



Efficient removal of heavy metal ions from aqueous solution using salicylic acid type chelate adsorbent

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ABSTRACT

In this study, 5-aminosalicylic acid was successfully grafted onto the poly(glycidyl methacrylate) (PGMA) macromolecular chains of PGMA/SiO₂ to obtain a novel adsorbent designated as ASA-PGMA/SiO₂. The adsorption properties of ASA-PGMA/SiO₂ for heavy metal ions were studied through batch and column methods. The experimental results showed that ASA-PGMA/SiO₂ possesses strong chelating adsorption ability for heavy metal ions, and its adsorption capacity for Cu²⁺, Cd²⁺, Zn²⁺, and Pb²⁺ reaches 0.42, 0.40, 0.35, and 0.31 mmol g⁻¹, respectively. In addition, pH has a great influence on the adsorption capacity in the studied pH range. The adsorption isotherm data greatly obey the Langmuir and Freundlich model. The desorption of metal ions from ASA-PGMA/SiO₂ is effective using 0.1 mol l⁻¹ of hydrochloric acid solution as eluent. Consecutive adsorption–desorption experiments showed that ASA-PGMA/SiO₂ could be reused almost without any loss in the adsorption capacity.

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1. Introduction

Industrial development has worsened the contamination of surface water and groundwater resulting from heavy metal ions, and has increased concern for the high toxic effect of such contamination to animals, plants, and human beings. Heavy metal ions could accumulate in living bodies and cause serious diseases even at very low concentration. Therefore, the effective removal of heavy metal ions from water is very important and has attracted considerable research and practical interest. Various methods or technologies, such as chemical precipitation, reverse osmosis, electrodialysis, coagulation, ion exchange and adsorption, etc., have been used to remove heavy metal ions from aqueous solutions [1–11]. Among these methods or technologies, adsorption with chelating resin, such as polymer microspheres or polymer/inorganic microgranules, has received more attention in recent years because this method is easy to handle, relatively low cost, and effective in removing heavy metal ions especially at low concentration.

To prepare a chelating resin, numerous researchers have experimentized. Some researchers have synthesized multifarious adsorbents through the polymerization of conventional chelating monomers such as acrylic acid, methacrylic acid, allylthiourea, vinylpyridine, vinylimidazole, etc. [12–16]. Others have synthesized firstly a polymer first, and then allowed it to react with low

molecular weight ligands to form chelating resins [17–25]. The modification of a natural polymer matrix by functionalization reactions has also been used to create a chelating resin [26–29].

Among the polymerizable monomers, glycidyl methacrylate (GMA) is a commercial industrial material. Poly(glycidyl methacrylate) (PGMA) has good mechanical strength, sustained acid and base resistance, ease of porosity formation, and high reactivity of the epoxy group. Thus, numerous chelating resins have been successfully prepared via an epoxy group reaction of PGMA with amines [30–37]. As regards the chemical structure, 5-aminosalicylic acid (5-ASA) possesses one carboxyl, one hydroxyl, and one amine group that can share two or three pairs of electrons with a single metal ion. 5-ASA can be easily introduced to the side chain of a polymer owing to the reactive amine hydrogen that responds to the epoxy groups.

In this study, the chemical structure of the adsorbent was well designed. First, GMA was grafted onto the silica gel surface to obtain the PGMA/SiO₂ composite material, which possesses higher chemical and mechanical property than PGMA microsphere. Then, the adsorbent ASA-PGMA/SiO₂ was obtained through ring-opening reactions between the amine of 5-ASA and the epoxide rings of PGMA. According to hard–soft acid–base (HSAB) theory by Pearson, namely the Pearson theory, soft metal ions show affinity to soft bases with donor atoms as O < N < S while hard metal ions show affinity to hard bases with donor atoms as O > N > S [38,39]. For hard metal ions, such as Cu²⁺, Cd²⁺, Zn²⁺ and Pb²⁺, the adsorbent ASA-PGMA/SiO₂ must have strong chelating adsorption ability. The adsorption ability of ASA-PGMA/SiO₂ for Cu²⁺, Cd²⁺, Zn²⁺ and Pb²⁺ was investigated. Experimental results showed

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that ASA–PGMA/SiO₂ displays excellent adsorption property and reusability.

