Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.837000

53 (2015) 230–237
January

Taylor & Francis
Taylor & Francis Group

Synthesis of polyacrylamide/modified silica composite hydrogels for synergistic complexation of heavy metal ions

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Received 20 April 2013; Accepted 17 August 2013

ABSTRACT

In this research, polyacrylamide (PAM)/modified silica (SiO_2-NH_2) composite hydrogels have been prepared via *in situ* free-radical polymerization. The gel fraction of the polymerization was studied by gravimetric method, and the mechanical property of the resultant hydrogels was examined using a tensile tester. It was indicated that both the gel fraction and the mechanical strength increased with the SiO_2-NH_2 content in the formulation. When the pH value of the buffer solution and the SiO_2-NH_2 content increased, the swelling ratio decreased. The composite hydrogels were used to remove heavy metal ions from aqueous solution under the noncompetitive condition. The effects of SiO_2-NH_2 content in the formulation and pH values of the feed solution on the adsorption capacity were investigated. The results showed that the adsorption capacity of the hydrogels decreased with the pH values but increased with SiO_2-NH_2 content in the formulation. Furthermore, the synergistic complexation of metal ions was found in the adsorption studies. The adsorption isotherm of the hydrogels could be well fitted into the Langmuir model. Regeneration studies suggested that metal rebinding capacity of the hydrogels did not change significantly through repeated applications compared with the first run.

Keywords: Composite hydrogel; Heavy metal ion; Adsorption; Synergistic complexation

1. Introduction

Composite hydrogels which are composed of organic (polymer)/inorganic network have received a great deal of attention as a new type of materials. Due to the combination of the advantages of organic and inorganic components, composite hydrogels have been widely used in many fields, such as in agriculture, construction, petroleum chemical industry, environmental protection, and biomedical areas [1–5].

Due to excellent water solubility, high reactivity and *in vitro* low toxicity, polyacrylamide (PAM) hydrogels have been widely used in many fields such as recovery of secondary oil, stabilization of mineral sedimentation, purification of wastewater and metal extraction [6,7]. In recent years, it was found that crosslinked hydrogel materials having functional groups, such as carboxyl, amine, and hydroxyl groups, could be used as complexing agents for the removal of metal ions from aqueous solutions. Main advantages of such materials are easy loading and, in

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most cases, stripping of cations with simple chemicals, reusability and the possibility of semicontinuous operation [8–10].

However, hydrogels prepared from either natural or synthetic sources usually exhibit poor mechanical properties. There are several ways to improve the mechanical properties of hydrogels, including copolymerization with hydrophobic monomers and formation of interpenetrating polymer network [11–13]. Alternatively, the reinforcement of the mechanical properties can be achieved by the introduction of an inorganic phase inside the polymer matrix in the form of nanoparticles. Their formation yields significant improvement of mechanical properties in nanocomposites, when a very good dispersion of nanoparticles is succeeded at the nanoscale [14,15].

Silica sol is a dispersion system of amorphous silica particles in water, which can be divided into acid and basic sols according to the pH value. Due to the strong surface activity of hydrogen groups on the surface of silica particles, they can mix and react with organic polymer. Thus, they were widely applied in organic and inorganic composites. Because of the presence of hydroxyl group, silica particles could form hydrogen bonds to construct a space stereo 3D mesh structure in the system [16]. Li et al. [17] synthesized multilayered poly(vinyl alcohol)/silica composites through silica colloid solution. The results indicated that the inorganic particles deriving from silica sol played an important role in improving the tensile strength and ductility.

In the previous report, Ramadan prepared hybrid silica/polyacrylamide aerogels for mercury removal from aqueous solutions. It was found that the aerogels were economically interesting adsorbents due to their noticeable adsorptive capacity after regeneration [18]. In this research, polyacrylamide (PAM)/modified silica (SiO_2-NH_2) composite hydrogels containing different contents of SiO_2-NH_2 were prepared using *in situ* free-radical polymerization. The gel fraction of the polymerization, and the swelling behavior, mechanical property of the resultant composite hydrogels were investigated. Adsorption properties of the hydrogels were examined for the removal of Cu(II), Cd(II), and Pb(II) ions from aqueous solutions under the noncompetitive condition. Finally, the regeneration abilities of the hydrogels were evaluated.

