

Absorbency and Adsorption of Poly(acrylic acid-co-acrylamide) Hydrogel

Jianjun Xie,^{1,2} Xinrong Liu,³ Jifu Liang³

¹Division of Polymer Materials, Institute of Material Science and Engineering, Central-South University of Forestry and Technology, Changsha 410004, Hunan, China

²Institute of Rheological Mechanics and Materials Engineering, Central-South University of Forestry and Technology, Changsha 410004, Hunan, China

³Institute of Polymer Materials, Xiangtan University, Xiangtan 411105, Hunan, China

Received 28 November 2005; accepted 4 March 2007

DOI 10.1002/app.26666

Published online 17 July 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Poly(acrylic acid-co-acrylamide) (PAAAM) hydrogels have been prepared from partly neutralized acrylic acid (AA) and acrylamide (AM) by solution polymerization, and their absorbency and adsorption in both CuCl₂ and FeCl₃ solutions have been investigated. PAAAM hydrogels and their complexes with Cu²⁺ or Fe³⁺ have been characterized by FTIR. The absorbency of PAAAM in both CuCl₂ and FeCl₃ solutions increases initially and then decreases as the absorbing time increases. The adsorption of PAAAM in both CuCl₂ and FeCl₃ solutions can be described by the pseudo-second order chemisorption kinetics proposed by Ho and McKay, and the equilibrium uptake of Cu²⁺ on PAAAM can well be fit with the Langmuir adsorp-

tion isotherm. However, the equilibrium uptake of Fe³⁺ on PAAAM increases as the initial Fe³⁺ concentration increases for Fe³⁺ concentration smaller than 5.625×10^{-3} mol/L, and then decreases with Fe³⁺ concentration. The largest uptakes for Cu²⁺ and Fe³⁺ are 247 and 173 mg/g, respectively. The results also show that the uptake of Cu²⁺ and Fe³⁺ on PAAAM increases remarkably when pH of the solution is changed from 2.3 to 4.2 and from 1.0 and 2.1, respectively. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 1606–1613, 2007

Key words: poly(acrylic acid-co-acrylamide); hydrogel; absorbency; ion adsorption; adsorption modeling

INTRODUCTION

Hydrogels, which are three-dimensional networks containing hydrophilic functional groups, cannot be dissolved in water but can absorb a large amount of water and even retain the absorbed water under some pressures. The absorbing properties of hydrogels are affected by many factors, such as the ion type and its strength,^{1–3} solution pH,^{4,5} temperature,⁵ etc. The effect of synthetic conditions on the absorbency of superabsorbents or hydrogels has been discussed widely,^{6–12} while the factors affecting the absorbing kinetics in different transition metal solutions were not investigated in detail so far. The poly(acrylic acid-co-acrylamide) (PAAAM) hydrogel is one of the most important absorbents, because its monomers are cheap¹³ and easy to polymerize to reach high molecular weight.

Heavy metal ions in wastewater generated from various industries, such as electroplating, leather tanning, mining, steel making, and pigments, exert a significant impact on human health and other living organisms when discharged into the environment. Adsorption is a very wide and effective method to remove heavy metal ions from industrial effluent.¹⁴ Copper and iron ions are two important transition metal ions, and their concentrations should be limited to a low level. Many types of adsorbents including activated carbon, oxide minerals, polymer fibers, resins, biosorbents as well as hydrogels have been used to adsorb metal ions or sequester trace amount of metal ions from various aqueous solutions.¹⁵ The polymer absorbents include poly(acrylic acid) (PAA),^{16,17} polyacrylamide (PAM) and its modified product,¹⁸ poly(2-hydroxyethyl-methacrylate) (PHEMA),¹⁷ chitosan,^{19–21} chitin,²⁰ poly(acrylamidoglycolic-acid-co-acrylamide),²² polyethyleneimine (PEI),^{23,24} biomass Rhizopus compounds,^{20,25} poly(*p*-chloromethyl-stryrene-ethyleneglycol-dimethacrylate),²⁶ aminopolycarboxylic acid-type cellulose²⁷ and partially hydrolyzed polyacrylamide-co-polyvinyl pyrrolidone,²⁸ and so on.

Oeztop et al.⁸ prepared poly(acrylamide/sodium-acrylate) (PAM/SA) copolymer using various cross-linkers and investigated swelling, diffusion, immobilization of yeast cells, and production of ethyl alcohol.

Correspondence to: J. Xie (xiejianjun12@sina.com.cn).

Contract grant sponsor: Project of Research Plan of Science and Technology of Hunan Province; contract grant number: 05NK3052.

Contract grant sponsor: Research Fund of a Talented Person of Central South University of Forestry and Technology.

Journal of Applied Polymer Science, Vol. 106, 1606–1613 (2007)
© 2007 Wiley Periodicals, Inc.

Duran et al.²⁹ synthesized PAAAM, using irradiation polymerization by changing AM initial compositions, and discussed the swelling behavior and adsorption of some textile dyes. It is concluded that the diffusion of the fluids into hydrogel is non-Fickian in character and that the crosslinked PAAAM hydrogels can be successfully used in the purification of wastewater containing certain textile dyes. Katime et al.³⁰ investigated theophylline release from PAAAM hydrogels and has observed that the release kinetics from the swollen PAAAM hydrogels was a non-Fickian diffusion-controlled process. Zhang et al.³¹ investigated the drug loading and release of the PAAAM/linear polyallylammonium chloride (PAAC). Li et al.³² prepared PAAAM hydrogels by the controlled hydrolysis of polyacrylamide in an alkaline solution of 10% sodium hydroxide. They tested the capacity of the copolymer hydrogels to bind various metal ions under a range of uptake conditions, with varying uptake time, pH, and ionic strength. The results have shown that ions such as Cu^{2+} and Cd^{2+} were bound more strongly to PAAAM hydrogels than the competing ions of Na^+ , K^+ , Ca^{2+} , and Mg^{2+} , particularly at $\text{pH} > 5$, and they can be efficiently eluted (>94%) in 2 mol/L HNO_3 solution. Therefore, it can be used for the recovery and separation of Cu^{2+} and Cd^{2+} ions and for trace environmental analysis applications such as the diffusion gradients in thin films (DGT) technique.

