

Study on Superabsorbent Composite. XII. Effect of Ion-Exchanged Attapulgite on Water Absorbency of Poly(acrylic acid)/Attapulgite Superabsorbent Composites

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ABSTRACT: A series of poly(acrylic acid)/attapulgite superabsorbent composites were prepared by aqueous polymerization, using *N,N'*-methylenebisacrylamide as a crosslinker and ammonium persulfate as an initiator. The effects of anion- and cation-exchanged attapulgite on water absorbency of superabsorbent composites were studied. The results showed that the anions and cations exchanged attapulgite can affect the physicochemical properties of attapulgite such as cation-exchange capacity and specific surface area, which in turn have influence on water absorbency of composites. Compared with that of monovalent cation-exchanged attapulgite,

the water absorbencies of superabsorbent composites prepared with Ca^{2+} , Al^{3+} , and Fe^{3+} -exchanged attapulgite are relative low. However, multivalent cations exchanged attapulgite would improve the reswelling capacities of the superabsorbent composites, which suggested that multivalent cations exchanged attapulgite could serve as an additional inorganic crosslinker in the polymeric network. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 3476–3482, 2007

Key words: superabsorbent composites; attapulgite; swelling

INTRODUCTION

Superabsorbents can absorb a large amount of water during a short period of time and the absorbed water can hardly be removed even under some pressure. Therefore, superabsorbents have great advantages over traditional water-absorbing materials such as cotton, pulp, and sponge, and have found a variety of valuable applications.^{1–3} Because of their excellent characteristics, these superabsorbents are widely used in many fields such as agriculture and horticulture,^{4,5} sanitary goods,⁶ sealing composites,⁷ medicine for drug delivery system,⁸ and so on.

Recently, the preparation of polymer/clay superabsorbent composites has received great attention because of their relative low production cost and high water absorbency.^{9,10} The preparation and the swelling behaviors of poly(acrylic acid)(PAA)/attapulgite superabsorbent composite have been reported in our previous study.^{11,12} In which, we know that the

water absorbency of the PAA/attapulgite superabsorbent composite in distilled water was greatly improved as compared with crosslinked PAA superabsorbent polymer. To further improve the synthetic performance of superabsorbent composite, we have also prepared superabsorbent composite based on organic attapulgite¹³ and acid- and heat-activated attapulgite.¹⁴ Results show that organic modification and activated of attapulgite also lead a change in physicochemical properties of attapulgite and in turn affect the performance of superabsorbent composite compared to that of untreated attapulgite.

Attapulgite is a kind of crystalloid hydrous magnesium–aluminum silicate mineral, having a special laminated chain structure in which there is a crystalline lattice displacement existed. Thus it makes the crystals contain uncertain quantities of Na^+ , Ca^{2+} , Fe^{3+} , and Al^{3+} , and present in the shape of needles, fibers or fibrous clusters. Similar to other layered silicates such as montmorillonite, kaolin, and mica, the cations on the surface and channel of attapulgite can be exchanged with external cations when attapulgite was treated with various salts solution, which may change the physicochemical properties of attapulgite. From this point of view, a series of ion-exchanged attapulgite with different kinds of salts solution was prepared in this study, and the effect of treated attapulgite on the water absorbencies of PAA/attapulgite superabsorbent composites was investigated.

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It would develop a new approach for improvement of the performance of superabsorbent composite.

EXPERIMENTAL

Materials

Acrylic acid (AA, chemically pure, Shanghai Wulian Chemical Factory, Shanghai, China) was distilled under reduced pressure before use. Ammonium persulfate (APS, analytical grade, Xi'an Chemical Reagent Factory, Xi'an, China) was recrystallized from water. *N, N'*-methylenebisacrylamide (MBA, chemically pure, Shanghai Chemical Reagent Factory, Shanghai, China) was used as purchased. Attapulgit powder (supplied by Linze Colloidal, Gansu, China) was milled through a 320-mesh screen. Other agents used were all analytical grade and all solutions were prepared with distilled water.

