

Synthesis of Montmorillonite/Poly(acrylic acid-co-2-acrylamido-2-methyl-1-propane sulfonic acid) Superabsorbent Composite and the Study of its Adsorption

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Received October 7, 2011, Accepted February 16, 2012

A novel superabsorbent composite was prepared by intercalation polymerization of acrylic acid (AA) and 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS) in the presence of montmorillonite (MMT), using ammonium persulfate (APS) as an initiator and *N,N'*-methylenebisacrylamide (MBA) as a cross linker. The superabsorbent composite was characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), X-ray diffraction (XRD) and thermogravimetric analysis (TGA). Maximum absorbency of the composite in distilled water and 0.9% sodium chloride solution was 722 and 108 g/g, respectively. The composite was used for removal of heavy metal ions from aqueous solutions. Maximum amount of adsorption for Ni²⁺, Cu²⁺ and Pb²⁺ was 211.0, 159.6 and 1646.0 mg/g, respectively, and the adsorption was in accordance with both Langmuir and Freundlich model. The composite could be regenerated and reused in wastewater treatment.

Key Words : Synthesis, Montmorillonite, Superabsorbent composite, Adsorption

Introduction

In recent years, more and more wastewater with heavy metal ions has been discharged into the environment with the rapid development of industry. Many of the heavy metal ions, *i.e.*, ions of zinc, copper, nickel, mercury, cadmium, lead and chromium, are toxic and non-degradable. Because of their high solubility in the aquatic conditions, heavy metal ions can be accumulated in living tissues and cause various diseases and disorders. Therefore, removal of heavy metal ions from aqueous solutions is always widely focused. Many methods have been used to remove heavy metal ions, such as chemical precipitation,¹ membrane,² coagulation and flocculation,³ electrochemical treatment,⁴ ion-exchange⁵ and adsorption.⁶ Among these methods, adsorption shows particular advantages over others for its high efficiency, good selectivity, low cost and easy regeneration. With proper adsorbents, adsorption can be a promising technique for the removal of certain types of contaminants.

Superabsorbent resins are new kinds of functional polymeric materials which have three-dimensional networks with flexible chains. With their porous structures and hydrophilic functional groups, superabsorbent resins can not only absorb and retain water but also adsorb metal ions and ionic dyes from industrial wastewater. Therefore, they are widely used in agriculture, horticulture, hygienic products, drug-delivery systems and effluent treatment.⁷⁻¹⁰ Clay minerals with layered structures such as montmorillonite, kaolin, attapulgite, mica and vermiculite, have been used to prepare superabsorbent composites. Su *et al.*¹¹ prepared MMT/PAA superabsorbent composite and found that incorporation of MMT into PAA could improve the water absorbency, swelling ability and thermal stability of products. Li *et al.*¹² intro-

duced attapulgite into poly(acrylic acid-co-acrylamide) copolymer and found that when the content of attapulgite increased from 0 to 10 wt %, absorbency of water and 0.9% NaCl solution increased from 684 and 72 g/g to 1414 and 117 g/g, respectively. Güçlü *et al.*¹³ studied the effect of reaction conditions, including treatment time, pH values and initial concentration of metal ions, on the adsorption capacity of Cu²⁺ and Pb²⁺ on MMT/ starch-graft-acrylic acid superabsorbent nanocomposite. Bao *et al.*¹⁴ synthesized MMT/sodium carboxymethyl cellulose-g-poly(AA-co-AM-co-AMPS) superabsorbent hydrogel and investigated swelling behaviors of the product. However, study on the preparation and application of MMT/P(AA-co-AMPS) superabsorbent composite has not been reported.

AMPS is a hydrophilic monomer containing nonionic and anionic groups, which can react with the heavy metal ions and thereby improve the adsorption capacity and salt tolerance of the product. Meanwhile, as AMPS can be dissociated in a wide range of pH values, composites derived from AMPS always exhibit independent swelling behaviors from pH values.