The aim of this study is to prepare PAAAM hydrogels for absorbency and adsorption and to investigate their absorbency and adsorption behaviors in CuCl_2 and FeCl_3 solutions. The main factors affecting the absorbency and adsorption of Cu^{2+} and Fe^{3+} on PAAAM that are investigated are adsorption time, initial concentrations of Cu^{2+} and Fe^{3+} , and the solution pH.

EXPERIMENTAL

Materials

Acrylic acid (AA) was distilled in vacuum and stored in a refrigerator, both acrylamide (AM) and potassium peroxydisulfate (KPS) were recrystallized before use, other reagents including *N,N'*-methylene bisacrylamide (NMBA), NaOH, HCl, CuCl_2 , and FeCl_3 were used as received. NaOH was dissolved in distilled water to 12 and 1 mol/L, respectively, and HCl was dissolved in distilled water to 1 mol/L, while CuCl_2 and FeCl_3 were dissolved in distilled water to desired concentration. All of the materials were of analytical grade and provided by Shanghai Chemical Reagent Factory (Shanghai, China).

Preparation of PAAAM

PAAAM hydrogels were prepared from partly neutralized AA and AM by solution polymerization and were optimized by orthogonal experimental method.³³ The optimized compositions for the maximum absorbency in distilled water and in 0.9 wt % NaCl solution are as follows. The mass ratio of AA and AM is 6 : 1, the total mass percent of both monomers is 25%, the neutralized degree of AA is 60%, and the mass percentages of the cross-linker, and the initiator with respect to the total mass of the monomers are 0.01 and 0.1%, respectively.³³

First, a predetermined amount of 12 mol/L NaOH solution was added drop-wise to the stirred aqueous AA solution in a beaker cooled with an ice-water bath for a partial neutralization. Then, properly weighed AM, NMBA, and KPS masses were added into the beaker. Second, the reaction solution was heated for 2 h at 333 K, 2 h at 343 K, and 3 h at 353 K. After the polymerization, the product was cut into small pieces and dried in vacuum oven at 323 K, until the mass of product was constant. Finally, the dried product was pulverized and milled. The particle sizes for all of the samples used for the experiment were in the range of 60–100 mesh.

FTIR spectra

FTIR spectra of dried PAAAM hydrogel and its complexes with metal ions were obtained using a FTIR spectrophotometer (Spectrum one, PerkinElmer). PAAAM (0.02 g) and KBr (1.0 g) were thoroughly mixed and pressed to form a tablet, and then the spectrum was recorded.

Absorbency experiment

At room temperature, 0.4 g PAAAM was immersed in distilled water and in 0.9 wt % NaCl solution for absorbency or in about 500-mL metal salt solutions having defined concentrations for simultaneous batch absorbency and adsorption experiments. The swollen hydrogel was weighed after the desired time, and then the absorbency Q was calculated as follows:

$$Q = (W_2 - W_1)/W_1 \quad (1)$$

where Q is the absorbency in gram water/gram dried hydrogel (Q_s and Q_w are the absorbency of the PAAAM hydrogel in 0.9% NaCl solution and in distilled water, respectively). W_1 and W_2 are the weights of the dried hydrogel and the swollen hydrogel in grams, respectively.

TABLE I
Factors and Their Levels in the Orthogonal Experiments

Factor levels	[M] (%)	R	N (%)	[C] (%)	[I] (%)
I	25	12 : 1	90	0.01	0.05
II	30	9 : 1	80	0.02	0.1
III	35	6 : 1	70	0.03	0.2
IV	40	3 : 1	60	0.04	0.4

Adsorption experiment

Batch adsorption experiments were carried out at room temperature in a 500-mL beaker. The effects of the adsorption time, the initial concentrations of the copper ions, and iron ions in the adsorption media, and the solution pH values on the metal ions adsorption were studied. The solution pH values were adjusted with 1 mol/L HCl or 1mol/L NaOH solutions. The amount of absorbed metal ions was determined based on the following eq. (2) as a difference between metal ions concentrations before and after the adsorption. The adsorption percentage was calculated according to eq. (3). The concentration of metal ions was determined with an atomic absorption spectrum instrument (Z-8000, Shimadzu).

$$q = (C_0 - C) \times V/W_1 \quad (2)$$

$$A = (C_0 - C)/C_0 \times 100\% \quad (3)$$

where q is the equilibrium uptake (mg/g), A the adsorption percentage, C_0 and C the initial and the final metal ions concentrations (mg/ml), respectively, V the solution volume (mL), and W_1 the weight of PAAAM hydrogel (g).