2. Experiments

2.1. Materials and instruments

Silica was purchased from Ocean Chemical Company, Ltd. (120–160 mesh, about 125 μm in diameter, pore size: 6 nm, pore volume: 1.0 ml g⁻¹, surface area: 350 m² g⁻¹, Qingdao, China). GMA was purchased from Ruijinte Chemical Ltd. (Tianjin, China, AR grade) and purified by distillation under vacuum. 3-Methacryloylpropyl trimethoxysilane (MPS) was purchased from Nanking Chuangshi Chemical Aux Ltd. (Jiangsu, China, AR grade). Azoisobutyronitrile (AIBN) was purchased from Shanghai Chemical Reagent Plant (Shanghai, China, AR grade) and recrystallized by standard procedures. 5-ASA and other reagents were purchased from Beijing Chemical Plant (Beijing, China, AR grade).

Instruments used in this study were as follows: STA449 thermogravimetric analyzer (TGA, Netzsch Company, Germany), WYX-9001 atomic absorption spectrophotometer (AAS, Analytical Instrument Factory of Shenyang, China), Perkin-Elmer1700 infrared spectrometer (Perkin-Elmer Company, American), PHS-2 acidimeter (The Second Analytical Instrument Factory of Shanghai, China), and THZ-92C constant temperature shaker (Boxun Medical Treatment Equipment Factory of Shanghai, China).

2.2. Preparation and characterization of adsorbent ASA–PGMA/SiO₂

To prepare the adsorbent ASA–PGMA/SiO₂, 10 g of silica gel particles activated with methane sulfoacid and 15 ml of coupling agent MPS were added into 200 ml of a mixed solvent of ethanol and water (v/v = 1:1). The contents were maintained for 24 h at 50 °C, resulting in the formation of the surface-modified particles MPS–SiO₂, on which polymerizable double bonds were attached chemically. Afterwards, 6 g of particles MPS–SiO₂ and 20 ml of GMA were added into 400 ml of dimethyl formamide. Graft polymerization was performed by initiating AIBN (1.4 wt% of monomer) under N₂ atmosphere at 70 °C for 24 h. The product particles were extracted with dimethylsulfoxide in a Soxhlet apparatus to remove the polymers attaching physically onto the particles and then dried under vacuum. Subsequently, 1 g of PGMA/SiO₂ and 6 g of 5-ASA were added into 100 ml of sodium hydroxide aqueous solution with pH of 12. The ring-opening reaction between the amine of 5-ASA and the epoxide ring of PGMA was allowed to take place at 80 °C for 24 h, and finally, the adsorbent ASA–PGMA/SiO₂ was obtained.

The preparation process of ASA–PGMA/SiO₂ is expressed in Scheme 1. The grafting degree of ASA–PGMA/SiO₂ was determined by the TGA method. The adsorbent ASA–PGMA/SiO₂ used in this study have a grafting degree of 0.168 g g⁻¹.

2.3. Batch adsorption

2.3.1. Measurement of kinetic adsorption curve

About 0.1 g of ASA–PGMA/SiO₂ and 25 ml of aqueous metal ion solution with an initial concentration (C₀) of 10 mmol l⁻¹ (pH of 5) were directly introduced into a conical flask. This conical flask was placed into a shaker with a constant temperature and then shaken. At different time, the concentration (C_t) of metal ion solution was determined by atomic absorption spectrophotometer. Adsorption capacity (Q) was calculated according to the following equation.

$$Q = \frac{V(C_0 - C_t)}{m} \quad (1)$$

where Q (mmol g⁻¹) is the adsorption capacity, V (l) is the volume of the metal ion solution, and m (g) is the weight of the adsorbent ASA–PGMA/SiO₂.

2.3.2. Measurement of adsorption isotherm

About 0.1 g of ASA–PGMA/SiO₂ and 25 ml aqueous solution of metal ion with different initial concentrations (C₀ = 2, 4, 6, 8 and 10 mmol l⁻¹) and the same pH of 5 were directly introduced into several conical flasks. These conical flasks were placed into a shaker with a constant temperature and then shaken. After reaching the adsorption equilibrium (2 h), the equilibrium concentration (C_e) of metal ion solution was determined by atomic absorption spectrophotometer. Equilibrium adsorption capacity (Q_e) was calculated according to the following equation.

$$Q_e = \frac{V(C_0 - C_e)}{m} \quad (2)$$

2.4. Column adsorption and elution experiment

In the column experiment, 1.4824 g of ASA–PGMA/SiO₂ was placed in a glass column 8 mm in diameter and with a bed volume (BV) of 2 ml. The metal ion solution with a concentration of 10 mmol l⁻¹ and pH of 5 was allowed to flow gradually through the column at a rate of five bed volumes per hour (5 BV h⁻¹). The effluent with one bed volume was collected, the metal ion concentration was determined, and the dynamics adsorption curve was measured. Leaking adsorption capacity and saturated adsorption capacity were also calculated.