Ion-exchange of attapulgit

Ion-exchanged attapulgit samples were obtained according to the following procedure: (1) Ion kind series: 10.0 g natural attapulgit powder was immersed in 100 mL 0.1M salt solution at 20°C for 6 h. The salts used have the same cation (Na⁺) or anion (Cl⁻) including NaCl, NaNO₃, NaAc, NaHCO₃, NaH₂PO₄, Na₂CO₃, Na₂SO₄, Na₂HPO₄, Na₃PO₄, CaCl₂, FeCl₃, and AlCl₃. (2) AlCl₃ concentration series: 10.0 g natural attapulgit powder was immersed in 100 mL AlCl₃ solution of various concentration (0.01, 0.05, 0.1, 0.5, and 1.0M) at 20°C for 6 h. All the above ion-exchanged attapulgit samples were washed with distilled water until pH = 6, and then dried at 105°C for 8 h before use.

Preparation of poly(acrylic acid)/attapulgit superabsorbent composite

The PAA/attapulgit superabsorbent composite was synthesized by graft copolymerization reaction of AA on attapulgit micropowder using MBA as a crosslinker and APS as an initiator in aqueous solution. A series of the samples were prepared by the following procedure: Typically, acrylic acid (7.2 g) was dissolved in 39 mL of distilled water and then neutralized at 5°C with 12 mL of sodium hydroxide solution (5M) in a four-neck flask equipped with a stirrer, a condenser, a thermometer, and a nitrogen line. Attapulgit powder (3.14 g) was added to the above partially neutralized monomer solution. Under nitrogen atmosphere, the crosslinker MBA (20.9 mg) was added to the AA-clay mixture solution and the mixed solution was stirred on a water bath at room temperature for 30 min. The water bath was then heated slowly to 70°C with vigorous stirring after

the radical initiator APS (104.7 mg) was introduced to the mixed solution. After 3 h of the reaction, the resulting product was washed several times with distilled water and then dried in a vacuum oven at 70°C to a constant weight. Thus the superabsorbent composite was prepared after the dried product was milled and screened. All samples used had a particle size in the range of 40–80 mesh.

Water absorbency measurement

A weighted quantity of the superabsorbent composite was immersed in distilled water or 0.9 (w/w)% NaCl solution at ambient temperature to reach the swelling equilibrium. Swollen samples were then separated from unabsorbed water by screening, and the swollen sample was allowed to drain on the sieve for 10 min. The sieve was then weighed to determine the weight of the swollen sample. The Q_{H_2O} of the samples was calculated using the following equation:

$$Q_{H_2O} = (m_2 - m_1) / m_1 \quad (1)$$

where m_1 and m_2 are the weights of the dry sample and the water-swollen sample, respectively. The water absorbency (Q_{H_2O}) or ($Q_{0.9(w/w)\%NaCl}$) was calculated as grams of water per gram of sample. All the tests were carried out thrice carefully under the same conditions and the average values were reported. The standard deviation for reported data is smaller than 2%.

Measurement of swelling rate

Fifty milligram of the sample was immersed in excess amount of distilled water at room temperature and kept for different time durations until equilibrium was reached. Then the swollen sample was allowed to drain on a sieve for 10 min. The water absorbency was obtained by weighing the swollen samples at various time intervals. The water absorbency was calculated according to eq. (1).

Reswelling ability

The specimen (50 mg) was immersed in certain milliliter of water to ensure the swelling equilibrium was achieved. The swollen gel was placed in an oven at 100°C until the gel was dried thoroughly. Equal milliliter of water was added to the dried gel and placed in the oven again. Similar procedure was repeated and then saturated absorbency of the sample after several times of reswelling were obtained.

