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# Evaluation of ammonium removal using a chitosan-g-poly (acrylic acid)/rectorite hydrogel composite

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ABSTRACT

This paper concerns the removal of ammonium ions ($NH_4^+$) from aqueous solution using a hydrogel composite chitosan grafted poly (acrylic acid)/rectorite prepared from *in situ* copolymerization. The effects of rectorite content, contact time, pH, $NH_4^+$ concentration and temperature on the adsorption capacity were discussed. Langmuir, Freundlich, Tempkin and Redlich–Peterson isotherms were used to describe the experimental data. The results indicate that the adsorption equilibrium can be achieved within 3–5 min and, the hydrogel composite has a higher adsorption capacity for $NH_4^+$ in a wide pH levels ranged from 4.0 to 9.0. No significant changes in the adsorption capacity are found over the temperature range studied. The adsorption mechanism of $NH_4^+$ onto hydrogel composite was proposed, and the reusable ability of this hydrogel adsorbent was evaluated.

## 1. Introduction

Eutrophication of water body is a major, global environmental problem. Its main cause is disposal of nutrients (N and P) directly from wastewater plants or indirectly from agriculture runoff and leaching from sludge deposited in landfill fields [1]. Nitrogen compounds are very essential elements for living organisms. However, when they are more than needed, they can contribute to accelerated eutrophication of lakes and rivers, dissolved oxygen depletion and fish toxicity in receiving water, leading thus a number of health problems involving living species such as humans and animals [2]. Therefore, it is desirable that these nutrients should be removed before they are returned to the environment.

Ammonium nitrogen ($NH_4^+$) is the most commonly encountered nitrogenous compounds in wastewaters. In order to remove $NH_4^+$, several technologies have been tested, namely biological treatment [3], chemical precipitation [4], supercritical water oxidation [5], steam-stripping [6], microwave radiation [7], ion exchange [8] and adsorption [9]. Among these recipes, adsorption technology has received much attention and is considered to be a robust and effective technique used in water and wastewater treatments due to its economical advantages, low energy input and easy operation. The success of an adsorption technology depends on the choice of an appropriate adsorbent [10]. Due to the comparable low cost of application, most clays, which are hydrated aluminum-silicate minerals, have been used in removing $NH_4^+$ contaminant, such as sepiolite [11,12]. Natural zeolites are important inorganic cation exchangers that exhibit higher affinity for $NH_4^+$ and then are investigated widely for $NH_4^+$ removal [8,13]. Thanks to highly developed porous structure and large specific area, activated carbons show also considerable adsorption capacity towards $NH_4^+$ [9]. These adsorbents have been developed and studied for $NH_4^+$ removal, but the adsorption kinetics are slow and the adsorption capacity is also limited only via ion exchange or porous adsorption. In addition, only under optimum pH condition, the higher adsorption capacity for $NH_4^+$ would be obtained. The regeneration of developing adsorbents is also a limiting factor governing the adsorption cost.

Hydrogels are slightly crosslinked polymeric networks that enable the adsorption of many pollutants and recently, this type of adsorbents has attracted more attention due to its high-capacity and fast-responsive within a few minutes [14–16]. Considering the limitations of pure polymeric hydrogels, such as poor gel strength and stability, some inorganic clay minerals including attapulgite, montmorillonite, vermiculite and sepiolite have been incorporated into hydrogel matrix [17–20]. Clays are natural, abundant, and inexpensive materials that have high mechanical strength and chemical resistance. So, the preparation of organic–inorganic hydrogel composite has attracted increasing attention.

Chitosan (CTS) is produced commercially by deacetylation of chitin. Due to the presence of chemical reactive groups (primary, secondary hydroxyl groups and highly reactive amino groups), CTS can be easily modified by chemical reactions, in particular crosslinking and grafting, by which some novel functions can be

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introduced into this biopolymer [21] and the resulting product can then be useful in many other applications. Recently, Wang and co-workers used chitosan as the backbone to graft poly (acrylic acid), obtaining a hydrogel composite, and found that this hydrogel had a potential application for the fast removal of Cu(II) from the aqueous solution [22]. In addition, chitosan-grafted-poly (acrylic acid)/montmorillonite had also been used as the adsorbent to remove methylene blue and the maximum adsorption capacity was found to be 1859 mg/g even when 30 wt% montmorillonite was introduced [23]. These studies were aimed at removal of cationic pollutants, such as heavy metals or toxic dyes. However, no information was involved for removing $NH_4^+$ from the aqueous solution.

Rectorite (REC) is a regularly interstratified clay mineral with alternate pairs of dioctahedral mica-like layers (nonexpansible) and dioctahedral montmorillonite-like layers (expansible) in a 1:1 ratio [24]. The introduction of REC into the polymer matrix can not only improve the thermal stability of corresponding polymer [25], but also reduce the product cost. Moreover, previous study by our group proved that poly (acrylic acid) chain can graft onto the backbone of CTS, forming a hydrogel composite with REC being embedded within the polymeric networks [26]. Consequently, the aim of this study is: (i) to prepare a series of hydrogel composite containing REC; (ii) to evaluate the potential of as-prepared hydrogels for $NH_4^+$ removal; (iii) to investigate the regeneration and reusable ability of this hydrogel composite for the treatment of water body containing $NH_4^+$.