The elution experiment was performed using hydrochloric acid solution with a concentration of 0.1 mol l⁻¹ as eluting agent. The flow rate of the eluting agent was controlled at 1 BV h⁻¹. The eluent with one bed volume was collected, the metal ion concentration was determined, and the elution curve was plotted.

2.5. Repeated use experiment

Repeated usability (i.e., regenerability) is an important factor for an effective adsorption material. Desorption of the adsorbed metal ion from ASA–PGMA/SiO₂ was also studied by batch experiment using 0.1 mol l⁻¹ of hydrochloric acid solution as eluent. The ASA–PGMA/SiO₂ adsorbed metal ion was placed in the eluent and stirred continuously at room temperature (20 °C) for 5 h. The final metal ion concentration in aqueous phase was determined. Desorption ratio was calculated from the capacity of metal ion adsorbed on the ASA–PGMA/SiO₂ and the final metal ion concentration in the eluent. In order to test the reusability of ASA–PGMA/SiO₂, the metal ion adsorption–desorption procedure was repeated 10 times using the same ASA–PGMA/SiO₂.

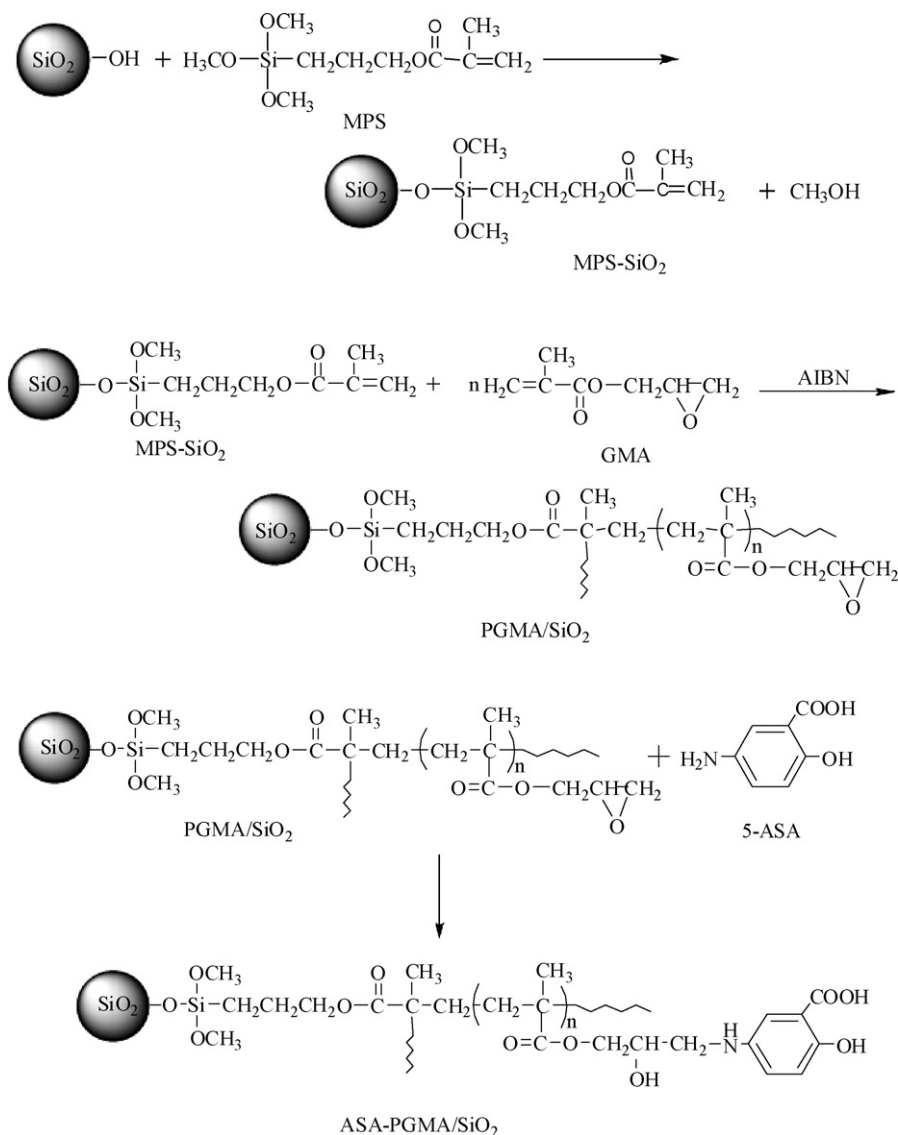
3. Results and discussion

3.1. Preparation and characterization of adsorbent ASA–PGMA/SiO₂

To confirm the effectiveness of PGMA grafting onto the silica gel microgranules and 5-ASA grafting onto the PGMA/SiO₂ microgranules, FTIR spectra (Fig. 1) of the SiO₂, MPS–SiO₂, PGMA/SiO₂, and ASA–PGMA/SiO₂ microgranules were obtained.