In this article, MMT/P(AA-co-AMPS) superabsorbent composite has been synthesized by intercalation polymerization of AA and AMPS in the presence of MMT, using APS as an initiator and MBA as a crosslinker in an aqueous solution. The superabsorbent composite was characterized by FTIR, SEM, XRD and TGA. The effect of reaction conditions such as the mass ratio of AA to AMPS, the content montmorillonite as well as the neutralization degree of AA on water and saline absorbency was investigated. Water retention of superabsorbent composite was also tested. Finally, the sorption behavior of Ni²⁺, Cu²⁺ and Pb²⁺ on the superabsorbent composite was studied.

Experimental

Materials. APS, analytical reagent grade, from Tianda Chemical Reagent Factory, Tianjin, China, was recrystallized from water before use. Sodium montmorillonite (MMT-Na) was prepared by hydro-separating¹⁵ and milled through a 200-mesh screen before use. All the other reagents were analytical reagent grade or chemically pure and used directly without further purification.

Preparation of MMT/P(AA-co-AMPS) Superabsorbent Composite. MMT/P(AA-co-AMPS) was prepared according to the following procedures: 7.2 g of AA was dissolved in 20 mL distilled water and neutralized to a certain degree with sodium hydroxide solution whose concentration was 6.25 mol/L. Then a certain amount of AMPS was added to the neutralized AA solution and stirred for 10 min. The mixture was poured into a four-necked flask equipped with a stirrer, a condenser, a thermometer, and a nitrogen line. After that, MMT-Na powder was dispersed in the above mentioned AA-AMPS mixed solution and stirred vigorously for 30 min before the addition of MBA solution (0.01 g/mL, 0.45 mL) under nitrogen atmosphere. After stirring at 40 °C for 20 min on a water bath, the mixture was slowly heated to 75 °C and then 0.58 mL of APS solution (0.1 g/mL) was added in. The reaction mixture was stirred at 75 °C for 3 h. The resulting rubbery gel was removed from the reaction vessel, cut up into small pieces and dried at 60 °C until constant weight.

Characterization. IR spectra of the superabsorbent composite were recorded on a Nicolet-380 Fourier Transform Infrared Spectrometer in a range of 4000-400 cm⁻¹ using KBr pellets. The morphology analysis of the composite was carried out on the KYKY-2800B SEM instrument (China) using an acceleration voltage of 20 kV after coating the sample with gold film. XRD patterns were obtained from D/Max 2500PC X-ray diffractometer (Japan), and the tests were carried out using Cu K α radiation ($\lambda = 0.154$ nm), scanning from 0° to 50° at 10°/min under a voltage of 40 kV and a current of 30 mA. Thermal stability studies were performed on TGA/SDTA-851° thermogravimetric analyzer (Mettler-Toledo Company, Switzerland), at a heating rate of 10 °C/min using dry nitrogen purge.

Measurement of Absorbency. 0.5 g of dried powder composite was dispersed in 500 mL distilled water or 100 mL 0.9% NaCl solution at ambient temperature. After reaching the swelling equilibrium, the swollen composite was filtered by a 100-mesh nylon sieve. Absorbency of the composite was calculated according to Eq. (1):

$$Q = \frac{m_2 - m_1}{m_1} \quad (1)$$

Where m_1 and m_2 were the weights of the dried composite and swollen composite, respectively. Q was calculated as grams of liquid per gram of composite.

Adsorption Studies. A certain amount of MMT/P(AA-co-AMPS) superabsorbent composite was weighed in parallel and added to three kinds of solutions containing Ni²⁺, Cu²⁺ and Pb²⁺ with different initial concentrations, respectively.

After quiescence for 24 h at room temperature, the swollen composites were filtered and the solutions were obtained to determine the concentrations of metal ions after adsorption. Concentrations of metal ions were determined on a TAS-986 atomic absorption spectrometer (AAS, Beijing Purkinje General Instrument Co., Ltd., China), which was equipped with a flame atomizer and an air compressor, in a wavelength ranged from 190-900 nm. The adsorption capacity of heavy metal ions on the superabsorbent composite was calculated according to Eq. (2):

$$q = \frac{(C_0 - C_{eq})V}{m} \quad (2)$$

Where q was the amount of metal ions adsorbed onto unit amount of the composite (mg/g); C_0 and C_{eq} were the concentrations of metal ions in the initial solution and in the aqueous phase after adsorption, respectively (mg/mL); V was the volume of the aqueous phase (mL), and m was the weight of the superabsorbent composite charged (g).