2. Experimental

2.1. Materials

Acrylamide (AM) was purchased from Sigma–Aldrich Chemicals. Silica (mean grain size: 8 nm) was obtained from Tianjin Guangfu Fine Chemical Research Institute, China. *N,N′*-methylene bisacrylamide (MBA) and ammonium persulfate (APS), used as a crosslinking agent and an initiator, were purchased from Sigma–Aldrich Chemicals and used without further purification. Copper nitrate [$Cu(NO_3)_2 \cdot 3H_2O$], cadmium nitrate [$Cd(NO_3)_2 \cdot 4H_2O$], and lead nitrate [$Pb(NO_3)_2 \cdot 6H_2O$] used in adsorption experiments were purchased from Shanghai Chemical Reagents Co., China. In order to improve the metal ion adsorption capacity, silica was modified by the amination reaction using the method as described in the literature [19,20]. The structure of the modified silica (SiO_2-NH_2) is shown in Fig. 1.

2.2. Preparation of PAM/modified silica composite hydrogels

A mixture of AM, modified silica (SiO_2-NH_2), and distilled water was stirred vigorously to produce a homogeneous and transparent solution. Then MBA (5% w/w based on AM) and APS (1% w/w based on AM) were added into the solution as the crosslinker and initiator. Table 1 shows the feed formulations for the composite hydrogels. The mixture of each formulation was introduced between two glass plates (7.5 cm × 2.5 cm) and was heated for 30 h in a constant temperature water bath at 65℃ until the monomer AM was completely polymerized. The hydrogels were extracted with water for 24 h. Subsequently, the hydrogels were kept in distilled water, and the composite hydrogels were obtained.

Fig. 1. The structure of the modified silica (SiO_2-NH_2).

Table 1
Feed formulations for the composite hydrogels

Formulation	Feed wt.%			
	AM	SiO_2-NH_2	MBA[a]	APS[b]
1	100	0	5	1
2	95	5	5	1
3	90	10	5	1
4	85	15	5	1
5	80	20	5	1
6	75	25	5	1

Notes: [a]5% w/w based on AM; [b]1% w/w based on AM.

2.3. Gel fraction

To investigate the gel content of the hydrogels, the dried hydrogels were extracted with water for 24 h at 100˚C in order to extract the soluble parts of the hydrogel. The insoluble part, that is, the gelled part, was dried and weighed. This extraction cycle was repeated until the weight became constant. The gel fraction in the hydrogel was determined from the following equation:

$$\text{Gel } (\%) = \frac{W_e}{W_d} \times 100\% \tag{1}$$

where W_d and W_e represent the weights of the dry hydrogel and the gelled part after extraction, respectively.

2.4. Swelling ratio studies

Swelling ratio (SR) was determined by the gravimetric method at 25˚C. Dried composite hydrogel samples were immersed in 0.01 mol/L citrate buffer solution for 24 h, and the weight of the wet sample (W_w, g) was measured after carefully removing moisture on the surface with filter paper. The weight of the dried sample (W_d,g) was determined after drying samples at 105˚C for 24 h. The SR of samples was calculated as follows:

$$\text{SR } (\%) = \frac{W_w - W_d}{W_d} \times 100\% \tag{2}$$

2.5. Mechanical property studies

Stress/strain measurements were carried out using an Instron series IX materials testing system at room temperature. Dog-bone shaped samples were cut from the hydrogels (5 mm wide at the narrowest point with a gage length of 15 mm). Thickness of the samples was measured with a digital micrometer having a precision of 1 μm. A crosshead speed of 10 mm/min was used, and at least, triplicate was tested for each sample.

2.6. Adsorption capability studies

Adsorption studies were carried out in magnetically stirred (160 rpm), thermostated (25˚C) cylindrical glass vessels in batch conditions. The sample was added into Cu(II), Cd(II), or Pb(II) ion solutions to determine the metal ion adsorption capacity of the samples under noncompetitive conditions. The pH of the metal feed solutions was adjusted using 0.01 mol/L citrate solution before the hydrogels were applied for the adsorption process. Amount of the residual metal ion in the solution was determined using a Thermo Elemental-X Series Inductively Coupled Plasma-Mass Spectrometer after 24 h [8]. Amount of adsorbed metal ion (Q, mmol/g) was calculated from the following equation:

$$Q = \frac{(C_0 - C)V}{m} \tag{3}$$

where C_0 (mmol/L) and C (mmol/L) were the metal ion concentrations in the initial solution and after the adsorption for different periods of time, respectively. V (L) was the volume of the solution added and m (g) was the amount of sample used.