TABLE I
Effect of Anions on Water Absorbencies of the Superabsorbent Composites in Distilled Water and in 0.9 (w/w)% NaCl Solution

Valence of anions	Anions	Q_{eq} (g g ⁻¹)	$Q_{0.9(w/w)\% NaCl}$ (g g ⁻¹)	CEC	SSA
Monovalent	NO ₃ ⁻	661	61	23.4	50.1
	Ac ⁻	633	63	23.5	56.9
	HCO ₃ ⁻	664	63	23.3	63.6
	Cl ⁻	675	70	23.0	70.0
	H ₂ PO ₄ ⁻	614	67	11.7	86.1
Divalent	CO ₃ ²⁻	633	61	20.9	76.2
	SO ₄ ²⁻	647	65	20.7	69.7
	HPO ₄ ²⁻	649	66	24.1	54.8
Trivalent	PO ₄ ³⁻	585	60	21.9	57.8

Characterization

IR spectra of samples were taken as KBr pellets using a Thermo Nicolet NEXUS TM spectrophotometer.

RESULTS AND DISCUSSION

Effect of anions on water absorbencies of superabsorbent composites

The effect of attapulgite treated with salt solutions that contain different valence of anions and a common cation (Na⁺) on water absorbency of superabsorbent composites in distilled water and in 0.9 (w/w)% NaCl solution is shown in Table I. Cation-exchange capacity (CEC) and specific surface area (SSA) of attapulgite samples were determined by the ammonium acetate method¹⁵ and the glycol aether (C₄H₁₀O₂) method,¹⁶ respectively. As can be seen, when attapulgite treated with monovalent anionic solutions such as NO₃⁻, Ac⁻, CO₃²⁻, Cl⁻, and H₂PO₄⁻, the superabsorbent composite incorporated with attapulgite treated with NaCl solutions possesses the highest water absorbency. Compared to that of nature attapulgite, the treated attapulgite have lower CEC and higher SSA. The superabsorbent composite based on H₂PO₄⁻ exchanged attapulgite, which have relatively lower CEC and higher SSA, exhibits the lower water absorbency. In general, a relatively higher CEC and SSA are of benefit for improving water absorbency in distilled water.¹⁴ In this case, however, this opposite observation may be attributed to the fact that NaH₂PO₄ solution is an acidic solution and could acid-activate attapulgite to produce more reactive —OH on its surface. It has been reported that —OH on the surface of attapulgite could react with acrylic acid and act as crosslinker in the polymeric network,¹¹ and then decrease water absorbency in distilled water according to Flory's network theory.¹⁷ When attapulgite treated with divalent anionic solutions such as CO₃²⁻, SO₄²⁻, and HPO₄²⁻, the water absorbencies of superabsorbent

composites increase with increase of CEC of attapulgite and decrease of SSA of attapulgite. In the case of PO₄³⁻, the water absorbency is relatively lower, which may be due to the fact that PO₄³⁻ exchanged attapulgite has the relative lower SSA. The results obtained from Table I show that the treated attapulgite with different valence of anion and a common cation may not the greatly affect on water absorbency of superabsorbent composites because of the fact that attapulgite can be exchanged with external cations on the surface and channel of attapulgite.¹⁸

Effect of cations on water absorbencies of the superabsorbent composites

There are cations on the surface and channel of attapulgite, thus, cations in solution could exchange with them through a cation-exchange process, and then alter the composition of attapulgite.^{14,18} Figure 1 presents the effect of attapulgite treated with various cationic solutions with common anion (Cl⁻) on

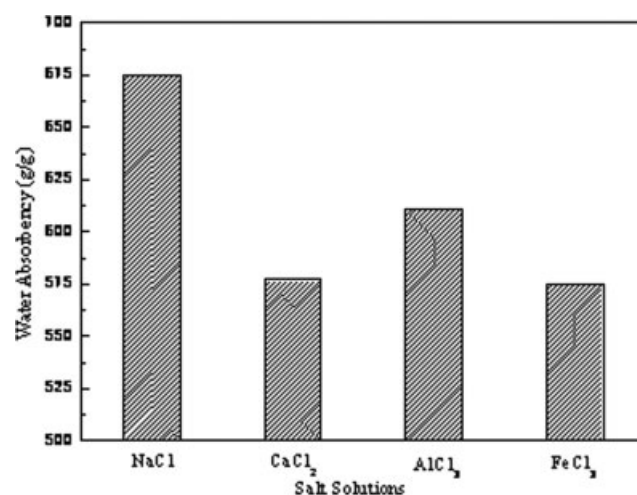


Figure 1 The effect of attapulgite treated with various cationic solutions with common anion (Cl⁻) on water absorbency of superabsorbent composite in distilled water.