## 2. Methods

### 2.1. Materials

Acrylic acid (AA, chemically pure, Shanghai Shanpu Chemical Factory, Shanghai, China) was distilled under reduced pressure before use. Ammonium persulfate (APS, analytical grade, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), N,N′-methylene-bisacrylamide (MBA, chemically pure, Shanghai Yuanfan additives plant, Shanghai, China), and chitosan (CTS, degree of deacetylation is 0.90, average molecular weight is $3 \times 10^5$, Zhejiang Yuhuan Ocean Biology Co., Zhejiang, China) were used as received. Rectorite (REC, Mingliu Rectorite Co. Ltd., Hubei, China) was milled through a 320-mesh screen prior to use.

A 1000 mg/L stock standard solution of $NH_4^+$ was prepared by dissolving an appropriate amount of ammonium chloride (dried to constant mass at 100–105 °C) in 1000 mL of distilled water. The working solutions containing different concentrations of $NH_4^+$ were prepared by stepwise dilution of the stock solutions. The initial pH value was adjusted by addition of 0.1 and 1.0 mol/L NaOH or HCl solution to designed value (Mettler Toledo FE20 pH-meter). Other reagents used were all analytical grade and all solutions were prepared with distilled water.

### 2.2. Preparation of hydrogel composite

0.5 g CTS was dissolved in 30 mL 1% (v/v) acetic acid in a 250 mL four-neck flask equipped with a stirrer, a condenser, a thermometer and a nitrogen line. After removal of oxygen, 0.1 g APS was introduced to initiate CTS to generate radicals. Ten minutes later, the mixture consisted of 3.6 g AA, 0.1 g MBA and certain amount of REC was added. The oil bath was kept at 65 °C for 3 h to complete the polymerization reaction. When the reaction was finished, the resulting granular product was cooled to room temperature and neutralized with 6.0 mol/L NaOH solution to pH 7.0. The swollen product was dehydrated with methanol and then dried at 60 °C to a constant weight. The obtaining product is denoted as CTS-*g*-PAA (without REC) and CTS-*g*-PAA/REC (with REC), respectively. The hydrogels were milled and all samples used for adsorption test were passed through 200-mesh stainless screen with a particle size of 75 μm.

### 2.3. Adsorption experiment

$NH_4^+$ adsorption experiments were performed under 120 rpm with an orbital shaking THZ-98A. The experiments were carried out in a series of 50 mL conical flasks containing 0.05 g hydrogel adsorbent and 25 mL $NH_4^+$ solutions. On reaching equilibrium the adsorbents were separated by centrifugation at 4500 rpm for 10 min. The $NH_4^+$ concentration in the solution was measured according to Nessler's reagent colorimetric method. The adsorption capacity of hydrogels for $NH_4^+$ was calculated from the following equation:

$$q_e = \frac{C_0V_1 - C_eV_2}{m} \tag{1}$$

where $q_e$ is the adsorption capacity of $NH_4^+$ onto adsorbent (mg N/g), $C_0$ is the initial $NH_4^+$ concentration (mg N/L), $C_e$ is the equilibrium $NH_4^+$ concentration (mg N/L), $m$ is the mass of adsorbent used (mg), $V_1$ and $V_2$ are the volumes of $NH_4^+$ solution before and after the adsorption (mL). All assays were carried out in triplicate. The limit of experimental error was ±5%.

For the adsorption kinetic studies, a series of solutions containing 100 mg N/L $NH_4^+$ were allowed to contact with 0.05 g hydrogels with different amount of REC. At different intervals (3, 5, 10, 30, 60 min), the adsorbents were separated by centrifugation and the solutions were analyzed for residual $NH_4^+$ concentration. The effects of pH on $NH_4^+$ adsorption onto as-prepared hydrogels were studied at pH range from 2.0 to 10.0 for an initial $NH_4^+$ concentration of 100 mg N/L and contact time of 30 min. To investigate the adsorption isotherms, a series of $NH_4^+$ solutions with different concentration (10–1000 mg N/L) were kept in contact with 0.05 g hydrogels for 30 min at natural pH (6.0–7.0). Temperature effect on adsorption for determination of temperature-dependence was also studied for five temperatures: 23, 30, 37, 44, 51 °C.

### 2.4. Desorption, regeneration and reusable ability

The desorption of $NH_4^+$ loaded on as-prepared hydrogels was done using sodium hydroxide as the desorbing agent. A fixed amount (0.05 g) of each adsorbent was contacted separately with 25 mL 0.1 mol/L sodium hydroxide solution and kept stirring with a magnetic bar at room temperature. Then, the desorbed amount of $NH_4^+$ was obtained. Preliminary experiments proved that $NH_4^+$ adsorbed onto hydrogel composite could be completely desorbed within 10 min using 0.1 mol/L NaOH solution as the desorbing agent. After that, the achieved hydrogel was washed with distilled water for several times for another adsorption. A similar procedure was repeated and the adsorption capacity after several times was then achieved. Here, the regeneration ratio is defined as the ratio of re-adsorbed $NH_4^+$ amount to initial adsorbed one by which the regeneration ability of this hydrogel composite can then be evaluated.