In the infrared spectrum of PGMA/SiO₂, the characteristic absorptions of the epoxide rings appear at 905 cm⁻¹ and the characteristic absorptions of the carbonyl group at 1732 cm⁻¹ is enhanced. These show that PGMA macromolecules have been grafted onto the silica gel surface and PGMA/SiO₂ microgranules have been formed.

The characteristic absorption peaks of benzene ring appear at 1485 and 1589 cm⁻¹, the characteristic absorption peak of



Scheme 1. Synthesis process of adsorbent ASA-PGMA/SiO₂.

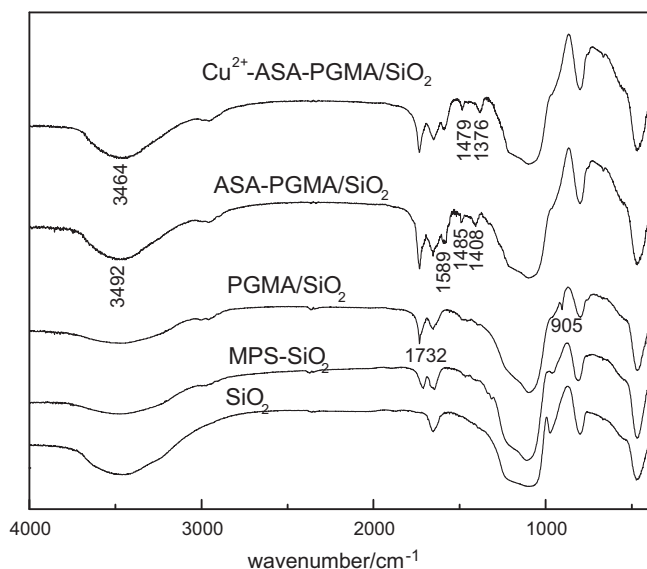


Fig. 1. FTIR spectra of every microgranules.

bend vibration of C–N bond appear at 1408 cm⁻¹, the characteristic absorption peak of epoxide rings at 905 cm⁻¹ disappear, and the characteristic absorption peak of N–H bond at 3492 cm⁻¹ is enhanced. These show that 5-ASA has reacted with the PGMA of PGMA/SiO₂ microgranules, and ASA-PGMA/SiO₂ microgranules have been formed.

Additionally, in the infrared spectrum of ASA-PGMA/SiO₂ loaded with Cu²⁺ (Cu²⁺-ASA-PGMA/SiO₂), the characteristic absorption peak of bend vibration of C–N bond at 1408 cm⁻¹ and the characteristic absorption peak of N–H bond at 3492 cm⁻¹ shift to lower wave numbers 1376 cm⁻¹ and 3464 cm⁻¹, respectively. When the N → Cu²⁺ chelate bond is formed, the electron cloud of N atom will transfer to Cu²⁺, and the energy of C–N bond and N–H bond will decline. Thus, the characteristic absorption peaks of C–N bond and N–H bond shift to a lower wave number, proving the presence of chelation between N atom and Cu²⁺.