Desorption Studies. The heavy metal ions adsorbed on the superabsorbent composite were desorbed by stirring the swollen composite in 100 mL of HNO₃ aqueous solution (0.1 mol/L) for 24 h at room temperature. After filtration, the concentration of the metal ions in the aqueous phase was determined by AAS. Desorption ratio was calculated from the amount of metal ions initially loaded on the composite and the final metal ion concentrations in the desorption medium, according to Eq. (3):

$$\text{Desorption ratio (\%)} = \frac{\text{Amount heavy metal ions desorbed into the elution medium}}{\text{Amount heavy metal ions absorbed on to the superabsorbent}} \times 100 \quad (3)$$

Results and Discussion

IR Spectra. The IR spectra of MMT, P(AA-co-AMPS) copolymer and MMT/P(AA-co-AMPS) superabsorbent composite, containing 15 wt % of MMT.

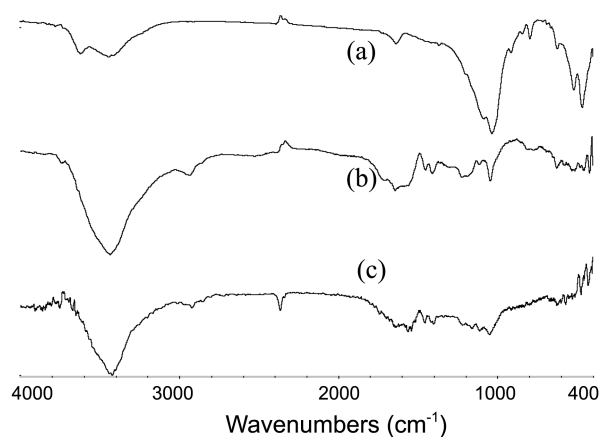


Figure 1. IR spectra of (a) MMT, (b) P(AA-co-AMPS) copolymer and (c) MMT/P(AA-co-AMPS) superabsorbent composite, containing 15 wt % of MMT.

posite (15 wt % MMT) were shown in Figure 1.

It could be seen that MMT exhibited two broad absorption bands at 3624 cm^{-1} and 3446 cm^{-1} , attributed to the stretching vibration of H-OH bond in silanol and water molecules adsorbed on the surface of MMT.¹⁶ The band at 1036 cm^{-1} represented the stretching vibrations of Si-O bond. The sharp band at 795 cm^{-1} with inflexion at 779 cm^{-1} indicated the presence of quartz in the sample. In the case of P(AA-co-AMPS) copolymer, the band at 1644 cm^{-1} was corresponded to the stretching vibration of C=O double bond, and that at 1453 cm^{-1} was the vibration of C-N. The band at 1115 cm^{-1} and 1047 cm^{-1} were ascribed to the asymmetric and symmetric vibration of S=O, respectively, which were the characteristic absorption of AMPS. The band at 1223 cm^{-1} was the absorption of C-O, and that at 2939 cm^{-1} was ascribed to the $-\text{CH}_2-$ group on the polymeric chain. However, the characteristic peaks of C=C disappeared, which confirmed the formation of P(AA-co-AMPS) copolymer. As for MMT/P(AA-co-AMPS), the band at 2936 cm^{-1} was attributed to $-\text{CH}_2-$, produced by polymerization of AA and AMPS. The band at 1655 cm^{-1} and 1400 cm^{-1} were ascribed to the asymmetric and symmetric vibration of RCOO^- in AA, 1568 cm^{-1} was the vibration of N-H in AMPS, 687 cm^{-1} and 631 cm^{-1} were the bending vibrations of Si-O and Al-O-Si in MMT, respectively.