RESULTS AND DISCUSSION

Optimal polymerization conditions for the absorbency

The optimal conditions to obtain PAAAM for the best absorbency have been investigated through the typical orthogonal experiments. In Tables 1-4, are given the levels of the affecting factors and the absorbency results of the orthogonal experiments at the reaction temperature 323 K. It is seen from the results given in Table 2 and the range analyses in Tables 3 and 4 that the best polymerization conditions are as follows: the mass ratio of AA to AM is 6 : 1, the total mass percentage of both monomers is 25%, the neutralized degree of AA is 60%, and the mass percentages of the cross-linker and the initiator with respect to the total mass of the monomers are 0.01 and 0.1%, respectively.³³ The important affecting factors are the mass percentages of all monomers, the initiator, and the cross-linker. Considering the cooperative effect of the reaction temperature and the initiator concentration

TABLE II
Results from the Orthogonal Experiments

No.	[M] (%)	R	N (%)	[C] (%)	[I] (%)	Q_s	Q_w
1	25	12 : 1	90	0.01	0.05	121	2345
2	25	9 : 1	80	0.02	0.1	109	1318
3	25	6 : 1	70	0.03	0.2	92	992
4	25	3 : 1	60	0.04	0.4	76	985
5	30	12 : 1	80	0.03	0.4	75	699
6	30	9 : 1	90	0.04	0.2	71	535
7	30	6 : 1	60	0.01	0.1	131	2207
8	30	3 : 1	70	0.02	0.05	100	1765
9	35	12 : 1	70	0.04	0.1	72	666
10	35	9 : 1	60	0.03	0.05	72	794
11	35	6 : 1	90	0.02	0.4	71	730
12	35	3 : 1	80	0.01	0.2	86	1077
13	40	12 : 1	60	0.02	0.2	66	706
14	40	9 : 1	70	0.01	0.4	72	835
15	40	6 : 1	80	0.04	0.05	64	385
16	40	3 : 1	90	0.03	0.1	68	799

Q_s and Q_w are the absorbency of the PAAAM hydrogel in 0.9% NaCl solution and in distilled water, respectively.

on the polymerization rate, we have applied the temperature programming method to search the optimum experimental conditions of the absorbency, while keeping constant all the other parameters. It is found that the temperature programming is 2 h at 333 K, 2 h at 343 K, and 3 h at 353 K, and the maximum absorbencies of the obtained PAAAM hydrogel in distilled water and in 0.9 wt % NaCl aqueous solution were 2710 and 133 g/g, respectively.

FTIR spectroscopy analysis

To study the complexes of the PAAAM hydrogel with metal ions Cu^{2+} and Fe^{3+} , we have recorded their FTIR spectra (Fig. 1). Several peaks of plain PAAAM can be assigned as follows: 3449 cm^{-1} (ν O—H) in —COOH, 2954 cm^{-1} (ν N—H) symmetric in —CONH₂, 1675 cm^{-1} (ν C=O) symmetric in —CONH₂, 1566 cm^{-1} (ν C—O) asymmetric in —COO(H), 1454 cm^{-1} (ν C—N) in —CONH₂, 1403 cm^{-1} (ν C=O) symmetric in —COO(H). The adsorption band between 3000 and 3700 cm^{-1} is very broad in

TABLE III
Range Analysis of Absorbency of PAAAM in 0.9 wt % NaCl Solutions

Factor levels	[M] (%)	R	N (%)	[C] (%)	[I] (%)
I	398	334	331	410	357
II	377	324	334	346	379
III	301	358	336	307	315
IV	270	330	345	283	295
I/4	99.5	83.5	82.75	102.5	89.25
II/4	94.25	81	83.5	86.5	94.75
III/4	75.25	89.5	84	76.75	78.75
IV/4	67.5	82.5	86.25	70.75	73.75
Ranges	32	8.5	3.5	31.75	21

TABLE IV
Range Analysis of Absorbency of PAAAM in Distilled Water

Factor levels	[M] (%)	R	N (%)	[C] (%)	[I] (%)
I	5640	4416	4409	6464	5289
II	5206	3482	3479	4519	4990
III	3267	4314	4258	3284	3310
IV	2725	4626	4692	2571	3249
I/4	1410	1104	1102.25	1616	1322.25
II/4	1301.5	870.5	869.75	1129.75	1247.5
III/4	816.75	1078.5	1064.5	821	827.5
IV/4	681.25	1156.5	1173	642.75	812.25
Ranges	728.75	286	303.25	973.25	510

the absorbing water hydrogel, because of the functional groups having hydrogen bonding interaction with water from two different monomers. When the PAAAM is complexed with the metal ions, some adsorption wave numbers are shifted, because of the interaction effects of metal ions with $-COO(H)$ and/or $-CONH_2$. For example, for the adsorption of Cu^{2+} and Fe^{3+} , the adsorption wave number of $C=O$ in $-CONH_2$ has been shifted from 1675 to 1717 cm^{-1} and 1716 cm^{-1} , respectively, and that of $C=O$ in $-COOH$ has been shifted from 1566 to 1612 cm^{-1} and 1583 cm^{-1} , respectively.