3.2. Kinetic adsorption curve

The kinetic adsorption curve is shown in Fig. 2. The adsorption reached equilibrium at 2 h, and the saturated adsorption capacity for Cu²⁺, Cd²⁺, Zn²⁺ and Pb²⁺ reached 0.42, 0.40, 0.35, and

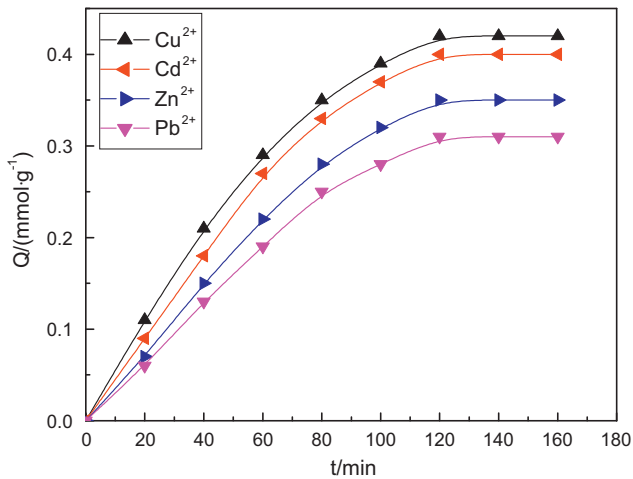


Fig. 2. Kinetic adsorption curve of ASA-PGMA/SiO₂ for metal ions temperature: 35 °C; pH=5.

0.31 mmol g⁻¹, respectively. This adsorption capacity is higher than that of other adsorbents, such as SG-PS-azo-IM (for Cu²⁺ 0.15 mmol g⁻¹; for Zn²⁺ 0.05 mmol g⁻¹; for Pb²⁺ 0.12 mmol g⁻¹) [1], GH-T-P (for Zn²⁺ 0.05 mmol g⁻¹; for Pb²⁺ 0.1 mmol g⁻¹; for Cd²⁺ 0.1 mmol g⁻¹) [8], oxidized coir fibers (for Zn²⁺ 0.1 mmol g⁻¹) [9], Dowex 50 W (for Cu²⁺ 0.02 mmol g⁻¹; for Pb²⁺ 0.02 mmol g⁻¹) [10], and PSDC (for Cu²⁺ 0.14 mmol g⁻¹; for Pb²⁺ 0.2 mmol g⁻¹) [40]. The composite adsorbent ASA-PGMA/SiO₂ clearly has very strong adsorption ability and high affinity for metal ions. This can be attributed to the chelating interaction between the 5-ASA on ASA-PGMA/SiO₂ and heavy metal ions, and the interaction mechanism will be discussed below.

3.3. The influence of pH value on adsorption capacity

To avoid forming hydroxide precipitates, the adsorption of adsorbent for metal ions was conducted at pH below 5. The adsorption performances of PGMA/SiO₂ and ASA-PGMA/SiO₂ adsorbent for metal ions at different solution pH values are shown in Fig. 3.

In contrast with the PGMA/SiO₂ that did not adsorb any metal ions in the pH range studied, the ASA-PGMA/SiO₂ adsorbent showed a pH-dependent adsorption behavior. There is nearly no adsorption at the pH of 1, and the adsorption capacity of ASA-PGMA/SiO₂ for metal ions increases significantly with the

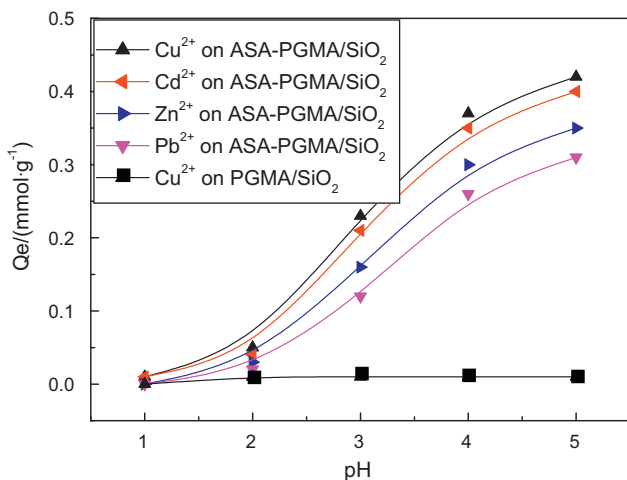


Fig. 3. The influence of pH on the adsorption capacity temperature: 35 °C; adsorption time: 2 h.