2.7. Regeneration studies

The metal-complexed hydrogels were freed from metals by treating with 1 mol/L HCl for 1 h. The acid-treated hydrogels were filtered and washed with distilled water and bicarbonate solution to remove HCl. The concentration of desorbed metals was determined as mentioned peviously. The desorption ratio was calculated as follows: desorption ratio = (amount of metal ion desorbed into solution/amount of metal ion bound to hydrogels) × 100%. A second metal binding cycle was repeated with these regenerated hydrogels. Reuse of the composite hydrogels = (amount of metal ion adsorpted in the second run/amount of metal ion adsorpted in the first run) × 100%.

3. Results and discussion

3.1. Gel fraction

The gel fraction plays an important role in the metal ion adsorption and can be controlled by the composition of the composite hydrogel [21]. Fig. 2 illustrates the gel fraction of the composite hydrogels, which was determined as a function of modified silica (SiO_2-NH_2) content in the formulation. It was observed that, the gel fraction for all composites was higher than 91% and increased with the SiO_2-NH_2 content in the formulation. The results indicated that the molecular interactions such as hydrogen bonding between SiO_2-NH_2 and PAM in the composites increased with the SiO_2-NH_2 content in the formulation [15,21].

3.2. Mechanical property

Tensile testing was carried out to investigate mechanical properties of the composite hydrogels.

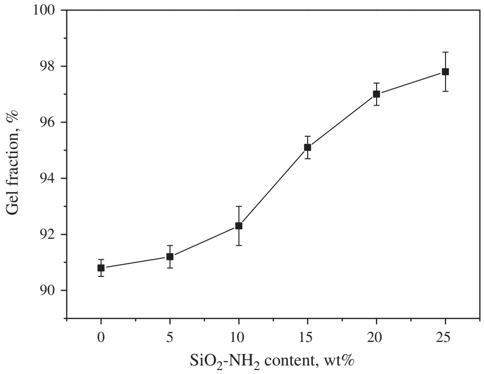

Fig. 2. Gel fraction of the composite hydrogels as a function of SiO_2-NH_2 content in the formulation.

Fig. 3 shows that the mechanical strength of the PAM/SiO_2-NH_2 composites as a function of SiO_2-NH_2 content in the formulation. It was seen that the mechanical strength of the composites was substantially enhanced by the addition of silica particles. PAM/SiO_2-NH_2 composites with high SiO_2-NH_2 content possessed higher strength because that the incorporation of a hard ceramic phase supported applied loads and restricted surface deformations [16]. In this study, when the SiO_2-NH_2 content in the formulation increased, the gel fraction increased, leading to the increase in the mechanical strength [21]. The high mechanical strength of the composite hydrogels would potentially facilitate the metal ion adsorption applications.

3.3. Swelling ratio

Fig. 4 shows the SR of the composite hydrogels as a function of SiO_2-NH_2 content and the pH value of the buffer solution at room temperature. The SR of composite hydrogels decreased with the increase in SiO_2-NH_2 content. The maximum SR of the composite hydrogels was reached with the least amount of SiO_2-NH_2 content in the formulation as shown in Fig. 4. This was attributed to the stronger hydrophilicity of PAM than SiO_2-NH_2 [15]. It also could be seen that the SR of the hydrogels increased as the pH value of the buffer solution decreased. At low pH values, because protonation of amino groups was enhanced, electrostatic repulsion made the hydrogel network more looser. Therefore the hydrogels could absorb more amount of water.

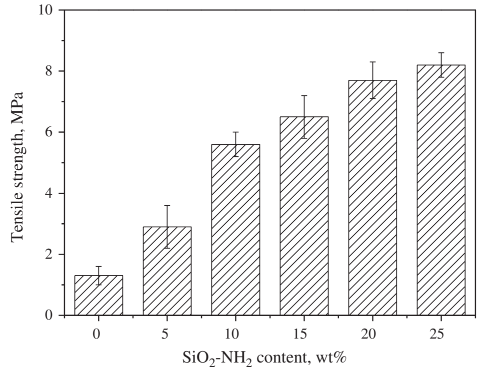

Fig. 3. Mechanical strength of the PAM/SiO_2-NH_2 composites.