## 3. Results and discussion

### 3.1. Effect of REC content on adsorption capacity

With the rapid development of organic–inorganic materials, polymer–clay composites have received considerable interest. Clay minerals are low cost materials and the introduction of inorganic clay component can reduce the cost of material, meanwhile, the interactions between them have effects on the properties of both clay and polymer systems [27]. In this section, the effects of REC

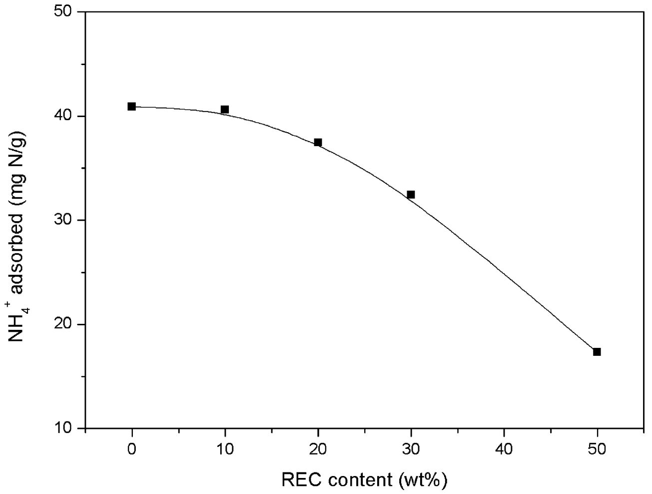

**Fig. 1.** Adsorption capacity as a function of REC content in the hydrogel composite. Adsorption conditions: contact time, 30 min; initial $NH_4^+$ concentration, 100 mg N/L; natural pH (6.0–7.0); 120 rpm; 30 °C.

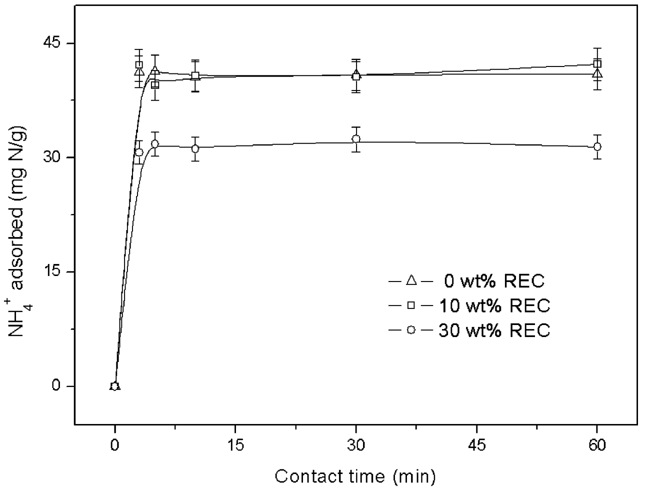

**Fig. 2.** Adsorption kinetics of CTS-g-PAA and CTS-g-PAA/REC. Adsorption conditions: initial $NH_4^+$ concentration, 100 mg N/L; natural pH (6.0–7.0); 120 rpm; 30 °C.

content on the adsorption capacity were investigated, as shown in Fig. 1. It is observed that the adsorption capacity is 40.90, 40.61, 37.46, 32.43 and 17.3 mg N/g for CTS-*g*-PAA, CTS-*g*-PAA/REC (10 wt%), CTS-*g*-PAA/REC (20 wt%), CTS-*g*-PAA/REC (30 wt%), and CTS-*g*-PAA/REC (50 wt%), respectively. During the experiment, it is found that REC has a poor adsorption capacity for $NH_4^+$ and only a value of 1.54 mg N/g is observed. In this case, if REC and CTS-*g*-PAA are physically mixed, the adsorption capacity for $NH_4^+$ is calculated to be 36.96, 33.03, 29.09 and 21.22 mg N/g when REC percent is 10, 20, 30 and 50 wt%, respectively. The difference in the adsorption capacity between chemically reacted and physically mixed is clear with increasing the REC content in the hydrogels. Generally, an appropriate addition of clay particles can improve the polymeric networks and contribute to the higher swelling ratio of a hydrogel in aqueous solution [17,28], which is beneficial for the adsorption. Furthermore, the addition of REC can reduce the production cost of the adsorbents, and accordingly, the superiority of CTS-*g*-PAA/REC over CTS-*g*-PAA is clearly observed.

### 3.2. *Effect of contact time on the adsorption capacity*

Contact time is an important parameter because this factor can reflect the adsorption kinetics of an adsorbent for a given initial adsorbate concentration. Activated carbon is undoubtedly the most commonly used adsorbent for the treatment of pollutants, however, the adsorption equilibrium requires the contact time of 2 h for $NH_4^+$ removal [9]. Clinoptilolite has a high affinity for $NH_4^+$, and is one of the most important natural zeolites, however, the equilibrium time would be obtained as 40 min [8]. But for hydrogel adsorbents, the adsorption equilibrium can be achieved within 3–5 min, meaning their fast adsorption kinetics (Fig. 2). As-prepared adsorbent belongs to hydrogels whose main feature is the ability to absorb water quickly due to the hydrophilic networks. After the initial faster hydration of the polymer networks, concentration gradient of $NH_4^+$ is formed at gel–water interface, thereby the diffusion of $NH_4^+$ from the aqueous solution into the hydrogel is started and bound immediately to the swollen polymeric networks as a result of electrostatic attraction. During this process, the swollen polymeric networks can diminish the diffusion limitation, leading thus the adsorption system to reach equilibrium within a few minutes. Also, it is clear that apart from comparable adsorption capacity, the adsorption rate is not influenced by introducing 10 wt% REC into the hydrogel.