Morphology. The SEM images of P(AA-co-AMPS) co-

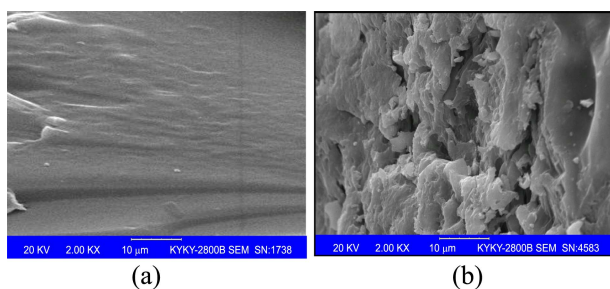


Figure 2. Scanning electron micrographs of (a) P(AA-co-AMPS) copolymer and (b) MMT/P(AA-co-AMPS) superabsorbent composite, containing 15 wt % of MMT.

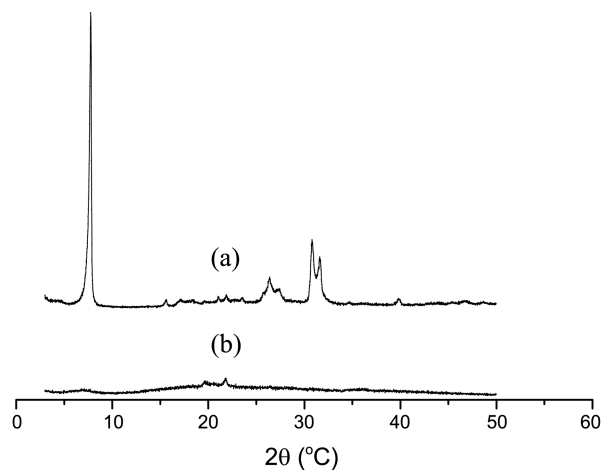


Figure 3. XRD patterns of (A) MMT and (B) MMT/P(AA-co-AMPS) superabsorbent composite, containing 15 wt % of MMT.

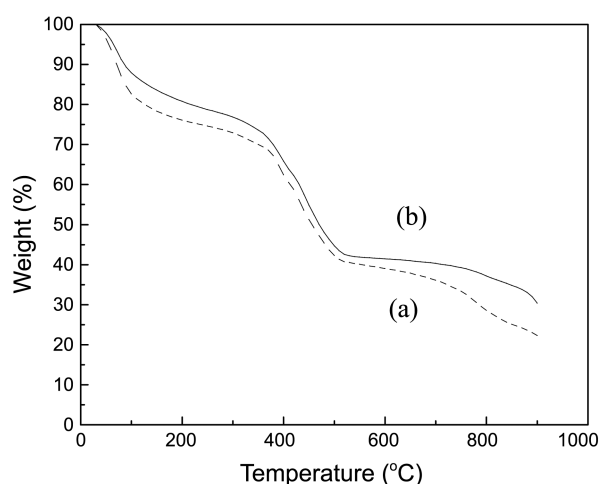


Figure 4. TGA curves of (a) P(AA-co-AMPS) copolymer and (b) MMT/P(AA-co-AMPS) superabsorbent composite, containing 15 wt % of MMT.

polymer and MMT/P(AA-co-AMPS) superabsorbent composite were shown in Figure 2. It could be seen that the surface of P(AA-co-AMPS) was tight and smooth, while that of MMT/P(AA-co-AMPS) was porous and coarse, which was beneficial for the permeation of solute molecules and the adsorption of metal ions into the polymeric network.¹⁷

XRD Analysis. The XRD patterns of MMT and MMT/P(AA-co-AMPS) superabsorbent composite were presented in Figure 3.

It was obvious that MMT showed a strong peak at $2\theta = 7.78^\circ$ which was corresponded to an interlayer spacing of 1.135 nm, calculated according to the formula $2d\sin\theta = n\lambda$.¹⁸ However, in the case of MMT/P(AA-co-AMPS) the peak disappeared, indicating that MMT sheets were exfoliated completely and dispersed evenly in the polymeric network.¹⁹

TGA Curves. TGA curves of P(AA-co-AMPS) copolymer and MMT/P(AA-co-AMPS) superabsorbent composite were presented in Figure 4.