TABLE II
CEC and Specific Surface Area of Attapulgite Treated with Various Cationic Solutions

Cations	CEC (mmol 100 g ⁻¹)	SSA (m ² g ⁻¹)
Nature	30.0	49.0
NaCl	23.0	70.0
CaCl ₂	18.1	78.4
AlCl ₃	14.7	100.1
FeCl ₃	18.5	177.3

water absorbency of superabsorbent composite in distilled water. It can be seen from Figure 1 that the water absorbency decrease in the order $\text{Na}^+ > \text{Al}^{3+} > \text{Ca}^{2+} \approx \text{Fe}^{3+}$ -treated attapulgite. This observation may be due to the fact that divalent or trivalent cations take part in the crosslinking of superabsorbent composite polymeric network and then in turn increase the crosslinking density. For example, when attapulgite treated with CaCl_2 solution, more Ca^{2+} could exchange with other cations (such as Na^+ and Mg^{2+}) on the surface and in the channels of attapulgite. As reported in a previous literature,¹⁹ Ca^{2+} may react with COO^- groups bonded in PAA polymeric chains. This could form more intramolecular and intermolecular complex and then increase the effective crosslinking density of corresponding superabsorbent composites, which is responsible for the decrease of water absorbency. This result also suggested that Ca^{2+} , Al^{3+} , and Fe^{3+} -exchanged attapulgite could serve as an inorganic crosslinker in the polymeric network.

Compared with that of nature attapulgite from Table II, Na^+ , Ca^{2+} , Al^{3+} , and Fe^{3+} -treated attapulgite have a relatively lower CEC and higher SSA. The water absorbency of superabsorbent composite with Fe^{3+} -treated attapulgite is equal to Ca^{2+} -treated attapulgite. SSA of Fe^{3+} -treated attapulgite is higher than that of Ca^{2+} -treated attapulgite, but CEC are almost equality. So the CEC may be main factor of divalent or trivalent cations exchanged attapulgite on water absorbency of superabsorbent composite. However, the water absorbency of superabsorbent composite with Al^{3+} -treated attapulgite obtains the deregulation result. On the one hand, Al^{3+} -treated attapulgite have a relatively lower CEC. On the other hand, AlCl_3 solution is a Lewis acid and could provide a relative acidic environment in the polymerization process and then increases water absorbency compared to that of Fe^{3+} and Ca^{2+} -treated attapulgite.

To investigated the inorganic crosslinking function in the polymeric network of divalent or trivalent cations exchanged attapulgite on water absorbency of superabsorbent composite, superabsorbent composites prepared with different salt-exchanged attapulgite such as NaCl, CaCl_2 , AlCl_3 , and FeCl_3 are

characterized by the infrared spectra in Figure 2. It can be seen that the absorption peaks at 1573–1579 cm^{-1} , which is corresponding to $-\text{COO}^-$ of acrylate unit, is moved to high frequency from monovalent cation (Na^+) to divalent cation (Ca^{2+}) to trivalent cations (Fe^{3+} and Al^{3+}). It is indicated that $-\text{COO}^-$ may react with multivalent cations and then make a change in the infrared spectrum of carboxylate groups. Besides, The absorption peaks at 1029–1037 cm^{-1} , which is corresponding to the Si–O stretching of attapulgite, is moved to low frequency from Na^+ to Al^{3+} , it is also indicated that the exchange reaction between cations on the surface and channel of attapulgite with cations in external solutions has been carried out, which in turn affect the stretching of Si–O.