### 3.3. *Effect of pH values on the adsorption capacity*

Generally, pH value is one of the most important parameters controlling the adsorption process. In order to determine the effects of pH values on $NH_4^+$ removal, experiments were carried out using various pH levels in the range of 2.0–10.0, as shown in Fig. 3. It appears that the adsorption capacity of hydrogel adsorbent remains a constant within the pH range of 4.0–9.0 for CTS-*g*-PAA and CTS-*g*-PAA/REC (10 wt%). When pH is lower than 4.0 or above than 9.0, the adsorption capacity shows a slight decrease. But for CTS-*g*-PAA/REC (30 wt%), the adsorption capacity seems to be constant within pH of 4.0–6.0. When pH value is lower than 4.0, a slight decrease in adsorption capacity is observed. While for pH lying between 8.0 and 10.0, a slight increase is visible. For all the hydrogels, the adsorption capacity for $NH_4^+$ exhibits a sudden decrease in the stronger acid condition (pH 2.0). These phenomena may be correlated with the dissociation constant (pKa) of poly (acrylic acid). Owing to a small amount of CTS used in the preparation of adsorbent and most of the active amino groups of CTS have participated in the copolymerization, –COOH groups within the polymeric networks play the vital role controlling the nature of this hydrogel. pKa of poly (acrylic acid) is about 4.7 [29], then the carboxylic acid groups can be easily

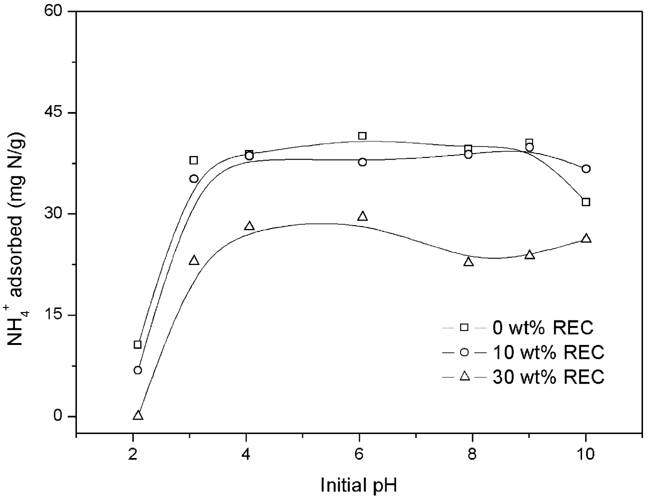

**Fig. 3.** Effects of pH on adsorption capacity of CTS-g-PAA and CTS-g-PAA/REC. Adsorption conditions: contact time, 30 min; initial $NH_4^+$ concentration, 100 mg N/L; 120 rpm; 30 °C.

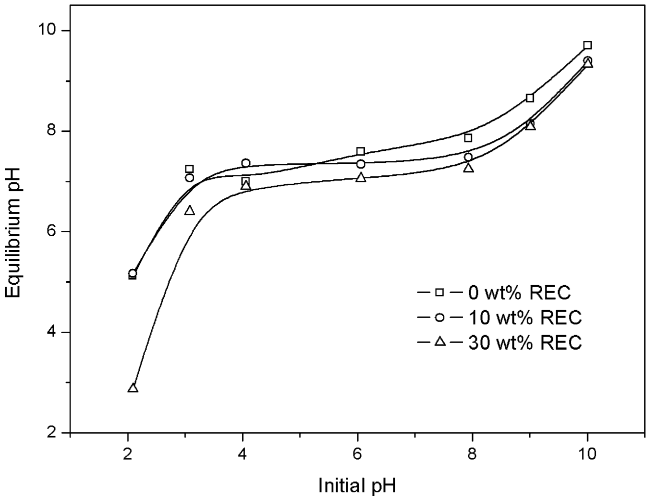

**Fig. 4.** Relationship between equilibrium pH and initial pH values for $NH_4^+$ adsorption.

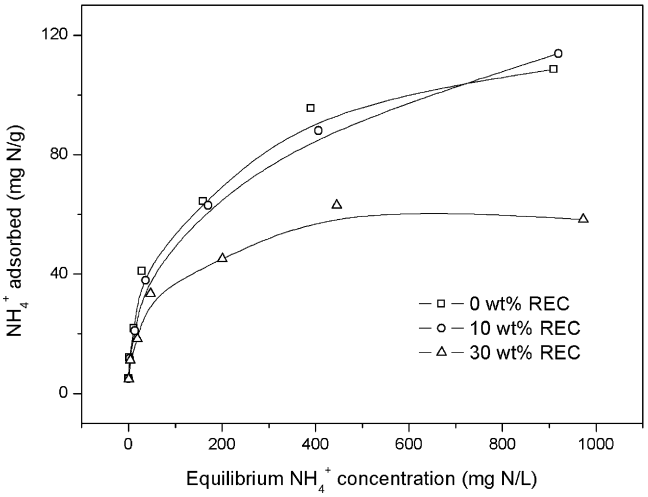

**Fig. 5.** Adsorption isotherms of CTS-*g*-PAA and CTS-*g*-PAA/REC. Adsorption conditions: contact time, 30 min; natural pH (6.0–7.0); 120 rpm; 30 °C.