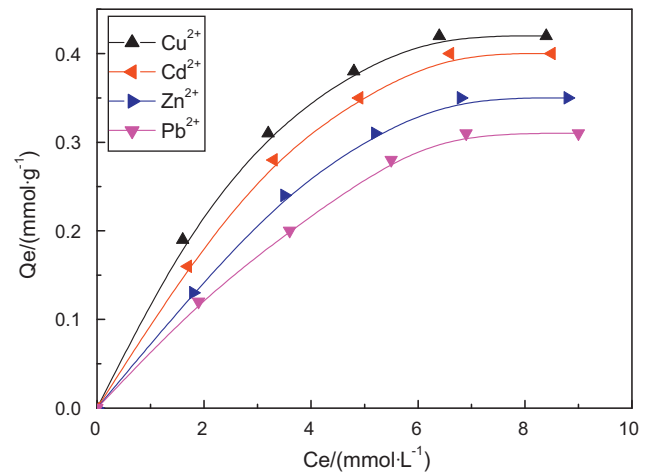


Fig. 4. Adsorption isotherms of ASA-PGMA/SiO₂ for metal ions temperature: 35 °C; adsorption time: 2 h; pH=5.

increase of the solution pH values. This phenomenon may be explained from several aspects. First, carboxylate ions (COO⁻), amine groups (-NH-) and hydroxyl (-OH) within ASA-PGMA/SiO₂ adsorbent are the functional groups for metal ion adsorption. At low solution pH values (high acidic environment), a relatively high concentration of protons would compete strongly with the metal ions for the action sites, and thus the adsorption capacity of ASA-PGMA/SiO₂ for metal ions is significantly decreased. On the other hand, the protonation of the action sites would lead to a strong electrostatic repulsion to the metal cation ions to be adsorbed. As a result, it becomes difficult for heavy metal ions to make contact with the adsorbent surfaces and allow adsorption to take place; poor adsorption performance therefore occurs at low solution pH values. With the increase of solution pH values (lowered proton concentrations), the competition effect of the protons with the metal ions for the action sites become less significant, and the ionization degree of the carboxylate ions and hydroxyl is enhanced. These reduce the electrostatic repulsion to the metal cation ions. Hence, more metal ions can be adsorbed onto the surfaces of the ASA-PGMA/SiO₂ adsorbent, resulting in the increase of metal ion adsorption on the adsorbent with the increase of solution pH values.

Low adsorption capacity at low pH indicates that the spent adsorbent can be regenerated in a strong acidic solution.

3.4. Adsorption isotherm

The adsorption isotherms of ASA-PGMA/SiO₂ for different metal ions are shown in Fig. 4. Equilibrium adsorption amount increases rapidly with the increase of equilibrium concentrations. This implies that ASA-PGMA/SiO₂ possesses very strong adsorption ability and high affinity for heavy metal ions.

The Freundlich adsorption equation and its logarithmic form are follows:

$$Q_e = kC_e^{1/n} \quad (3)$$

$$\ln Q_e = \ln k + \frac{1}{n} \ln C_e \quad (4)$$

The Langmuir adsorption equation is as follows:

$$Q_e = Q_m \frac{bC_e}{1 + bC_e} \quad (5)$$

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{bQ_m} \quad (6)$$

Table 1
The related constant and linear regression coefficient of Langmuir–Freundlich fitting.

Fitting model		Adsorbate			
		Cu ²⁺	Cd ²⁺	Zn ²⁺	Pb ²⁺
Langmuir	<i>b</i>	0.239	0.149	0.100	0.091
	<i>R</i> ²	0.9952	0.9897	0.9834	0.9898
	<i>Q_m</i>	0.58	0.51	0.48	0.42
Freundlich	<i>k</i>	0.149	0.116	0.087	0.075
	<i>n</i>	1.722	1.464	1.321	1.239
	<i>R</i> ²	0.9826	0.9818	0.9824	0.9946

where, Q_m (mmol g⁻¹) is the saturated adsorption amount, and b is the combine constant.

The data in Fig. 4 are treated using the Freundlich and Langmuir adsorption equations. The related constant and linear regression coefficients are displayed in Table 1.

The combine constant of the Freundlich and Langmuir adsorption equations decreases in the sequence of Cu²⁺, Cd²⁺, Zn²⁺, Pb²⁺, and this order is in accordance with the order of adsorption capacity. The linear regression coefficient is very close to 1, indicating that the adsorption of ASA–PGMA/SiO₂ for metal ions is a typical monomolecular layer adsorption.