Both of the samples showed two degradation stages. The

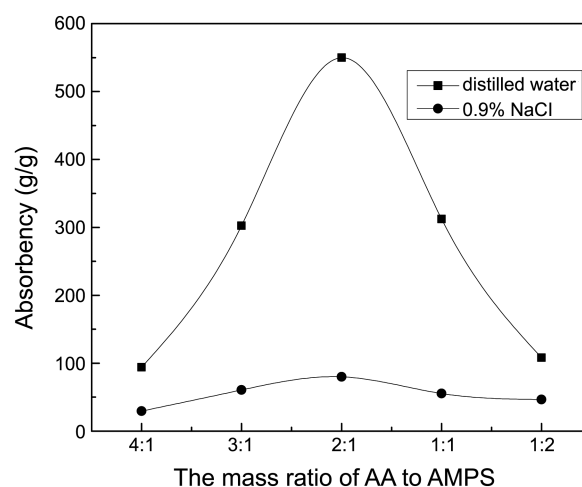


Figure 5. Effect of mass ratio of AA to AMPS on absorbency. Conditions: APS 0.8%, MBA 0.05%, MMT 10%, neutralization degree of AA 70%.

first stages of the two samples were in the range of 30-100 °C, ascribed to the loss of water. The second degradation stages ranged from 350-520 °C, ascribed to the decomposition of the polymer chains. The decomposition temperatures of P(AA-co-AMPS) and MMT/P(AA-co-AMPS) were 357 °C (weight loss 30.5%) and 354 °C (weight loss 26.8%), respectively. At 520 °C, weight loss of P(AA-co-AMPS) was 59.4% whereas that of MMT/P(AA-co-AMPS) was 57.6%. Meanwhile, at 900 °C, the residue of P(AA-co-AMPS) and MMT/P(AA-co-AMPS) were 21.8% and 28.5%, respectively. It indicated that MMT particles could act as physical barrier which obliged the gas molecules to bypass the MMT particles before passing through the polymer matrix.²⁰ As a result, thermal stability of the composite was improved.

Effect of Reaction Conditions on Absorbency.

Mass Ratio of AA to AMPS: The effect of mass ratio of AA to AMPS on absorbency was demonstrated in Figure 5. With the increase of AMPS content in the two monomers absorbency of both water and saline increased and reached maximum as the mass ratio of AA to AMPS was 2:1. Further increase of AMPS content led to a decrease of absorbency. Since with the increase of AMPS content the number of hydrophilic groups such as -CONH and -SO₃H increased accordingly. As a result, the synergistic effect produced by -CONH and -SO₃H on AMPS, together with that of -COONa and -COOH on AA increased,²¹ which brought about great enhancement of absorbency. However, when the mass ratio of AA to AMPS was below 2:1, which meant that AMPS content was over one-third of total monomers, absorbency decreased in respect that the electrostatic repulsion between ions weakened and the three-dimensional network compacted. In addition, as AMPS contained quaternary carbon atoms and -SO₃H groups which were enormous in size, stretching of the polymer chains would be obstructed and absorbency would decrease accordingly.

MMT Content: The effect of MMT content on absor-

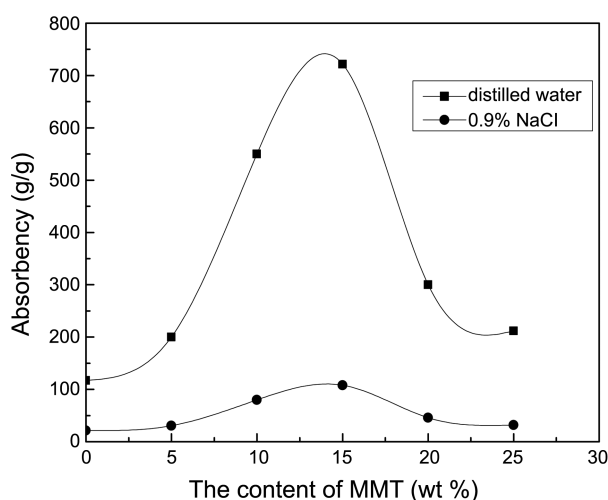


Figure 6. Effect of MMT content on absorbency. Conditions: APS 0.8%, MBA 0.05%, mass ratio of AA to AMPS 2:1, neutralization degree of AA 70%.