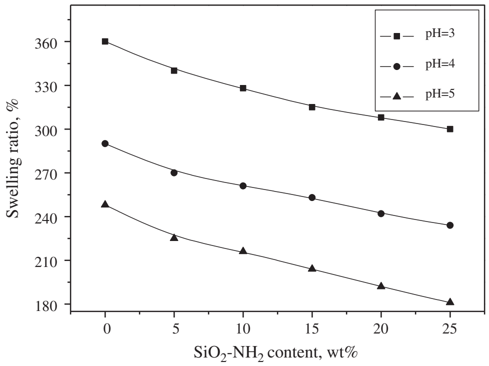

Fig. 4. SRs of the composite hydrogels as a function of SiO_2-NH_2 content in the formulation.

3.4. Adsorption studies

Metal ion adsorption capacity of SiO_2-NH_2 and crosslinked PAM network at different pH values is listed in Table 2. Figs. 5 and 6 respectively, illustrate the influence of SiO_2-NH_2 content in the formulation and pH values of the feed solution on the adsorption capacity of the composite hydrogels. The theoretical adsorption values of composite hydrogels, which were used to reach certain conclusions about the incorporation of SiO_2-NH_2 on the adsorption capacity, were also calculated. Briefly, theoretic values in Figs. 5 and 6 were obtained as follows: Firstly, metal ion adsorption capacity of SiO_2-NH_2 and crosslinked PAM obtained from Table 1 was used in calculations. Then, the values

Table 2
Metal ion adsorption capacity of SiO_2-NH_2 and PAM at different pH values from the single metal ion solution (0.005 mol/L), mmol/g

Metal ions	SiO_2-NH_2			PAM		
	pH = 3	pH = 4	pH = 5	pH = 3	pH = 4	pH = 5
Pb (II)	7.1	12.4	16.2	0.38	0.69	1.09
Cu (II)	6.4	10.8	13.1	0.33	0.67	0.84
Cd (II)	4.1	6.9	8.4	0.21	0.37	0.5

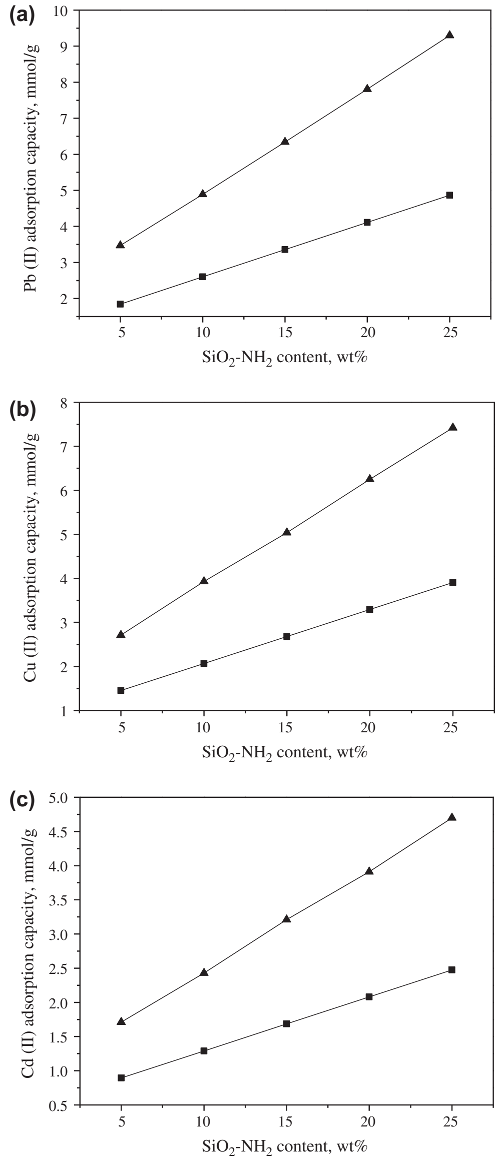

Fig. 5. Influence of SiO_2-NH_2 content in the formulation on (a) Pb(II), (b) Cu(II), (c) Cd(II) adsorption capacity, fixing pH at 5; (filled squares) theoretic values, (filled triangles) experimental values.