Effect of Al^{3+} -exchanged attapulgite solution concentration on water absorbency of the superabsorbent composite

As aforementioned, the cations bonded on attapulgite may act as an additional crosslinker in polymer network. To further study the effect of treatment of attapulgite with different cationic solution concentration on water absorbency of superabsorbent composite, Al^{3+} was selected as a model and attapulgite treated with AlCl_3 solution with different concentrations. As shown in Figure 3, the water absorbency of superabsorbent composite decreases with increase of concentration of AlCl_3 solution. According to Flory's network theory,¹⁷ the swelling ratio of the hydrogel has a relation to the ionic osmotic pressure, crosslinked density, and affinity of the hydrogel with water. When the crosslinker content increased, the crosslinking density of the superabsorbent composite also increased. This would result in a decrease in the space between the polymer chains and lead a

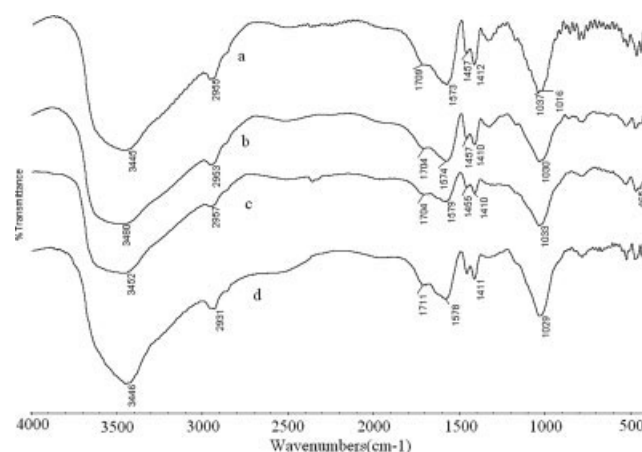


Figure 2 The infrared spectra of superabsorbent composites prepared with different salt-exchanged attapulgite such as (a) NaCl, (b) CaCl_2 , (c) AlCl_3 and (d) FeCl_3 .

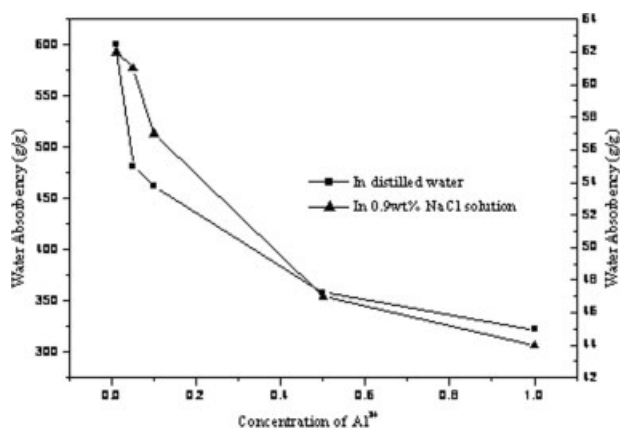


Figure 3 The effect of Al³⁺-exchanged attapulgite solution concentration on water absorbencies of the superabsorbent composites.

decrease in water absorbency. In this case, the Al³⁺-exhibited the same action as a crosslinker and the results were in good accordance with Flory's network theory.

Swelling rate

The swelling rate of superabsorbent composites prepared with different kinds of salt solutions treated attapulgite was determined and are shown in Figure 4. It is indicated that the swelling rate of all superabsorbent composites samples are high in 0–10 min. In 10–30 min, the swelling rate of superabsorbent composite prepared with NaCl-exchanged attapulgite is higher than that of superabsorbent composite prepared with multivalent salt solutions treated attapulgite. It was reported by Lee and Yeh²⁰ that the initial