Absorbency of PAAAM in $CuCl_2$ and $FeCl_3$ solutions

Since the absorbency of hydrogel is influenced by the ion type and concentration as well as pH in solution,^{1,2} the absorbency of PAAAM in $CuCl_2$ and $FeCl_3$ solutions has been investigated by keeping constant the ionic strength of solutions, I , defined as

$$I = \frac{1}{2} \sum m_i z_i^2 \tag{4}$$

where m_i and z_i are the mass mole concentration and charge of ion i , respectively. Figure 2 shows the absorbency of PAAAM in $CuCl_2$ and $FeCl_3$ solutions at the ionic strength, $I = 0.009$ mol/kg. It is seen that

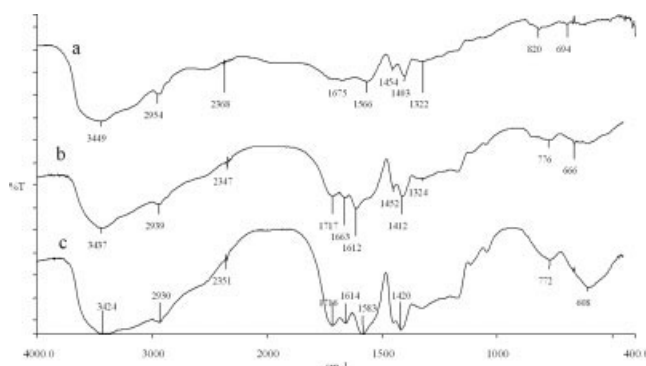


Figure 1 FTIR of PAAAM: (a) plain PAAAM; (b) Cu^{2+} loaded PAAAM; (c) Fe^{3+} loaded PAAAM.

the absorbency of PAAAM in $CuCl_2$ and $FeCl_3$ solutions first increases and then decreases as the swelling time increases. During the absorbing process of PAAAM in $CuCl_2$ and $FeCl_3$ solutions, both the absorbing and the chelating of PAAAM with metal ions occur simultaneously, that is, the swelling and the chelating are the competing processes. Because at the beginning of the absorbing process, the osmotic pressure of PAAAM hydrogel is large, the swelling is stronger than the chelating, and the absorbency of PAAAM increases. As the absorbing time increases, the osmotic pressure of the PAAAM hydrogel decreases, and the absorbency of PAAAM also decreases, while the chelating increases. It has been found that at the same ionic strength, the absorbency of PAAAM in the $FeCl_3$ solution is larger than that in the $CuCl_2$ solution. This can be explained by the fact that at the same ionic strength, from eq. (4), the concentration of Fe^{3+} is only the half of the concentration of Cu^{2+} . Therefore, the chelating amount of PAAAM for Fe^{3+} is smaller than that for Cu^{2+} ; as a result, the absorbency of PAAAM in $FeCl_3$ solution is larger than that in $CuCl_2$ solution.

Adsorption kinetics

Usually, the adsorption process can be divided into three consecutive phases. The first phase is that the adsorbate particles move to the surface of adsorbent, the second phase is that the adsorbate diffuses into the holes of adsorbent, and the last phase is the reactive adsorption, i.e., the adsorbate reacts with the functional groups of adsorbent. Generally speaking, the adsorption process is controlled by the first and/or the second phases.

The adsorption kinetics of Cu^{2+} and Fe^{3+} on PAAAM hydrogel has been investigated and the results are shown in Figure 3. As can be seen, the

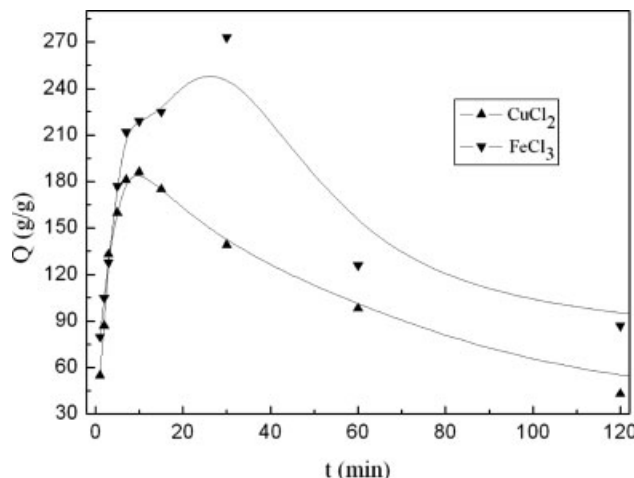


Figure 2 Absorbency of PAAAM (Q) as a function of the absorbing time (t). $I = 0.009$ mol/kg.

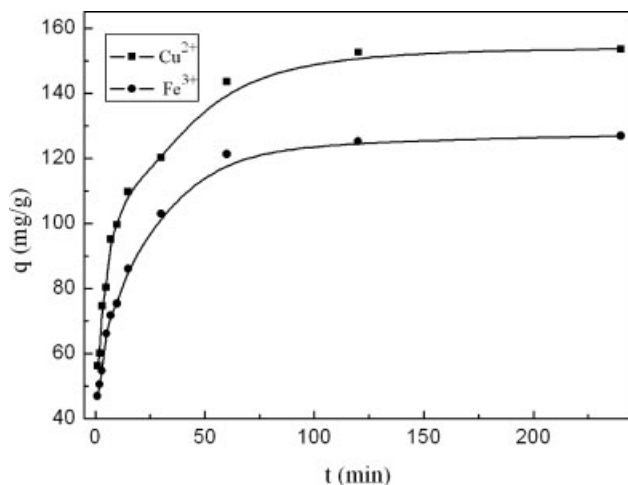


Figure 3 Adsorption kinetics of Cu^{2+} and Fe^{3+} ions on PAAAM hydrogel. Initial concentration of Cu^{2+} or Fe^{3+} : 0.0025 mol/L; adsorption time: 12 h; pH \approx 6.0; room temperature; mass of the PAAAM hydrogel: 0.40 g.

adsorption uptakes for both Cu^{2+} and Fe^{3+} increase with time, but the adsorption rates obviously decreases with time, and then the adsorptions reach their equilibrium gradually in about 2 h. To evaluate the mechanism of the adsorptions, several models have been used to interpret the experimental data:

- i. The diffusion equation model,³⁴

$$\frac{q_t - q_0}{q_e - q_0} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{4D_e n^2 \pi^2 t}{d_{p,e}^2}\right) \quad (5)$$

where q_0 is the initial adsorbed amount, q_t and q_e the adsorbed amount at time t and at equilibrium, respectively, D_e the effective diffusivity, and $d_{p,e}$ the swelling diameter of the gel particle at equilibrium. Equation (5) is the solution of the diffusion equation within a sphere where the mass transfer rate is expressed by the Crank-Nicholson method, i.e., the relationship between adsorption capacity (q_t) and the adsorption time (t).