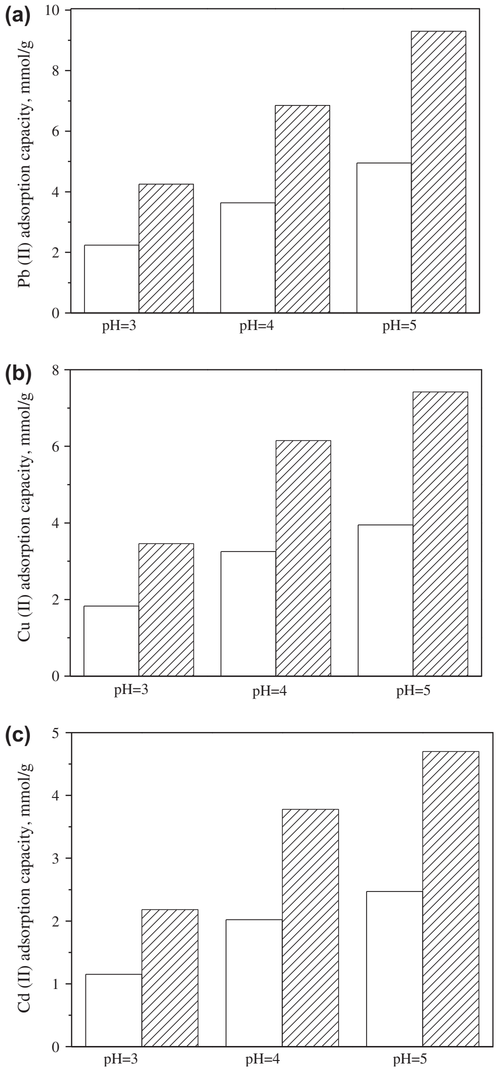

Fig. 6. Effect of pH values on (a) Pb(II), (b) Cu(II), (c) Cd (II) adsorption capacity of the composite hydrogel derived from SiO_2-NH_2 content of 25% in the formulation; (open bars) theoretic values, (filled bars) experimental values.

of SiO_2-NH_2 and PAM contents in the formulation were multiplied by adsorption values of each respective inorganic or polymer adsorbents. Finally, both values were added to obtain theoretical results [22].

In order to investigate the relationship between adsorption capacity of the hydrogels and SiO_2-NH_2 content in the formulation, the adsorption studies of the hydrogels for Cu(II), Cd(II), and Pb(II) ions were conducted from single solutions (0.005 mol/L) fixing pH at 5. It was seen that the adsorption capacity increased with the SiO_2-NH_2 content in the formulation for all metal ions. The results may be attributed to the fact that SiO_2-NH_2 exhibited higher adsorption capacity compared with PAM. Therefore, the highest sorbing capacity for metal ions was observed for the hydrogel derived from the highest SiO_2-NH_2 content in the formulation.

The influence of pH values on the metal ion adsorption capacity was studied at various pH values with the hydrogel derived from SiO_2-NH_2 content of 25% in the formulation. The distribution of metal species in aqueous solution as a function of pH reveals that metal ions precipitate in the forms of metal oxides or hydroxides at $pH > 6$ [8,10]. Hence, the experiments were conducted at $pH = 3$, 4, and 5. From the results shown in Fig. 6, the adsorption of metal ions was strongly dependent on the pH values. High adsorption at higher pH values showed that metal ions interacted with –NH_2 group by chelating.

Furthermore, it was found that the experimental value was larger than the corresponding theoretical value for the metal ion adsorption. The phenomena may be explained by synergistic complexation of metal ions with SiO_2-NH_2 and PAM in the composites. Synergism is defined as the cooperative action of different ligands in producing an effect greater than the sum of the effects of all ligands acting separately. In this research, not only –NH_2 groups from the pure SiO_2-NH_2 or PAM could coordinate to metal ions separately, but also both of the –NH_2 groups from the SiO_2-NH_2 and PAM could cooperate in the complexation of metal ions, leading to the enhanced amount of metal ion adsorption [13,22].

3.5. Adsorption isotherms

Adsorption isotherms describe how adsorbates interact with adsorbents and provide estimation of adsorption capacity of the adsorbents. Fig. 7 shows the experimental equilibrium isotherms for the adsorption of metal ions on composite hydrogels. The results clearly indicated that with an increase in initial metal ion concentration, the adsorption capacity of hydrogels increased significantly. At lower initial concentrations, the adsorption capacities increased almost linearly, implying that the sample surfaces possessed enough active sites for adsorption and the amount of adsorption in these cases were dependent on the number of metal ions that were transported from the bulk solution to the surface of samples. On the other hand, at higher initial concentrations, the adsorption capacities no longer increased linearly, suggesting that the number of adsorption sites on the surfaces of the samples limited the adsorption capacities.