ionized above pH value of 4.7. Due to the rapid adsorption of $NH_4^+$ onto hydrogels, the equilibrium pH value is thus considered to be the governed factor influencing the ionization degree of –COOH groups. Owing to the buffer action of –COOH and $–COO^-$ groups, one can speculate that after the adsorption, the equilibrium pH values would remain a constant in a certain extent, which can be testified from Fig. 4. However, in the stronger acidic region, some $–COO^-$ groups are transformed to –COOH groups, leading the electrostatic attraction between adsorbent and adsorbate to diminish, and accordingly, the adsorption capacity decreases. Nevertheless, some –COOH groups have been ionized and therefore considerable adsorption capacity is also observed. At higher pH values, $NH_4^+$ are neutralized by hydroxyl ion rendering it uncharged [8], together with increased ion strength, resulting in a decreasing adsorption capacity for $NH_4^+$. But for other adsorbents, pH is expected to have an impressive effect on $NH_4^+$ removal as it can influence both the character of adsorbate and adsorbent itself, and then, there is often an optimum pH value for $NH_4^+$ adsorption at that point, a maximum adsorption capacity is found [13,30]. From the experimental data, it is observed that by introducing inorganic REC particles into the polymeric networks, the adsorption capacity seems not to be affected significantly, especially in basic pH values. This behavior is not clear at this time. Nevertheless, one can conclude that this hydrogel composite can be used in a wide pH range.

### 3.4. *Effect of $NH_4^+$ concentration on the adsorption capacity*

In this section, the efficiency of the hydrogels was evaluated by measuring the adsorption isotherms by batch technique using initial $NH_4^+$ concentrations between 10 and 1000 mg N/L. As shown in Fig. 5, one can observe a convexly upward curvature of the isotherms due to the very high preference of hydrogel adsorbent for $NH_4^+$.

Fitting of adsorption isotherm equations to experimental data is often an important aspect of data analysis. In this study, four typical isotherms were used for fitting the experimental data:

$$\text{Langmuir equation}: \quad q_e = \frac{q_m b C_e}{1 + b C_e} \tag{2}$$

$$\text{Freundlich equation}: \quad q_e = K C_e^{1/n} \tag{3}$$

$$\text{Tempkin equation}: \quad q_e = b \ln(a C_e) \tag{4}$$

$$\text{Redlich–Peterson equation}: \quad q_e = \frac{K_r C_e}{1 + a C_e^b} \tag{5}$$

where $q_e$ is the equilibrium adsorption capacity of $NH_4^+$ onto adsorbent (mg N/g), $C_e$ is the equilibrium $NH_4^+$ concentration (mg N/L), the other parameters are different isotherm constants, which can be determined by non-linear regression of the experimental data. The estimated model parameters with correlation coefficient ($R^2$) were summarized in Table 1. It is evident that the suitability of isotherms for fitting the experimental data is in the following order: Redlich–Peterson > Freundlich > Langmuir > Tempkin. This is because that Redlich–Peterson model is a combination of Langmuir equation as a limit for high concentration and Freundlich's for low concentration, and then this model can be used extensively in a wide concentration range and be believed to be applicable to a large class of adsorption [31]. Here, *K* value is related to the adsorption capacity of an adsorbent and $q_m$ denotes the monolayer adsorption capacity of an adsorbent. The higher values for *K* indicate higher

**Table 1**
Estimated isotherm parameters for $NH_4^+$ adsorption.

| Adsorbents | Langmuir | | | Freundlich | | |
|---|---|---|---|---|---|---|
| | $q_m$ (mg N/g) | *b* (L/mg) | $R^2$ | *K* (L/g) | *n* | $R^2$ |
| CTS-g-PAA | 109.2 | 0.01607 | 0.9582 | 12.67 | 3.100 | 0.9810 |
| CTS-g-PAA/REC (10 wt%) | 123.8 | 0.0072 | 0.9516 | 12.67 | 3.100 | 1 |
| CTS-g-PAA/REC (30 wt%) | 61.95 | 0.02411 | 0.9579 | 10.24 | 3.686 | 0.9309 |

| Adsorbents | Tempkin | | | Redlich–Peterson | | | |
|---|---|---|---|---|---|---|---|
| | *a* | *b* (L/g) | $R^2$ | *a* (L/mg) | *b* | $K_r$ (L/g) | $R^2$ |
| CTS-g-PAA | 0.5995 | 16.25 | 0.9553 | 0.3485 | 0.7494 | 7.161 | 0.9864 |
| CTS-g-PAA/REC (10 wt%) | 0.1242 | 23.06 | 0.9763 | 0.8681 | 0.6693 | 10.53 | 0.9958 |
| CTS-g-PAA/REC (30 wt%) | 1.591 | 8.100 | 0.9210 | 0.06408 | 0.9088 | 2.174 | 0.9621 |

