micromeritics Co., USA). Each run was performed with approximately 0.1 g of sample which was pretreated at 200°C under vacuum. The specific surface area was determined using Brunauer-Emmett-Teller (BET) method. Pore size distribution and total pore volume of the materials were evaluated from the adsorption branch of nitrogen isotherms by using the Barrett-Joyner-Halenda (BJH) method.

The potentiometric titration was carried out with an...
automatic potential titrator (716 DMS Titrino, Metrohm Co., Switzerland). AMPS-silica 0.05 g was dispersed in 50 mL of 0.1 mol/L or 0.01 mol/L NaNO₃ solution which was CO₂ free and mixture was shaken for 70 h. Titration experiments were then carried out with 0.01 mol/L HNO₃ or 0.01 mol/L NaOH solution. The temperature was kept at (25 ± 0.5)°C.

Fourier transform infrared spectroscopy (FT-IR) was used to determine the vibration frequency changes of the functional groups in the AMPS-adsorbents before and after Cu²⁺ loaded and after one adsorption-desorption cycle. The spectra were collected using FT-IR 5700 (Nicolet, USA) within the wavenumber range from 400 to 4000 cm⁻¹.

1.4 Copper adsorption experiments

A batch study on the adsorption of Cu²⁺ from aqueous solution onto the AMPS-silica adsorbent was employed. All adsorption experiments were carried out in triplicates under room temperature ((25 ± 0.5)°C).

The pH effect on the adsorption performance was examined in the pH range 2–6 (initial pH values) at an initial copper concentration of 63 mg/L. Adsorbent 0.05 g was added into 50 mL of Cu²⁺ solution, with the pH being adjusted to a desired value with 0.1 mol/L NaOH or HNO₃. The vial was shaken on a rotary shaker at 70 r/min for 1 h and the final Cu²⁺ concentration was analyzed by inductively coupled plasma-emission spectroscopy (ICP-OES) (Perkin-Elmer Optima 2000, USA).

The adsorption kinetics was studied with 0.01 mol/L NaNO₃ as the background electrolyte at pH 4.5. A 0.75 g of AMPS-silica was added into 250 mL Cu²⁺ solution with the initial concentration of 200 mg/L. Samples were taken with a syringe at various time intervals for the determination of Cu²⁺ concentration.

In the adsorption isotherm experiments, the solution pH was controlled at 4.5. The initial concentration of Cu²⁺ was varied form 6–220 mg/L. A 0.05 g of AMPS-silica was added into each 50 mL Cu²⁺ solution with different initial concentrations. Other procedures were the same as those used for pH effect determination.

1.5 Desorption experiments

Cu-loaded AMPS-silica (0.2 g) were stirred with 20 mL 0.1 mol/L HNO₃ solution at room temperature for 2 h to desorb the metal ions. The final metal ion concentration in the aqueous phase was determined by using ICP-OES. Thereafter, the AMPS-silica was washed with deionized water and again subjected to adsorption processes to determine its reusability. The adsorption-desorption cycle was repeated three times by using the same adsorbent.

2 Results and discussion

2.1 Adsorbent characterization

2.1.1 Thermogravimetric analysis

TGA of AMPS-silica, product A and silica gel were performed and results are shown in Fig. 1. The TGA profiles could indicate a difference in chemical composition of the products obtained from each step of the modification. For silica gel, the TGA profiles show a loss of moisture at 60–100°C (Fig. 1a). In the cases of product A and AMPS-silica (Figs. 1b and 1c), the profiles show a weight loss at 350–400°C, which could be attributed to the loss of organic groups from the silica gel surface. A difference in weight loss between product A and AMPS-silica indicated the variation in their composition. The loss of water from the silica surface appeared at 400–850°C. The overall loading of organics on the functionalized silica gel was calculated using weight loss data of silica gel and functionalized silica gel (Alekseev and Zaitsev, 2006; Evangelista et al., 2007) and the amount of organics grafted on the silica gel was found to be about 50 mg/g.

2.1.2 Brunauer-Emmett-Teller surface area

The N₂ adsorption-desorption isotherms and BJH pore size distribution of silica gel and AMPS-silica are shown in Fig. 2. It can be seen from Fig. 2a that both silica gel
Fig. 2 N$_2$ adsorption-desorption isotherms (a) and pore size distribution (b) of silica gel and AMPS-silica.

and AMPS-silica exhibited type-IV adsorption isotherms, indicating the presence of mesopores (Haber et al., 1994). The pore size distribution analysis (Fig. 2b) indicated that the modification of silica gel changed the distribution of pore size of the adsorbent, which clearly shifted to a smaller size as being compared to the unmodified silica gel. The silica gel has a uniform and a narrow range of pore size. After being modified, the pore surface was coated with the organic molecules and a significant change could be observed.