bency was shown in Figure 6. It indicated that when the content of MMT increased from 0 to 15%, absorbency of water and saline increased from 117 and 26 g/g to 722 and 108 g/g, respectively. This might be attributed to the graft copolymerization between monomers and -OH groups on the surface of MMT, which brought about copolymers with MMT as crosslinking points and thereby expanded the polymeric network.²² However, when the content of MMT was over 15%, the excessive crosslinking points would lead to exorbitant crosslinking density and a relatively smaller volume of the network. Consequently, absorbency decreased. In addition, excessive MMT particles might physically filled in the polymeric network, causing separation of MMT from P(AA-co-AMPS) copolymer and shrinkage of the composite,²³ thus, the absorbency decreased accordingly.

Neutralization Degree of AA: AA was always partially neutralized with alkalis like NaOH before polymerization due to its high reaction activity. The neutralization degree of AA played an important role in water and saline absorbency,

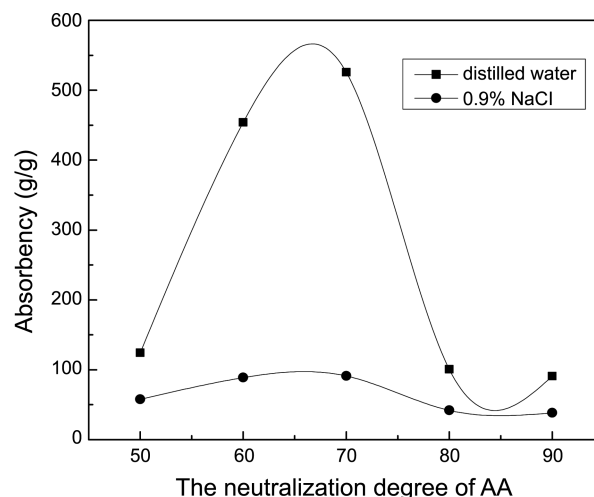


Figure 7. Effect of the neutralization degree of AA on absorbency. Conditions: APS 0.8%, MBA 0.05%, mass ratio of AA to AMPS 2:1, MMT 10%.

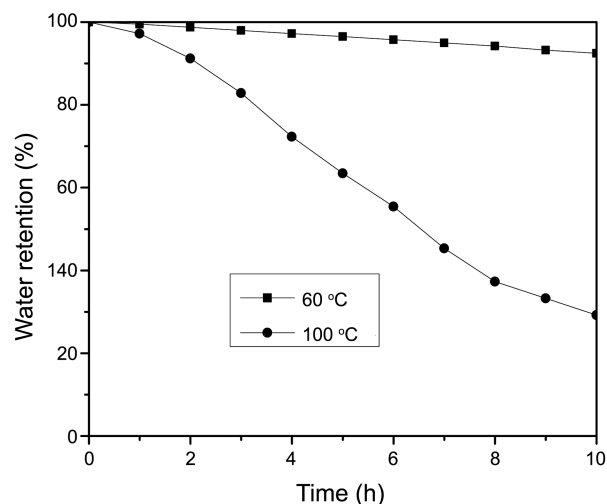


Figure 8. Water retention of MMT/P(AA-co-AMPS) superabsorbent composite.

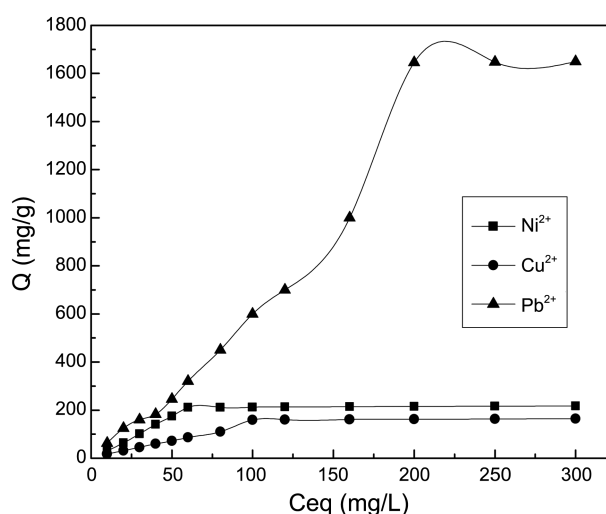


Figure 9. Adsorption of Ni^{2+} , Cu^{2+} and Pb^{2+} on MMT/P(AA-co-AMPS).