**Table 2**
$NH_4^+$ removal with different adsorbents studied and reported.

| Adsorbents | Adsorption conditions | | Monolayer adsorption capacity (mg/g) | Reference |
|---|---|---|---|---|
| | $NH_4^+$ concentration (mg/L) | Contact time | | |
| CTS-*g*-PAA/REC (10 wt%) | 10–1000 | 30 min | 123.8 | This work |
| Activated carbon | 35–280 | 2 h | 11.57 | [9] |
| Sepiolite | 150–7000 | 6 h | 25.49 | [12] |
| Volcanic tuff | 20–300 | 3 h | 13.64 | [30] |
| Zeolite 13 X | 5–400 | 30 min | 8.61 | [32] |
| Mordenite | 10–200 | 3 days | 9.479 | [33] |
| New Zealand clinoptilolite | 10–200 | 3 days | 6.588 | [33] |
| Natural Turkish clinoptilolite | 25–150 | 40 min | 8.121 | [34] |

affinity of hydrogel for $NH_4^+$. Values of the empirical parameter $1/n$ in the range $0.1 < 1/n < 1$ indicate a favorable adsorption. In addition, the monolayer adsorption capacity for $NH_4^+$ is 109.2, 123.8 and 61.95 mg N/g for CTS-*g*-PAA, CTS-*g*-PAA/REC (10 wt%) and CTS-*g*-PAA/REC (30 wt%), respectively. Clearly, by introducing 10 wt% REC into the hydrogel, the adsorption capacity is comparable with that of pure CTS-*g*-PAA. In addition, the adsorption capacity of hydrogel adsorbent was compared with other adsorbents reported, as listed in Table 2. Obviously, this hydrogel composite possessed much higher adsorption capacity for $NH_4^+$, enabling it a potential fast-responsive and high-capacity adsorbent for $NH_4^+$ removal.

### 3.5. Effect of temperature on the adsorption capacity

Temperature is a highly significant parameter in the adsorption process. A series of experiments at 23, 30, 37, 44, 51 °C were undertaken to study the effect of temperature on the adsorption capacity for $NH_4^+$, as shown in Fig. 6. The results suggest that the adsorption capacity is not affected by rising the adsorption temperature for CTS-*g*-PAA, while for CTS-*g*-PAA/REC, low temperature appears to benefit for the adsorption. However, the differences in adsorption capacity are not significant, and then we can conclude that the temperature has little effects on the adsorption capacity of $NH_4^+$ onto these hydrogel composites. Here, it should be mentioned that compared to CTS-*g*-PAA, CTS-*g*-PAA/REC (10 wt%) shows a comparable adsorption capacity when the temperature of $NH_4^+$ solution is below 30 °C, and at this point, the product cost would be reduced with the addition of inorganic REC particles while the adsorption ability is maintained.

### 3.6. Effect of ion strength on the adsorption capacity

From the viewpoint of practical application, it is more important to know the adsorption capacity of an adsorbent when it contacts with various saline solutions. Hence in this section, the adsorption capacity of CTS-*g*-PAA/REC (10 wt%) for $NH_4^+$ was investigated respectively in three cationic saline solutions (NaCl, $CaCl_2$ and $AlCl_3$), as shown in Fig. 7. It is clear that when the metal cation concentration is below 0.05 mmol/L, the adsorption capacity of CTS-*g*-PAA/REC shows a platform, and is observed to decrease a little compared with that in distilled water (40.61 mg N/g). Further increasing the cation concentration would result in an appreciable decrease in the adsorption capacity and the effects of multivalent cation are more impressive. This is attributed to that the counterion ions, especially multivalent cations would neutralize the negatively fixed-charged groups, thereby disabling CTS-*g*-PAA/REC to interact with the positive charged adsorbate. In spite of the increased ionic strength of solution leads to $NH_4^+$ absorption decreasing, CTS-*g*-PAA/REC has good adsorption capacity for $NH_4^+$ from saline water, and more than 30 mg N/g can be achieved even at higher concentration saline solutions (0.5 mmol/L), enabling it as a potentially feasible absorbent for $NH_4^+$ removal from saline environments.

In order to assess the efficacy of as-prepared hydrogel adsorbent in real water body, the adsorption efficacies for $NH_4^+$ in tap water and in natural water collected from Taihu Lake in Jiangsu were evaluated and compared with that in distilled water, as shown in inset in Fig. 7. The results indicate that the adsorption capacity shows a decreasing tendency in the order of distilled water, tap water and Taihu water. Nevertheless, the adsorption capacity is as high as 37.97 and 34.26 mg N/g, a little decrease compared with that in