In addition, it was found that the amount of adsorbed Pb(II) and Cu(II) was more than that of Cd(II). It is well known that the interactions between metal ions and ligands could depend on the many parameters such as nature of the functional groups attached to the adsorbent, the adsorbent composition and structure, nature and charge of the metal ion, and temperature and pH values of the external solution. In this study, the adsorption results were due to the functional groups (–NH_2 groups) of the composite hydrogels possessed higher affinity for Pb(II) and Cu(II) than that of Cd(II) [23,24].

The adsorption isotherm data were analyzed by the Langmuir isotherm model in the linearlized form:

$$\frac{C_e}{q_e} = \frac{K_s}{q_{max}} + \frac{C_e}{q_{max}} \tag{4}$$

where q_e was the equilibrium metal ion adsorption amounts on the hydrogels (mg/g), C_e was the equilibrium metal ion concentrations in the solution (mg/L), q_{max} was the maximum amount of metal ions that could be adsorbed on the hydrogels (mg/g), and K_s was a constant of the Langmuir model (mg/L). The plot of the experimental C_e/q_e against C_e for the experimental data in Fig. 7 is shown in Fig. 8.

All correlation coefficients were calculated to be larger than 0.99, indicating that the experimental data of these metal ion adsorption fitted well theoretical Langmuir relationship. The Langmuir isotherm model assumes that the adsorbed layer is one molecule in thickness and that all adsorption sites have equal energies and enthalpies of adsorption. As shown in

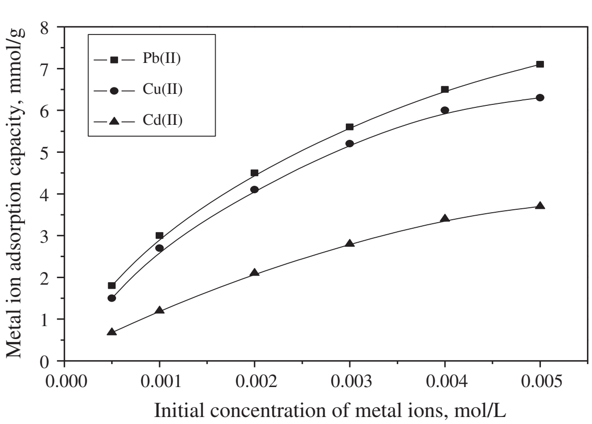

Fig. 7. Adsorption capacity for metal ions with various initial concentrations on the composite hydrogels at pH = 5.

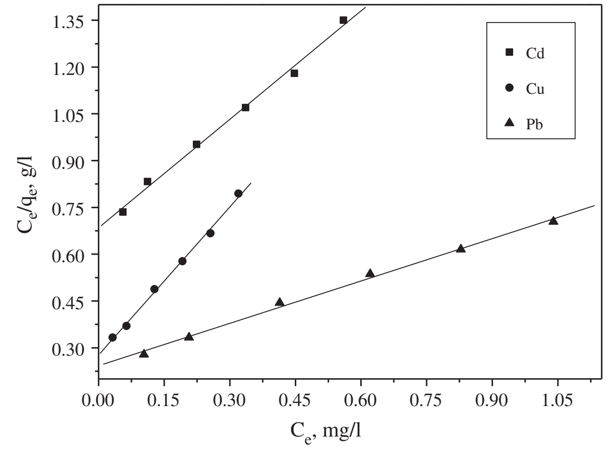

Fig. 8. Illustration of the experimental adsorption isotherm data presented in terms of the linearized Langmuir model.

Fig. 8, the adsorption isotherm results for composite hydrogels could be well described by the Langmuir mode, indicating that the metal ions were primarily adsorbed on the surface of the composite and the adsorbed layer was one molecule in thickness [25].

3.6. Adsorption kinetics

The rapid adsorption of metal ions by the adsorbent is of great importance for practical use, shortening the treatment of wastewater during filtration. The adsorption kinetics is to establish the time course of metal ion uptake on the composite hydrogels. The composite prepared with SiO_2-NH_2 content of 25% was selected for the adsorption kinetics studies. The change in amount of adsorbed metal ions with time for the hydrogels is shown in Fig. 9. It was observed that the adsorption process was very fast, and the equilibrium was approached within the first 10 min of the process. After this period, the adsorption rate was fairly slow, and saturation was reached within approximately 12 mins for all metal ions. This high initial rate suggested that the adsorption probably occurred mainly on the surface and the synergistic complexation of heavy metal ions as shown in Figs. 5 and 6 [26].