as shown in Figure 7. It was clear that the absorbency increased as the neutralization degree rose from 50% to 70% and decreased with further increase of neutralization degree. When the neutralization degree of AA was below 70%, the rate of polymerization could hardly be controlled for the high reactivity of AA. As a result, products with low molecular weight and low gel strength increased. In addition, with low neutralization degree, content of $-\text{COO}^-$ groups was low accordingly, the repulsive forces between anions in the polymer chains weakened due to the poorer polarity of $-\text{COO}^-$ in contrast with $-\text{COOH}$. Consequently, stretching of the polymer chains was confined and the pore space in the polymeric network narrowed. However, when the neutralization degree of AA was over 70%, polymerization could hardly take place for the low reactivity of the raw materials. Therefore, proper neutralization degree of AA was 70%.

Water Retention. Water retention of MMT/P(AA-co-AMPS) composite was determined by heating the swollen samples in an oven at different temperatures. As shown in Figure 8, the composite could keep 91.3% and 29.7% of distilled water after drying for 10 h at 60 °C and 100 °C, respectively. Since hydrogel was formed after absorbency, the movement of water molecules was restricted. Moreover, as MMT in the composite was monolayered and nano-scaled,²⁴ water molecules would have to bypass the silicate layer when passing through the composite. All of which contributed to the good water retention property of MMT/P(AA-co-AMPS).

Adsorption Capacity. Effect of initial concentration of heavy metal ions on the adsorption capacities of Ni^{2+} , Cu^{2+} and Pb^{2+} on MMT/P(AA-co-AMPS) was shown in Figure 9. It could be seen that the adsorption capacities were enhanced with the increase of initial concentration of heavy metal ions, especially for Pb^{2+} . Maximum amount of adsorption for Ni^{2+} , Cu^{2+} and Pb^{2+} was 211.0, 159.6 and 1646.0 mg/g, respectively. While under the same conditions, the adsorption capacity was found to decrease in the following order: $\text{Pb}^{2+} \gg \text{Ni}^{2+} > \text{Cu}^{2+}$.

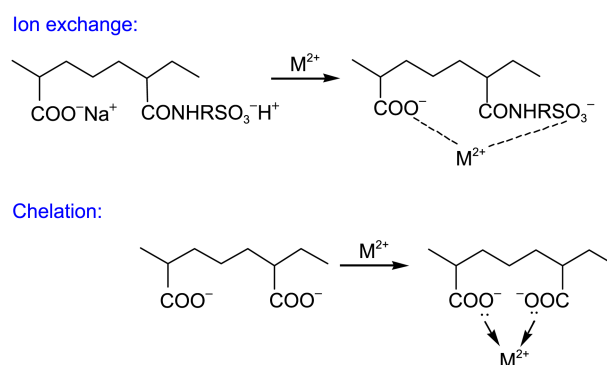


Figure 10. Possible mechanisms for the adsorption of heavy metal ions onto MMT/P(AA-co-AMPS) superabsorbent composite.

It was known that adsorption capacity was closely related to the ionic charges, hydrated ionic radius and the outermost electron configurations of the metal ions.²⁵ The ionic charges of the three ions were identical, however, the hydrated ionic radius and the outermost electron configurations of Pb^{2+} were much different from those of Ni^{2+} and Cu^{2+} . Pb was a main group element in the periodic table while Cu and Ni were in the transitional zone. The valence electron configuration of Pb^{2+} was $6s^2$, whereas that of Ni^{2+} and Cu^{2+} was $3d^8$ and $3d^9$, respectively. In addition, the hydrated ionic radius of Pb^{2+} was larger than that of Cu^{2+} and Ni^{2+} , the hydration energy of Pb^{2+} was just the other way round. Therefore, it was easier for hydrated Pb^{2+} to lose the coordinated water and form a stable valence electron configuration of $6s^2$ when combining with the adsorption sites of MMT/P(AA-co-AM) superabsorbent composite. Thus, the adsorption capacity of Pb^{2+} was much larger than that of Ni^{2+} and Cu^{2+} . The possible mechanisms for the adsorption of heavy metal ions onto the composite were schematically presented in Figure 10.