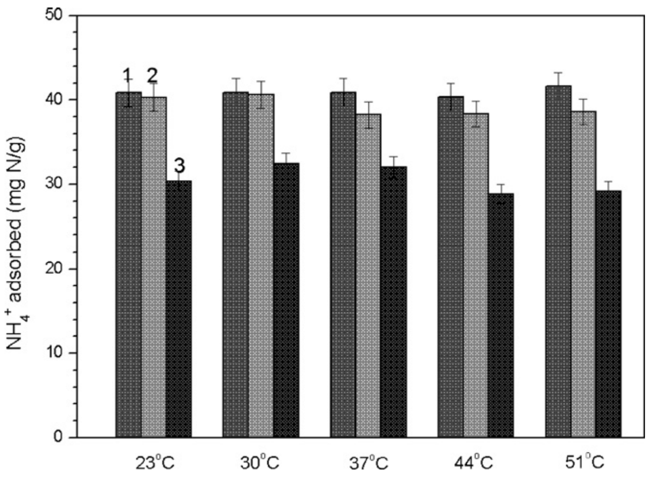

**Fig. 6.** Effect of temperature on adsorption capacity of CTS-*g*-PAA and CTS-*g*-PAA/REC. Adsorption conditions: contact time, 30 min; initial $NH_4^+$ concentration, 100 mg N/L; natural pH (6.0–7.0); 120 rpm. 1, CTS-*g*-PAA; 2, CTS-*g*-PAA/REC (10 wt%); 3, CTS-*g*-PAA/REC (30 wt%).

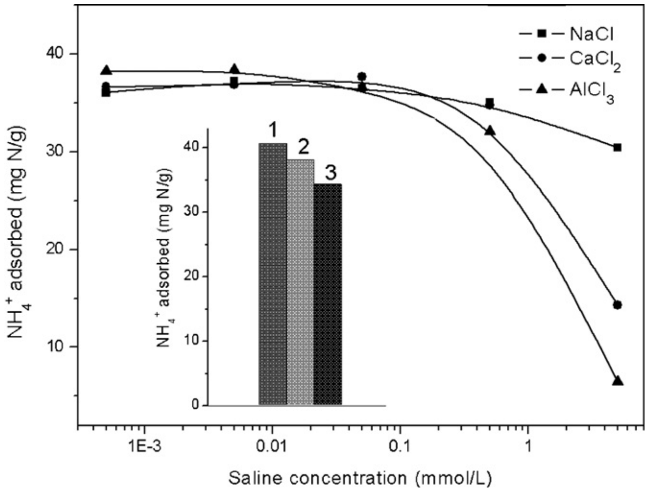

**Fig. 7.** Effect of ion strength on the adsorption capacity of CTS-*g*-PAA/REC (10 wt%). Adsorption conditions: contact time, 30 min; initial $NH_4^+$ concentration, 100 mg N/L; natural pH (6.0–7.0); 120 rpm; 30 °C. Inset is a comparison of adsorption capacity in different water body: 1, distilled water; 2, tap water; 3, Taihu Lake water.

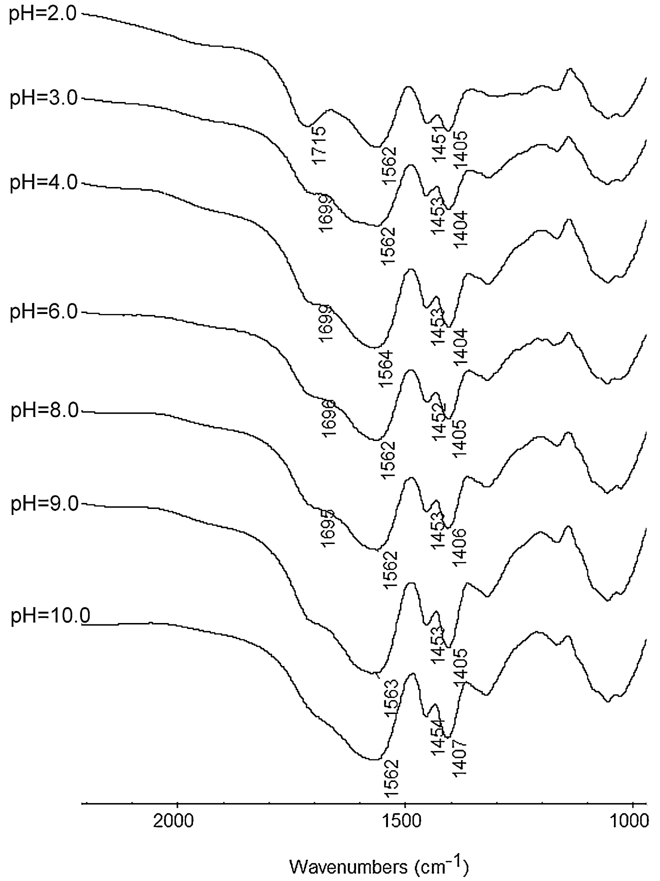

**Fig. 8.** FTIR spectra of CTS-*g*-PAA/REC (10 wt%) after adsorption at different pH values.

distilled water (40.61 mg N/g). The results suggest the suitability of developing adsorbent for $NH_4^+$ removal in real circumstance.