3.5. Dynamic adsorption curve

The dynamic adsorption curve of ASA–PGMA/SiO₂ for Cu²⁺ is

$$\text{desorption ratio} = \frac{\text{amount of metal ion desorbed to the elution medium}}{\text{amount of metal ion sorbed on adsorbent}} \times 100\% \quad (7)$$

shown in Fig. 5. When the Cu²⁺ solution passes through the column packed with ASA–PGMA/SiO₂ at a flow rate of 5 BV h⁻¹ upstream, the leaking appears only at 23 BV, the leaking adsorption amount to be calculated is 0.31 mmol g⁻¹, and the saturated adsorption amount is 0.41 mmol g⁻¹. Analogous to the static adsorption result, the dynamic adsorption capacity is also very high.

3.6. Elution curve

Good desorption performance of an adsorbent is important in its potential practical applications. Based on the results in Fig. 4, the ASA–PGMA/SiO₂ adsorbent does not adsorb heavy metal ions at the pH of 1, suggesting that adsorbed metal ions on the

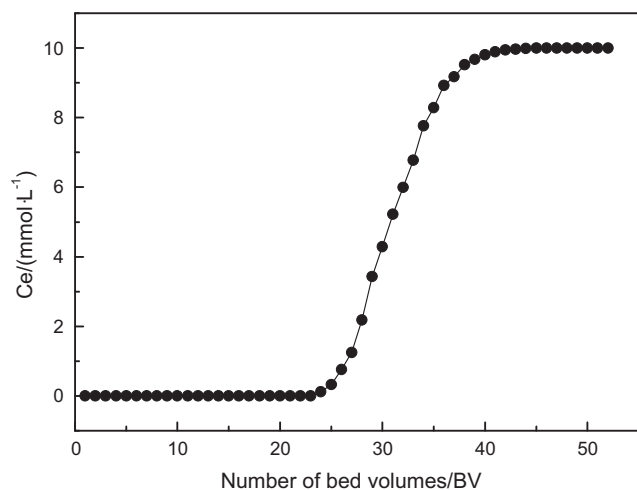


Fig. 5. Breakthrough curve of Cu²⁺ on ASA–PGMA/SiO₂ column temperature: 35 °C; pH=5.

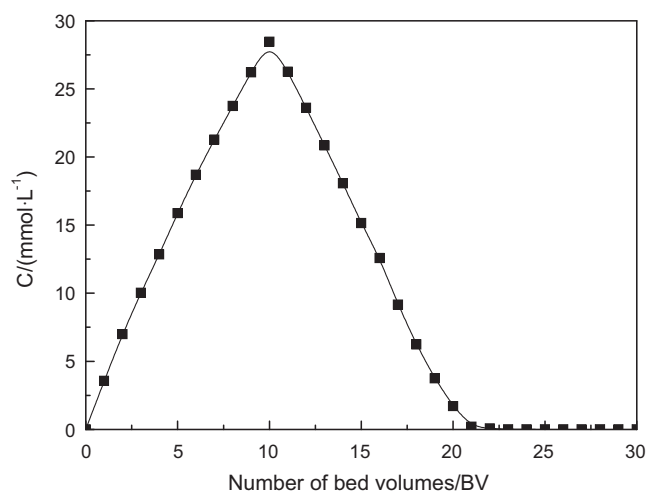


Fig. 6. Elution curve of ASA–PGMA/SiO₂ temperature: 35 °C.

ASA–PGMA/SiO₂ adsorbent may be desorbed in a strong acidic solution with a pH value of 1. Hydrochloric acid solution with a concentration of 0.1 mol l⁻¹ is used as the eluent, and the eluent at a rate of 1 BV h⁻¹ flows upstream through the column of ASA–PGMA/SiO₂ particles on which the adsorption of Cu²⁺ has reached saturation. The elution curve of ASA–PGMA/SiO₂ is shown in Fig. 6, and the desorption ratio was calculated as follows:

It can be seen that the shape of the desorption curve is cusped and without tailing, showing a fine elution result. Calculation results show that within 19 and 22 BV, Cu²⁺ is eluted from the ASA–PGMA/SiO₂ column with a desorption ratio of 98.93% and 99.57%, respectively. This fully reveals that ASA–PGMA/SiO₂ on which Cu²⁺ is adsorbed in saturation has outstanding elution property, and as a novel adsorbent, ASA–PGMA/SiO₂ has excellent reusing property.