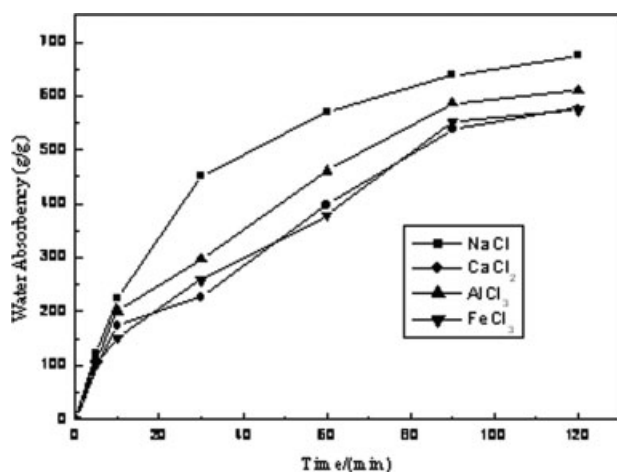


Figure 4 The swelling rate of superabsorbent composites prepared with different kinds of salt solutions treated attapulgite.

swelling rate is controlled by the diffusion process of water penetrated into the inside of gels. As aforementioned, attapulgite treated with divalent or trivalent cations solutions, for example Ca²⁺-exchanged attapulgite, could serve as an inorganic crosslinker in the polymeric network which in turn increase the crosslinking density of superabsorbent composite network. The more crosslinking density, the low diffusion rate of water penetrated into the inside of gels. So, the initial swelling rate of superabsorbent composite prepared with multivalent salt solutions treated attapulgite is lower than that of superabsorbent composite prepared with NaCl-exchanged attapulgite. After 30 min, the swelling rate of all samples become low and the maximum swelling capacity is obtained within about 120 min.

Reswelling test

As a kind of water absorbing material, the swelling–deswelling–reswelling property (gel strength) of superabsorbent composite is very important for its applications in many fields especially for agricultural and horticultural ones.²¹ The effect of treatment of attapulgite with different kinds of cationic solutions (NaCl, CaCl₂, AlCl₃, and FeCl₃) on swelling–deswelling–reswelling properties of superabsorbent composites is shown in Figure 5. Under the same preparation conditions, the superabsorbent composite prepared with CaCl₂, AlCl₃, and FeCl₃ aqueous solutions treated attapulgite can respectively, keep 81, 82, and 79% of their initial water absorbency after five times of swelling–deswelling–reswelling test, which is slight higher than that of superabsorbent composite prepared with NaCl-exchanged attapulgite, whereas only ~76% initial water absorbency

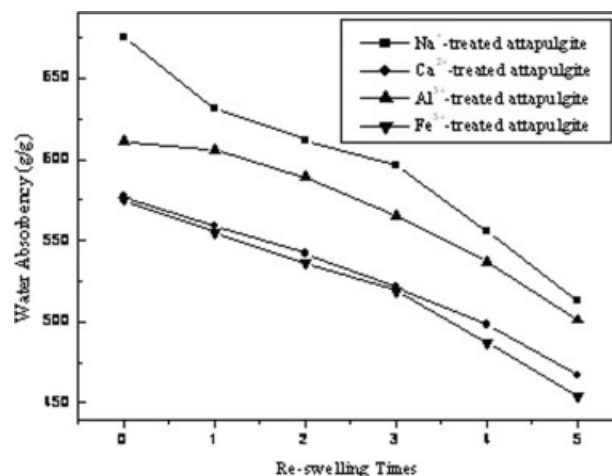


Figure 5 The effect of treatment of attapulgite with different kinds of cationic solutions (NaCl, CaCl₂, AlCl₃ and FeCl₃) on swelling–deswelling–reswelling properties of superabsorbent composites.

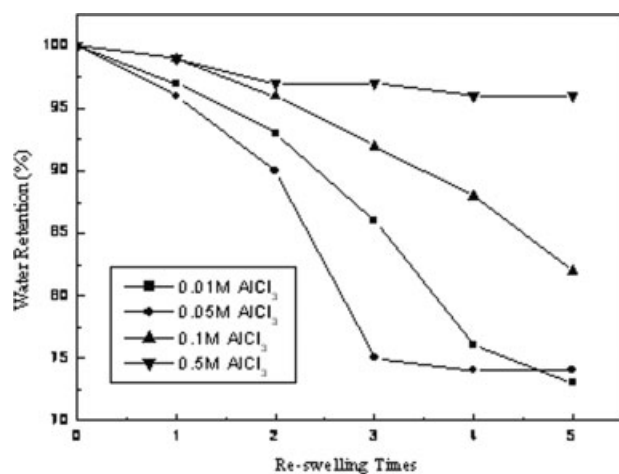


Figure 6 Effect of Al^{3+} -exchanged attapulgite solution concentration on water retention of the superabsorbent composites.