### *3.7. Adsorption mechanism*

For $NH_4^+$, the predominant adsorption mechanism may be related to the number of $-COO^-$ groups present within polymeric networks. The adsorption of $NH_4^+$ onto hydrogel is mainly due to the ionic interaction between positively charged $NH_4^+$ and negative adsorption sites of the adsorbent ($-COO^-$). The electrostatic attraction can be further testified by performing the adsorption experiment in a mixed solution containing positively charged $NH_4^+$ and negatively charged orthophosphate $PO_4^{3-}$. Preliminary experiments verified that after the adsorption, the residual $PO_4^{3-}$ concentration equaled to the initial $PO_4^{3-}$ concentration, that is, in the mixed solution containing $NH_4^+$ and $PO_4^{3-}$, CTS-*g*-PAA/REC could exclusively absorb $NH_4^+$ while $PO_4^{3-}$ was remained. This is a strong evidence that the electrostatic attraction is responsible for the adsorption of $NH_4^+$ onto CTS-*g*-PAA/REC. Paulino et al. utilized a hydrogel consisted of gum arabic, polyacrylate and polyacrylamide as the adsorbent to investigate its adsorption capacity for some dyes and concluded that in an aqueous mixture of orange II and methylene blue, this hydrogel adsorbed the methylene blue exclusively while orange II was remained [35]. Similar experiments strength the argument that the electrostatic attraction between the adsorbent and adsorbate would control the adsorption process.

Fig. 8 shows the FTIR spectra of CTS-*g*-PAA/REC adsorbed at different pH values. Clearly, in the stronger acid condition (pH 2.0), there are characteristic stretching bands of –COOH and $-COO^-$ groups lying respectively at 1715, 1562 and 1405 $cm^{-1}$. With increasing pH values from 2.0 to 4.0, the stretching vibration of –COOH groups gets weakened and the intensities of asymmetric/symmetric vibration absorption bands of $-COO^-$ groups show a gradual increase. Afterwards, it appears that the latter absorption bands remain unchangeable until pH 10.0 at this point, the stretching vibration of –COOH groups has disappeared. FTIR analysis results are consistent with that obtained from pH effects, confirming further that the electrostatic attraction between $-COO^-$ groups and $NH_4^+$ can describe the main adsorption process.

### *3.8. Evaluation of regeneration and reusable ability*

A good adsorbent, in addition to its high adsorption capacity, must also exhibit a good regeneration ability for multiple uses. In this work, desorption of adsorbed $NH_4^+$ onto hydrogel composite was studied using distilled water, 0.1 mol/L HCl, 0.1 mol/L NaCl or 0.1 mol/L NaOH solution as the eluents. The results suggest that 0.1 mol/L NaOH solution can give the highest recovery for $NH_4^+$ (approximate 100%). When $NH_4^+$ was removed, this recovered hydrogel composite was used again to adsorb $NH_4^+$ and the results showed that 0.1 mol/L NaOH can act as not only desorbing agent, but also regenerating agent. That is, the desorption of $NH_4^+$ and regeneration of hydrogels can be performed simultaneously using NaOH solution as both of desorbing and regenerating agents by which the craft can be simplified and the charge would be cut down. In addition, the simultaneous desorption and regeneration can be complete at room temperature within 10 min, a rather mild condition.

By consecutive adsorption–desorption cycles, it is found that the regeneration ratio is 112 (first), 101 (second), 115 (third) and 112 (fourth), respectively. Then, one can speculate that during the desorption and regeneration process, the adsorption sites would increase, i.e. additional adsorption sites are created by desorption and regeneration process. This is ascribed that some unionized –COOH groups within the hydrogel composite get ionized during the regeneration, resulting in more adsorption sites.

## 4. Conclusion

This hydrogel composite has proved its potential in $NH_4^+$ removal on a laboratory scale. The following conclusions can then be drawn from the experiment results: (i) The adsorption equilibrium can be obtained within 3–5 min, meaning fast adsorption kinetics for $NH_4^+$ removal; (ii) The monolayer adsorption is 109.2, 123.8 and 61.95 mg N/g for CTS-*g*-PAA, CTS-*g*-PAA/REC (10 wt%) and CTS-*g*-PAA/REC (30 wt%), respectively, meaning high adsorption capacity for $NH_4^+$ removal; (iii) This hydrogel can be extensively used in a wide pH range from 4.0 to 9.0 and external temperature has little effects on the adsorption capacity, suggesting that as-prepared adsorbent could be applicable to a large class of adsorption systems; (iv) Cations especially multivalent cations coexisted with $NH_4^+$ in the solution can produce some negative effects on the adsorption capacity of CTS-*g*-PAA/REC, it has however higher adsorption capacity for $NH_4^+$ and more than 30 mg N/g can be achieved even at higher concentration saline solutions (0.5 mmol/L), enabling it as a potentially feasible absorbent for $NH_4^+$ removal from saline environments and real circumstance; (v) During the desorption process for $NH_4^+$, the regeneration of this adsorbent can be realized. The regeneration condition is mild and the recovered adsorbent can be used again for $NH_4^+$ removal. In addition, more adsorption sites would be created during the regeneration; (vi) The electrostatic attraction between $-COO^-$ and $NH_4^+$ is considered to be the main adsorption mechanism; and (vii) CTS-*g*-PAA/REC (10 wt%) shows a comparable adsorption kinetic and adsorption capacity to that of pure organic hydrogel CTS-*g*-PAA. Then, the charge would be cut down. Additionally, it is expected that the addition of inorganic clay particles can also improve the hydrogel strength and enhance the thermal stability. It is no doubts that this hydrogel composite is promising in $NH_4^+$ removal from the aqueous solution.

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