- ii. The Fickian diffusion model,^[30,31,35]

$$q_t = k_d t^n \quad (n = 0.5 \text{ for Fickian diffusion of a cylindrical shapes}) \quad (6)$$

where k_d is adsorption rate constant. Equation (6) gives the amount of adsorption by diffusion-controlled dynamics as a function of time.

- iii. The pseudo-second order chemisorption kinetic rate equation,¹⁹

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

where k_2 is the adsorption rate constant. Equation (7) was proposed by Ho and McKay.¹⁹

The correlation coefficients (R) of the above eqs. (5)–(7) are 0.94, 0.90, and 0.999 for the adsorption of Cu^{2+} , and 0.97, 0.918, and 0.999 for the adsorption of Fe^{3+} , respectively. Therefore, eq. (7) gives the best fit to the experimental kinetic data.

From eq. (7), we have found that the k_2 values for the adsorption of Cu^{2+} and Fe^{3+} are very similar and equal to 0.0014 and 0.0015, respectively. When one compares the radius of Fe^{3+} (6.0×10^{-11} m) to that of Cu^{2+} (7.2×10^{-11} m), one may expect that the adsorption rate for the Fe^{3+} ions should be significantly larger than that for the Cu^{2+} ions. This may suggest that partial hydrolysis of Fe^{3+} ions (in the form of $\text{Fe}(\text{OH})_x$ in the solution) might occur (to be discussed further in the following), resulting in that the effective size of the Fe^{3+} ions becomes similar to that of the Cu^{2+} ions. From Figure 3, the equilibrium uptake of Cu^{2+} is larger than that of Fe^{3+} . This arises because Fe^{3+} and Cu^{2+} have different valency, and for the same amount of PAAAM, it requires more Cu^{2+} than Fe^{3+} for the complexation to reach the equilibrium. Note that during the complexation of $\text{Fe}(\text{OH})_x$ with $-\text{COO}(\text{H})$ groups on the PAAAM, OH^- is released from $\text{Fe}(\text{OH})_x$.

Effect of the initial concentration of metal ions

Figure 4 gives the experimental adsorption equilibrium isotherms of metal ions on PAAAM hydrogel determined after the contact time of 10 h at various initial Cu^{2+} or Fe^{3+} concentrations at pH \approx 6.0. First, from Figure 4, we can observe that the uptake of Cu^{2+} on PAAAM increases as the initial concentration of Cu^{2+} increases and becomes constant when

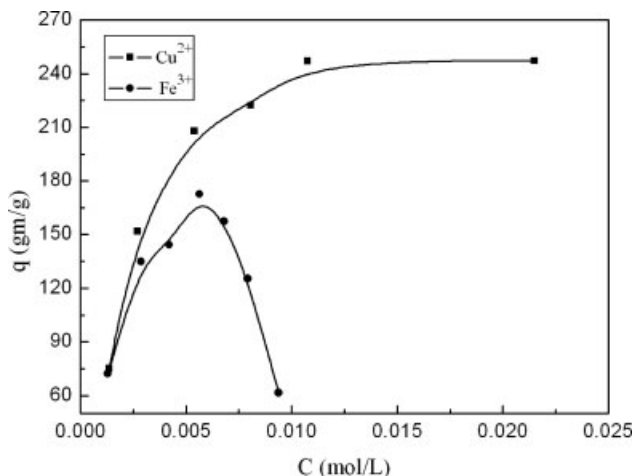


Figure 4 Adsorption isotherm of Cu^{2+} and Fe^{3+} on the PAAAM hydrogel. Adsorption time: 12 h; pH \approx 6.0; room temperature; mass of the PAAAM hydrogel: 0.40 g.

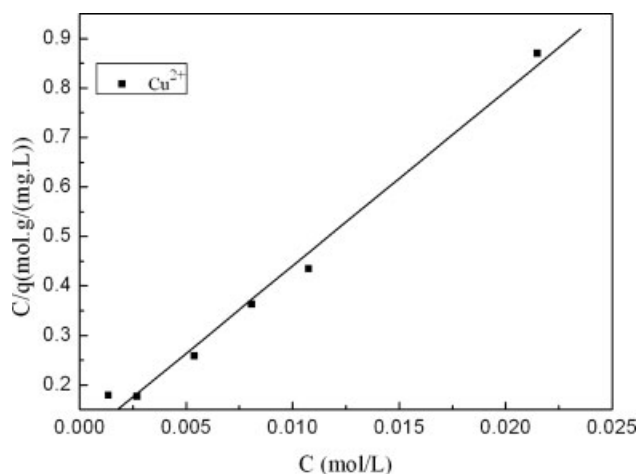


Figure 5 The quantity C/q plotted as a function of C , based on the linearized form of the Langmuir adsorption isotherm, eq. (8), in the case of Cu^{2+} . Adsorption time: 12 h; $\text{pH} \approx 6.0$; room temperature; mass of the PAAAM hydrogel: 0.40 g.

the concentration of Cu^{2+} is larger than 1.08×10^{-2} mol/L. Second, the uptake of Fe^{3+} on PAAAM also increases initially as the initial concentration of Fe^{3+} increases and reaches its maximum (173 mg/g) at the concentration of Fe^{3+} equal to 5.63×10^{-3} mol/L, and then it decreases sharply as the initial concentration of Fe^{3+} increases.