3.7. Reusability

In order to show the reusability of the ASA–PGMA/SiO₂, the adsorption–desorption cycle was repeated 10 times using the same material.

The adsorption–desorption cycle of ASA–PGMA/SiO₂ is shown in Fig. 7. Results clearly show that ASA–PGMA/SiO₂ could be used repeatedly without significantly losing its adsorption amount.

3.8. Practical application

To demonstrate its practical application value, the adsorbent ASA–PGMA/SiO₂ was used to dispose the plating copper wastewater by batch method. The initial Cu²⁺ concentration in plating copper wastewater is 12.5 mmol l⁻¹ and other metal ions are few.

In the batch study, 100 ml of plating copper wastewater was disposed using the adsorbent ASA–PGMA/SiO₂. The removal rate (R) of Cu²⁺ was calculated according to the following equation and shown in Fig. 8.

$$R = \frac{C_0 - C_e}{C_0} \quad (8)$$

For 100 ml of plating copper wastewater with an initial concentration of 12.5 mmol l⁻¹, the removal rate of Cu²⁺ could reach 98.0% when 1.4 g of ASA–PGMA/SiO₂ was used. This result clearly shows that ASA–PGMA/SiO₂ possesses potential application value.

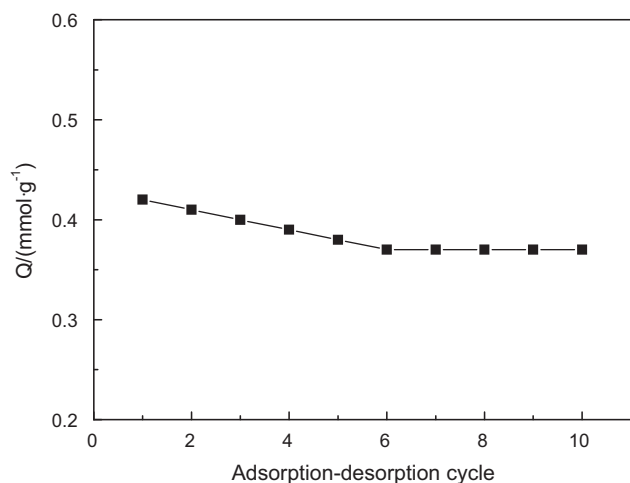


Fig. 7. Adsorption-desorption cycle of ASA-PGMA/SiO₂.

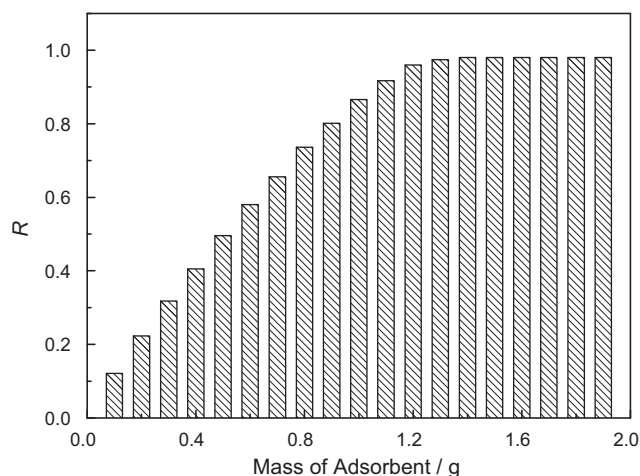


Fig. 8. The removal rate curve.

4. Conclusions

In this study, macromolecule PGMA was grafted onto micron-sized silica gel to prepare PGMA/SiO₂. The novel adsorbent ASA-PGMA/SiO₂ was also successfully obtained through ring-opening reactions between the amine of 5-ASA and the epoxide rings of PGMA. ASA-PGMA/SiO₂ has very strong chelating adsorption ability for hard metal ions, such as Cu²⁺, Cd²⁺, Zn²⁺ and Pb²⁺, according with the Pearson theory. The adsorption ability of ASA-PGMA/SiO₂ for metal ions is largely dependent on the solution pH value. In the studied pH value range, the adsorption capacity is the lowest at the lowest pH value (pH of 1) and the highest at the highest pH value (pH of 5). This study shows that ASA-PGMA/SiO₂ could dispose wastewater containing metal ions. Additionally, ASA-PGMA/SiO₂ has excellent reusability.

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