can be kept after five times of swelling–deswelling–reswelling test. The results indicated that the gel strength of superabsorbent composites prepared with divalent and trivalent cations exchanged attapulgite is slight higher than that of superabsorbent composites prepared with NaCl -exchanged attapulgite. Attapulgite treated with divalent or trivalent cations solutions, which is in good agreement with our conclusion aforementioned that multivalent cations bonded on attapulgite could serve as an inorganic crosslinker in the polymeric network result in an increase in the crosslinking density of superabsorbent composite network. Besides, the results showed that these superabsorbent composites may prove useful in recyclable superabsorbent materials.

Effect of Al^{3+} -exchanged attapulgite solution concentration on water retention of the superabsorbent composites

From Figure 5 we can see that the AlCl_3 exchanged attapulgite has a relative high influence on the reswelling property of superabsorbent composite. To further study Al^{3+} -exchanged attapulgite treated with different AlCl_3 solution concentrations on reswelling property of superabsorbent composites, the reswelling test of superabsorbent composites prepared with attapulgite respectively, treated with 0.01, 0.05, 0.1, and 0.5M AlCl_3 solutions were carried out and the results were presented in Figure 6. Clearly, with increasing the reswelling times, the water retention of all superabsorbent composites samples decreased. Also, the water retention of superabsorbent composites increased with the increase of the concentration of AlCl_3 solutions after five times of reswelling tests. The variation of water

retention with different AlCl_3 solutions concentrations may be due to the fact that further increased AlCl_3 solution concentration could form more intramolecular and intermolecular complex with hydrophilic groups, and then increase the effective crosslinking density of corresponding superabsorbent composites, which in turn increase the gel strength of superabsorbent composites and is responsible for the increase of water retention in reswelling test.

CONCLUSIONS

A series of superabsorbent composite, PAA/attapulgite, from acrylic acid (AA) and ion-exchanged attapulgite was prepared by aqueous polymerization, using *N, N'*-methylenebisacrylamide (MBA) as a crosslinker and ammonium persulfate (APS) as an initiator. When attapulgite was treated with different anionic solution with common cations (Na^+) such as NO_3^- , Ac^- , Cl^- , HCO_3^- , H_2PO_4^- , CO_3^{2-} , SO_4^{2-} , HPO_4^{2-} , and PO_4^{3-} , the different valence of anion obviously affect the physicochemical properties of ion-exchanged attapulgite such as CEC and SSA, which in turn have obvious influence on water absorbency. When attapulgite was treated with various cationic solutions with common anion (Cl^-), the water absorbency of superabsorbent composite decreased in the order $\text{Na}^+ > \text{Al}^{3+} > \text{Ca}^{2+} \approx \text{Fe}^{3+}$ -treated attapulgite. This observation may be due to the fact that divalent or trivalent cations take part in the crosslinking of superabsorbent composite polymeric network and then in turn increase the crosslinking density. Among the multivalent cations exchanged attapulgite, Al^{3+} -exchanged attapulgite exhibited excellent improvement on both water absorbency and reswelling abilities of corresponding superabsorbent composite. When attapulgite was treated with Al^{3+} solution, the water retention of superabsorbent composites increased with the increase of the concentration of AlCl_3 solutions after 5 times of reswelling tests. Under the same preparation conditions, the superabsorbent composite prepared with CaCl_2 , AlCl_3 , and FeCl_3 aqueous solutions treated attapulgite can respectively, keep 81, 82, and 79% of their initial water absorbency after five times of swelling–deswelling–reswelling test, which make the superabsorbent composites useful in recyclable superabsorbent materials.

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