For the adsorption of Cu^{2+} , it is found that the Langmuir model gives the best fit for the experimental data,^{21,34,37}

$$\frac{C}{q} = \frac{C}{q_0} + \frac{1}{q_0 b} \quad (8)$$

where C is the equilibrium or final concentration of Cu^{2+} in the solution (mol/L), q is the amount of Cu^{2+} absorbed per unit mass of the PAAAM at equilibrium concentration (mg/g), q_0 is the maximum uptake at monolayer coverage (mg/g), and b is the Langmuir adsorption equilibrium constant (L/mol) related to the energy of adsorption or the net enthalpy. Figure 5 shows the experimental data of C/q as a function of C , and the solid line is the fitting given by eq. (8). It is seen that the agreement is satisfactory, and the correlation coefficient (R) is 0.994. From the slope and interception of the line in Figure 5, we obtain the values of $q_{0,\text{cal}} = 253$ mg/g and $b = 0.0432$ L/mol. The obtained uptake $q_{0,\text{cal}}$ is very close to that determined experimentally, $q_{0,\text{exp}}$, which is 247 mg/g.

It is obvious that the adsorption curve of Fe^{3+} in Figure 4 cannot be described by the Langmuir adsorption isotherm. The abnormal adsorption behavior of Fe^{3+} on PAAAM for the Fe^{3+} concentration larger than 5.63×10^{-3} mol/L must be related to the hydrolysis of Fe^{3+} ions, to be discussed below.

Effect of pH on the metal ion adsorption

The system pH is a very important parameter affecting the adsorption and chelating of the metal ions in polymeric adsorbents,^{21,26,27,32,37-39} particularly affecting the formation of coordination bond between oxygen, nitrogen, or sulfur and metal atoms. Ionization of the chelating ligand and the stability of the metal-ligand complexes also vary with pH. Because of the easy hydrolysis of metal ions at higher concentration and higher pH of solutions, the effects of the system pH on the metal ion uptake on PAAAM hydrogel has been investigated at a fixed but small initial concentration of the single metal ions Fe^{3+} and Cu^{2+} ($\text{pH} < 5.0$).

Figure 6(a,b) shows the effect of pH on the uptake (q) and the adsorption percentage (A) of the metal ions Fe^{3+} and Cu^{2+} on PAAAM, respectively. The uptake of Fe^{3+} on PAAAM increases as pH increases

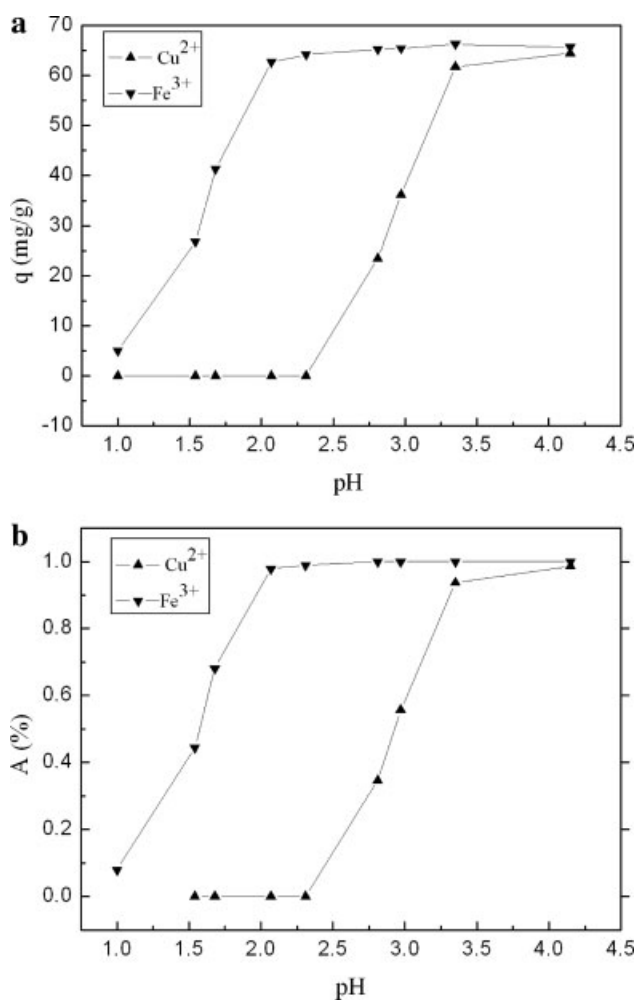


Figure 6 Experimentally measured dependence of (a) the adsorption uptake q and (b) the adsorption percentage A on the solution pH. Initial concentration of Cu^{2+} or Fe^{3+} : 0.001 mol/L; the adsorption time: 12 h; room temperature; mass of the PAAAM hydrogel: 0.40 g.

and approaches a defined value, $q = 65 \text{ mg/g}$ for $\text{pH} > 2.3$. For the Cu^{2+} ion, however, the uptake is very small when $\text{pH} < 2.3$, and the adsorption of Cu^{2+} starts to increase with pH only when pH is larger than 2.3 and approaches a constant value for $\text{pH} > 4.2$. This is in agreement with the Cu^{2+} uptake on cyclam modified poly(*p*-chloromethyl styrene-ethylene-glycol dimethacrylate), observed by Kavakli et al.,²⁶ and on the PAM-PAA, observed by Li et al.³² Similar results have also been obtained for the adsorption percentage A of Fe^{3+} and Cu^{2+} on PAAAM as shown in Figure 6(b).