3.7. Regeneration studies

The capacity of hydrogels to be used in repeated operations is greatly influenced by the ability to easily desorb the bound metals under suitable conditions. The composite hydrogels prepared with different silica content in the formulation were selected for the investigation of the desorption of metal ions. The data presented in Table 3 showed that the desorption ratio was higher than 97%, which meant that there was no difficulty in desorbing the metals from the composites, and both the strongly and weakly sorbed ions could be easily removed by the dilute acid. The dilute acid used for desorption leaded to breaking the coordination bonds between the metal ions and the ligands (–NH_2). Therefore, it leads to the release of the metal ions from hydrogels into solution.

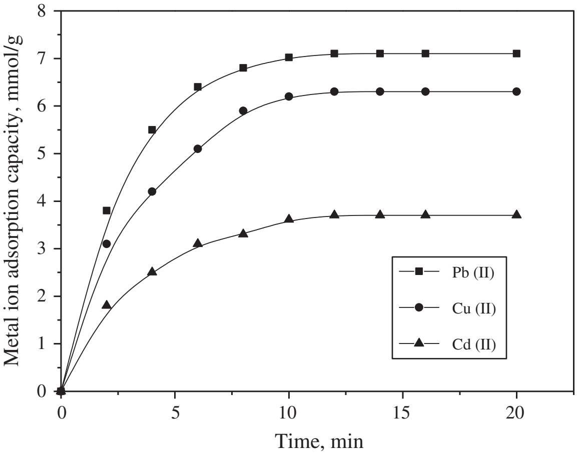

Fig. 9. Adsorption rates of metal ions by the composite hydrogel derived from SiO_2-NH_2 content of 25% in the formulation.

Table 3
Desorption ratio of metal ions, %

Sample	Cu (II)	Pb (II)	Cd (II)
Composite hydrogel 1[a]	98.3	97.7	97.6
Composite hydrogel 2[a]	97.5	98.1	97.3
Composite hydrogel 3[a]	97.9	97.9	98.7
Composite hydrogel 4[a]	98.3	98.3	97.9
Composite hydrogel 5[a]	98.0	98.5	98.2

Note: [a]Composite hydrogels 1, 2, 3, 4 and 5 were prepared with SiO_2-NH_2 content of 5, 10, 15, 20 and 25% in the formulation, respectively.

Table 4
Reuse of the composite hydrogels, %

Sample	Cu (II)	Pb (II)	Cd (II)
Composite hydrogel 1[a]	93.9	93.6	94.2
Composite hydrogel 2[a]	94.3	93.7	93.8
Composite hydrogel 3[a]	94.5	93.2	93.5
Composite hydrogel 4[a]	93.8	94.1	94.3
Composite hydrogel 5[a]	94.6	94.5	94.0

Note: [a]Composite hydrogels 1, 2, 3, 4 and 5 were prepared with SiO_2-NH_2 content of 5, 10, 15, 20 and 25% in the formulation, respectively.

Easy removal of metal ions from the binding sites demonstrated that the composite hydrogels might be reused several times without significant loss of the metal ion adsorption capacity. The hydrogels that regenerated with 1 mol/L HCl were used again in the adsorption of metal ions to observe the reuse properties. The results of Table 4 indicated that metal rebinding capacity of the hydrogels for all metals did not change significantly through repeated applications compared with the first run. This character of the possibility for reusing the hydrogels several times made them economically suitable for use.

4. Conclusion

In the current research, PAM/SiO_2-NH_2 composite hydrogels have been successfully prepared by *in situ* free-radical polymerization. The gel fraction and mechanical strength increased with the SiO_2-NH_2 content in the formulation. When the pH value of the buffer solution and the SiO_2-NH_2 content increased, the SR decreased. The metal ion adsorption capacity of the composites increased with the pH values of the feed solution and SiO_2-NH_2 content in the formulation. Furthermore, the synergistic complexation of metal ions was found in the adsorption studies. The Langmuir isotherm model could describe the adsorption isotherm of the composite hydrogels very well. The adsorption process for all metal ions was very fast, and the equilibrium was approached within the first 10 min of the process. Regeneration studies suggested that the composite hydrogels may be reused several times without significant loss of its metal ion capacity.

Acknowledgments

This project was supported by China Postdoctoral Science Foundation (No. 2012M520979) and Jiangsu Postdoctoral Science Foundation (No. 1201009B).

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