The surface area, pore volume and the average pore size of the modified adsorbents were determined and compared to the silica gel. As shown in Table 1, after functionalization, the decreases in BET surface, pore volume and average pore diameter was observed. This is probably due to the occupation of the functionalized molecules on the surface and inside the pores of the adsorbent.

Table 1

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>BET surface area (m$^2$/g)</th>
<th>Average pore diameter (nm)</th>
<th>Pore volume (m$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica gel</td>
<td>424.0</td>
<td>8.2</td>
<td>0.87</td>
</tr>
<tr>
<td>Product A</td>
<td>354.8</td>
<td>7.5</td>
<td>0.67</td>
</tr>
<tr>
<td>AMPS-silica</td>
<td>389.7</td>
<td>7.3</td>
<td>0.71</td>
</tr>
</tbody>
</table>

2.1.3 Potentiometric titration

The surface charge density ($\sigma_0$) of AMPS-silica is defined according to the uptake of protons by the surface. It was determined through the potentiometric titration experiments, and was calculated using Eq. (1) (Lim et al., 2008):

$$\sigma_0 = \frac{(c_A - c_B + C_{OH^-} - C_{H^+})F}{S \times a}$$

(1)

where, $c_A$ and $c_B$ (mol/L) are the concentrations of acid and base needed to reach a point on the titration curve; $C_{H^+}$ and $C_{OH^-}$ (mol/L) are the concentrations of $H^+$ and $OH^-$; $F$ (96490 C/mol) is the Faraday constant; $S$ (m$^2$/g) is the specific surface area of the sorbent; and $a$ (g/L) is the concentration of AMPS-silica.

According to the BET analysis, the specific surface area of the AMPS-silica is 389.7 m$^2$/g. The surface charge density as a function of solution pH at different ionic strengths (NaNO$_3$) is depicted in Fig. 3. It was observed that $\sigma_0$ decreased with increasing pH, and the zero point charge (pH$_{zpc}$) of AMPS-silica is 3.5.

As shown in Fig. 3, $\sigma_0$ is negative at pH > 3.5, implying that the adsorbent exhibited a high affinity for cation ions (i.e., Cu$^{2+}$), and $\sigma_0$ is positive at pH < 3.5, which is beneficial to the adsorption of anions onto AMPS-silica. The affinity is favorable for nonspecific adsorption of ions through Coulombic attraction between the ions and AMPS-silica. The surface charge density at ionic strength of 0.01 mol/L is virtually the same as that at ionic strength of 0.1 mol/L, indicating the minor effect of ionic strength on the surface charge density.

2.2 Adsorption of Cu$^{2+}$ onto AMPS-silica

2.2.1 Effect of pH on Cu$^{2+}$ adsorption

Solution pH is one of the important factors that affect the adsorption of metal ions. In this study, the effect of initial pH on Cu$^{2+}$ removal was investigated (Fig. 4). In contrast with the silica gel that did not adsorb any Cu$^{2+}$ in the pH range studied, the AMPS-silica showed a pH-dependent adsorption behavior and the adsorption of Cu$^{2+}$ increased significantly with the increase of solution pH.

Fig. 3 Surface charge density of AMPS-silica as a function of solution pH.


The dependence of Cu$^{2+}$ uptake on pH is related to the surface functional groups of the adsorbent. At low pH (e.g., pH 2), the –NH and –SO$_3$– groups in AMPS are protonated, therefore, the formation of specific interaction with metal ions is more pronounced. In addition, the surface charge density also played a significant role on Cu$^{2+}$ ions adsorption. Initial pH (4.5) facilitate the transportation of Cu$^{2+}$ onto AMPS-silica. pH 6, and adsorption experiments could not be performed at pH > 6 for Cu$^{2+}$ due to the insolubility of metal hydroxide.

2.2.2 Adsorption kinetics and isotherm of Cu$^{2+}$ onto AMPS-silica

Figure 5 presents the adsorption kinetics of Cu$^{2+}$ onto AMPS-silica. The adsorption of Cu$^{2+}$ is fairly rapid. It was observed that 90% uptake of Cu$^{2+}$ was achieved within 15 min, and the adsorption attained equilibrium after 30 min. The fast adsorption rate suggested that the readily available and easily accessible organic groups on AMPS-silica were probably due to the uniform pore channels in AMPS-silica, which facilitated the transportation of Cu$^{2+}$ during the adsorption.

To further demonstrate the dominant mechanism involved in the adsorption of Cu$^{2+}$ by AMPS-silica, the adsorption kinetic data were then fitted with the pseudo first- (Eq. (2)) and second-order (Eq. (3)) models.

\[
\frac{t}{q_t} = \frac{1}{q_e} + \frac{1}{k_2 q_e^2} t
\]

where, $q_t$ (mg/g) is the adsorption uptake at time $t$ (min); $q_e$ (mg/g) is the adsorption capacity at adsorption equilibrium; and $k_1$ (min$^{-1}$) and $k_2$ (g/(mg-min)) are the kinetics rate constants for the pseudo first- and second-order models, respectively.