The adsorption behavior of the PAAAM hydrogels depends on several parameters such as the adsorbent charge valency, the solution pH , and the solvation chemistry of the metal ions (e.g., ability to be hydrolyzed and to form polynuclear species³⁹). In general, pH affects the binding capacity by shifting the equilibrium of the coordination reaction and ion-exchange ability in two ways: changing the concentration of active ligands and the concentration of soluble metal ions. At very low pH (< 3.0), i.e., at high H^+ concentration, on one hand, there is a large amount of Fe^{3+} in solution; on the other hand, some amine groups $-\text{NH}_2$ on PAAAM are protonated and become $-\text{NH}_3^+$ due to the reaction with H^+ , and the stability of its metal ion complexes is decreased. Because of very high positive charges on the PAAAM hydrogel, the metal ions cannot contact PAAAM due to the charge repulsions. Also because of protonation, the carboxylic groups, $-\text{COO}(\text{H})$ inside the network of the PAAAM, cannot contact with the metal ions and have much less capacity of forming complexes than in their salt form.³² All these lead to a rather small adsorption of metal ions on PAAAM at low pH . Moreover, the interactions between Fe^{3+} and water can lead to very complicated solution chemistry and generate different types of Fe species such as Fe^{3+} , $\text{Fe}(\text{OH})^{2+}$, $\text{Fe}(\text{OH})_2^+$, and $\text{Fe}_2(\text{OH})_2^{4+}$,⁴⁰ which are difficult to form chelations with $-\text{COO}(\text{H})$ and $-\text{CONH}_2$. Such hydrolysis of Fe^{3+} ions becomes more severe when the concentration of Fe^{3+} in the solution is high, leading to even less chelating. This explains the Fe^{3+} uptake on PAAAM decreasing with an increase of Fe^{3+} concentration in the region of high Fe^{3+} concentrations in Figure 4. As the solution pH increases, the concentrations of $\text{Fe}(\text{OH})^{2+}$, $\text{Fe}(\text{OH})_2^+$, and $\text{Fe}_2(\text{OH})_2^{4+}$ increase; when the solution pH is greater than 4.5, there is almost only $\text{Fe}(\text{OH})_2^+$ complexes in solutions. Moreover, the carboxylic groups become progressively ionized and spaced along the polymeric chains, which increase the probability of the interactions between the carboxylic groups and metal ions in the solutions. However, if the solution pH is too high, particularly if the solution becomes basic, the metal ions would be easily hydrolyzed to form Fe^{3+} and OH^- coordinates or the metal ion

hydroxides with OH^- in the solution. For example, at $\text{pH} = 7$, 28% of Fe^{3+} are in the form of $\text{Fe}(\text{OH})_2^+$ and 71% in the form of $\text{Fe}(\text{OH})_3$.⁴⁰ Thus, poor adsorption of Fe^{3+} ions on PAAAM can occur at very high solution pH .

The hydrolysis of Cu^{2+} to form $\text{Cu}_2(\text{OH})_2^{2+}$ and mononuclear species $\text{Cu}(\text{OH})^+$, $\text{Cu}(\text{OH})_2$, and $\text{Cu}(\text{OH})_3^{3-}$ occurs in dilute solutions with increasing pH from 8 to 12, and even to form $\text{Cu}(\text{OH})_4^{2-}$ in more alkaline solutions.³⁷ In this study, since the adsorption experiments were carried out at $\text{pH} < 5.0$, copper ions exist mainly in the form of Cu^{2+} , i.e., the hydrolysis of Cu^{2+} does not occur significantly.³⁷ However, due to the above-mentioned amine group protonation, which induces an electrostatic repulsion for the Cu^{2+} ion contacts, the competition occurs between protons and Cu^{2+} ions for the adsorption sites. This explains why the adsorption capacity decreases as pH decreases for pH in the range between 4.3 and 2.1 in Figure 6. In addition, since the chelating constant of $-\text{COO}(\text{H})$ and $-\text{CONH}_2$ groups with Fe^{3+} is larger than that with Cu^{2+} ,³⁶ the adsorption of Fe^{3+} has been observed for $\text{pH} < 2.1$, while for Cu^{2+} it can occur only for $\text{pH} > 2.3$. This observation shown in Figure 6 indicates that one may separate Fe^{3+} and Cu^{2+} by adjusting pH between 2.1 and 2.3 through PAAAM hydrogel adsorption.

In addition, the adsorption of metal ions will depend on the number of sites available for metal ions attachment on PAAAM hydrogels. At the given experimental pH range, the $-\text{COO}(\text{H})$ groups on PAAAM hydrogels interact with metal ions Fe^{3+} and Cu^{2+} to form chemical bonds during the adsorption, while the $-\text{CONH}_2$ groups on PAAAM hydrogels chelate with metal ions Fe^{3+} and Cu^{2+} , possibly through complexation with the nitrogen atoms. The adsorption capacity cannot increase further after all the adsorption sites have been occupied by metal ions. This would explain the observed maximum and constant adsorption capacity in Figure 6.