Adsorption Isotherms. The equilibrium adsorption isotherms were one of the most important data to investigate the adsorption mechanism. The most widely used isotherms were the Langmuir and Freundlich models, as shown in Eqs. (4) and (5), respectively.

$$\frac{C_{eq}}{q} = \frac{1}{bq_{max}} + \frac{C_{eq}}{q_{max}} \quad (4)$$

$$\lg q = 1/n \lg C_{eq} + \lg K_F \quad (5)$$

Where b was the Langmuir constant (L/mg), q_{max} was the maximum adsorption capacity (mg/g). K_F was the Freundlich constant, suggesting the bonding degree between the adsorbate and adsorbent. The larger the value of K_F , the larger the adsorption capacity of adsorbents. $1/n$ was an indicator of adsorption intensity which reflected the non-linear degree of adsorption.

The data of Figure 9 were fitted according to Eqs. (4) and (5) using the least square method, respectively, and the corresponding parameters and related correlation coefficients (R^2 values) were shown in Table 1. It was obvious that the adsorption of Ni^{2+} , Cu^{2+} and Pb^{2+} on MMT/P(AA-co-AMPS) superabsorbent composite satisfied both Langmuir and

Table 1. Parameters of Langmuir and Freundlich isotherms for adsorption of Ni²⁺, Cu²⁺ and Pb²⁺ on MMT/P(AA-co-AMPS)

Metal ions	Langmuir constants			Freundlich constants		
	Q_{max} (mg/g)	b (L/mg)	R^2	K_F	n	R^2
Ni ²⁺	211	0.0140	0.9996	2.4826	0.9190	0.9996
Cu ²⁺	159.6	0.0094	0.9991	1.4478	0.9910	0.9956
Pb ²⁺	1646	0.0021	0.9968	0.7626	0.6980	0.9958

Freundlich models quite well.

Desorption. MMT/P(AA-co-AMPS) superabsorbent composites which had adsorbed the Ni²⁺, Cu²⁺ and Pb²⁺ with the maximum amount were desorbed in the solution of 0.1 M HNO₃. Determined by AAS, percent desorption of Ni²⁺, Cu²⁺ and Pb²⁺ was 90.3%, 95.6% and 84.5%, respectively. After desorption, the corresponding dry composites could still adsorb metal ions. The maximum of adsorption for Ni²⁺, Cu²⁺ and Pb²⁺ was 201.7, 148.6 and 1440.3 mg/g, respectively, after desorption once. These results indicated that MMT/P(AA-co-AMPS) superabsorbent composite could be regenerated and reused in wastewater treatment.

Conclusions

(1) MMT/P(AA-co-AMPS) superabsorbent composite was prepared by intercalation polymerization of AA and AMPS in the presence of MMT. Under the condition that the content MMT was 15%, mass ratio of AA to AMPS was 2:1 and the neutralization degree of AA was 70%, water and saline (0.9% NaCl) absorption reached maximum values of 722 and 108 g/g, respectively.

(2) The superabsorbent composite was used for the removal of heavy metal ions from aqueous solutions. Maximum adsorption amount for Ni²⁺, Cu²⁺ and Pb²⁺ was 211.0, 159.6 and 1646.0 mg/g, respectively, and the adsorption was consistent with both Langmuir and Freundlich model. In addition, the superabsorbent composite could be regenerated and had great prospect in wastewater treatment.

Acknowledgments. The authors are grateful to the Central and Local Characteristic Laboratory of Applied Chemistry, Department of Applied Chemistry, Shandong University of Science and Technology, for providing laboratory facilities

for this work.

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