The results showed that pseudo second-order model ($r^2 = 0.9920$, $k_2 = 0.0184$ g/(mg-min)) was better than the first-order model ($r^2 = 0.9594$, $k_1 = 0.219$ min$^{-1}$) to correlate the adsorption kinetics data. This suggested that the adsorption of Cu$^{2+}$ onto AMPS-silica was mainly dominated by chemical adsorption reactions.

2.2.3 Adsorption isotherm of Cu$^{2+}$ onto AMPS-silica

Adsorption isotherms provided valuable information on the interactions between Cu$^{2+}$ and AMPS-silica. Langmuir (Eq. (4)) and Freundlich (Eq. (5)) isotherms were used to fit the experimental data.

\[
q_e = \frac{K_L \times q_l \times C_e}{1 + K_L \times C_e}
\]

\[
q_e = K_F \times C_e^n
\]

where, $q_e$ (mg/g) is the amount of sorbate adsorbed per gram adsorbent at equilibrium, $C_e$ (mg/L) is the equilibrium concentration, $q_l$ (mg/g) is the saturation capacity of the adsorbent, $K_L$ (L/g) is the Langmuir isotherm constant, and $K_F$ and $n$ in the Freundlich model are constants.

The Langmuir and Freundlich isotherms for the adsorption of Cu$^{2+}$ onto AMPS-silica were displayed in Fig. 6. It is observed that the adsorption data fitted the Freundlich isotherm better with $r^2 = 0.993$ ($K_F = 0.52$ L/g, $n = 1.56$), followed by the Langmuir isotherm with $r^2 = 0.984$ ($K_L = 0.01$ L/g). These results probably suggested that Cu$^{2+}$ adsorption on the AMPS-silica followed a phenomenon...
exhibits a clear shift to a lower frequency at 1701.6 cm$^{-1}$ for Cu$^{2+}$ isotherm model fitting, the maximum adsorption capacity for Cu$^{2+}$ on AMPS-silica was calculated to be 19.9 mg/g at the solution pH 4.5.

2.3 Adsorption mechanism of Cu$^{2+}$ onto AMPS-silica

Figure 7 presents the FT-IR spectra of AMPS-silica, Cu$^{2+}$ loaded AMPS-silica, and AMPS-silica after one cycle of adsorption-desorption.

As shown in Fig. 7, although there is the possibility of overlapping between the N–H and the O–H stretching vibrations, the strong broad band at the wavenumber region of 3300–3500 cm$^{-1}$ is characteristic of the N–H stretching vibration. The decrease of absorbance in this band region after Cu$^{2+}$ adsorption indicates that the N–H vibration was affected due to the Cu$^{2+}$ adsorption. The absorbance at 1708.2 cm$^{-1}$ correspond to stretching vibrations of carbonyl double (C==O) bond. After Cu$^{2+}$ were adsorbed onto AMPS-silica, the carbonyl double bond stretching band exhibits a clear shift to a lower frequency at 1701.6 cm$^{-1}$. After the adsorbed Cu$^{2+}$ on AMPS-silica was desorbed, the carbonyl double bond stretching band was shift to 1708.2 cm$^{-1}$ again, which means that the desorption by 0.1 mol/L HNO$_3$ could refresh the adsorption site. Furthermore, the peak at 1635.5 cm$^{-1}$ can be attributed to the vibration of the nitrogen atoms (Constable, 1990; Clothup and Daly, 1990; Jin and Bai, 2002). Yetimoglu et al. (2007) has stated that the characteristic absorption peak of SO group could be easily regenerated using HNO$_3$ and would not affect its adsorption capacity.

3 Conclusions

The functionalized silica gel, AMPS-silica, could be synthesized by grafting AMPS onto the silica surface. AMPS-silica has a high BET surface area of 389.7 m$^2$/g. The removal of Cu$^{2+}$ by AMPS-silica increased with increasing pH. The pseudo-second-order model was fit the kinetics data better comparing with the pseudo first-order model, suggesting that chemical adsorption dominated the adsorption of Cu$^{2+}$. The adsorption of Cu$^{2+}$ onto AMPS-silica were well fitted by both Langmuir and Freundlich isotherms, and the maximum adsorption capacity for Cu$^{2+}$ was 19.9 mg/g. The FT-IR analysis demonstrated that carboxyl, sulfonic and amino groups were involved in the metal binding onto AMPS-silica. In addition, AMPS-silica could be easily regenerated using HNO$_3$ and would not affect its adsorption capacity.

Acknowledgments

This work was supported by the Foundation for Creative Research Groups of China (No. 50621804).

References