CONCLUSIONS

The PAAAM hydrogel has been synthesized by solution polymerization. Their absorbency and adsorption behaviors in CuCl_2 and FeCl_3 solutions have been investigated. It is found that at the same ionic strength, the absorbing capacity of the PAAAM hydrogel for Cu^{2+} and Fe^{3+} ions is significantly different, because of different chelating constant with $-\text{COO}(\text{H})$ and $-\text{CONH}_2$ groups. The relationship between the uptake (q_t) of metal ions Cu^{2+} and Fe^{3+} on PAAAM and adsorption time (t) can be interpreted by the expression, $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$. The effect of the initial metal ion concentration and solution pH on the uptake has been found to be substantial. The

adsorption isotherm of Cu^{2+} on PAAAM can be well explained by Langmuir adsorption isotherm. However, abnormal adsorption behavior of Fe^{3+} on PAAAM has been observed. In particular, the uptake of Fe^{3+} on PAAAM first increases and then decreases as the initial Fe^{3+} concentration increases. The latter is due to the hydrolysis of Fe^{3+} ions at large concentrations.

References

- Lee, W. F.; Wu, R. J. *J Appl Polym Sci* 1996, 64, 1099.
- Liu, Y.; Xie, J. J.; Zhang, X. Y. *J Appl Polym Sci* 2003, 90, 3481.
- Omidian, H.; Hashemi, S. A.; Sammes, P. G.; Meldrum, I. *Polymer* 1999, 40, 1753.
- Kang, H. M.; Xie, J. J. *J Appl Polym Sci* 2003, 88, 494.
- Zhao, Y.; Su, H. J.; Fang, L.; Tan, T. W. *Polymer*, 2005, 46, 5368.
- Omidian, H.; Hashemi, S. A.; Askari, F.; Nafisi, S. *J Appl Polym Sci* 1994, 54, 241.
- Zhou, W. J.; Yao, K. J.; Kurth, M. J. *J Appl Polym Sci* 1996, 62, 911.
- Oeztop, H. N.; Oeztop, A. Y.; Karadag, E.; Isikver, Y.; Saraydin, D. *Enzym Microbiol Technol* 2003, 32, 114.
- Mohan, Y. M.; Murthy, P. S. K.; Raju, K. M. *React Funct Polym* 2005, 63, 11.
- Bajpai, S. K.; Johnson, S. *React Funct Polym* 2005, 62, 271.
- Omidian, H.; Hashemi, S. A.; Sammes, P. G.; Meldrum, I. G. *Polymer* 1998, 39, 3459.
- Rintoul, I.; Wandrey, C. *Polymer* 2005, 46, 4525.
- Cui, Y. D.; Guo, J. W.; Liao, L. W.; Kang, Z. *J Chem Ind Eng (China)* 2001, 52, 601.
- Zhang, J. B.; Hong, J. M. *Tech Equip Environ Pollut Control (China)* 2001, 1, 46.
- Jianjun, X.; Jifu, L.; Xinrong, L.; Sai, L. *J Chem Ind Eng (China)* 2007, 58, 1762.
- Kirwan, L. J.; Fawell, P. D.; van Bronswijk, W. *Langmuir* 2003, 19, 5802.
- Moradi, O.; Modarress, H.; Noroozi, M. *J Colloid Interface Sci* 2004, 271, 16.
- Kasgoez, H.; Oezguemues, S.; Orbay, M. *Polymer* 2003, 44, 1785.
- Wu, F. C.; Tseng, R. L.; Juang, R. S. *Water Res* 2001, 35, 613.
- Sag, Y.; Aktay, Y. *Biochem Eng J* 2002, 12, 143.
- Ngah, W. S. W.; Enlud, C. S.; Mayanar, R. *React Funct Polym* 2002, 50, 181.
- Li, W.; Zhao, H.; Teasdale, P. R.; John, R. *Polymer* 2002, 43, 4803.
- Chanda, M.; Rempel, G. L. *React Funct Polym* 1997, 35, 197.
- Chanda, M.; Rempel, G. L. *Ind Eng Chem Res* 2001, 40, 1624.
- Bai, R. S.; Abraham, T. E. *Water Res* 2002, 36, 1224.
- Kavakl, C.; Tuncel, S. A.; Salih, B. *Separ Purif Technol* 2005, 45, 35.
- Akama, Y.; Yamada, K.; Itoh, O. *Anal Chim Acta* 2003, 485, 19.
- Kiatkamjornwong, S.; Suwanmala, P. *Radiat Phys Chem* 1998, 52, 217.
- Duran, S.; Solpan, D.; Gueven, O. *Nucl Instrum Method Phys Res* 1999, B151, 196.
- Katime, I.; Novoa, R.; de Apodaca, E. D.; Mendizabal, E.; Puig, J. *Polym Test* 1999, 18, 559.
- Zhang, Y. X.; Wu, F. P.; Li, M. Z.; Wang, E. J. *Polymer* 2005, 46, 7695.
- Li, W.; Zhao, H.; Teasdale, P. R.; John, R.; Zhang, S. *React Funct Polym* 2002, 52, 31.
- Liu, X. R.M.S. Thesis, Xiangtan University (People's Republic of China), 2006.
- Tokuyama, H.; Kanazawa, R.; Sakohara, S. *Separ Purif Technol* 2005, 44, 152.
- McKay, G.; Poots, R. E. *J Chem Technol Biotechnol* 1980, 30, 279.
- Huang, M. F. *Printing Dyeing* 2001, 1, 37.
- Deng, S. B.; Bai, R. B.; Chen, J. P. *J Colloid Interface Sci* 2003, 260, 265.
- Pekel, N.; Salih, B.; Guven, O. *Colloids Surf B: Biointerf* 2005, 42, 89.
- Kesenci, K.; Say, R.; Denizli, A. *Eur Polym J* 2002, 38, 1443.
- Martin, R. B. *J Inorg Boichem* 1991, 44, 141.