



Rapid and wide pH-independent ammonium-nitrogen removal using a composite hydrogel with three-dimensional networks

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ARTICLE INFO

Article history:

Received 11 August 2011

Received in revised form 18 October 2011

Accepted 19 October 2011

Keywords:

Ammonium

Composite hydrogel

Fast-responsive

Removal

Three-dimensional networks

ABSTRACT

Chitosan grafted poly(acrylic acid)/unexpanded vermiculite (CTS-*g*-PAA/UVMT), a granular composite hydrogel with three-dimensional networks, was prepared *via in situ* graft polymerization and evaluated as the adsorbent to remove ammonium-nitrogen (NH₄-N) from aqueous solution using batch adsorption experiments. The effects of various experimental parameters on NH₄-N removal, such as vermiculite content, pH, contact time, NH₄-N concentration and co-existing PO₄-P ion were investigated. The adsorption capacities in different water bodies including distilled water, tap water, well water and lake water were compared to study further the influence of ion strength on NH₄-N removal. The results indicate that the adsorption equilibrium can be achieved within a few minutes and the maximum, constant adsorption capacity can be observed in a wide pH range of 4.0–8.0. The adsorbent can exclusively adsorb NH₄-N in the mixing solution containing NH₄-N and PO₄-P, suggesting that the electrostatic attraction dominates the whole adsorption process. Five consecutive adsorption–desorption studies show that the composite hydrogel has higher adsorption and desorption efficiencies, suggesting the potential of the as-prepared adsorbent for NH₄-N removal.

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1. Introduction

Adsorption is a well-known separation process and recognized as an effective, efficient and economic method for water decontamination applications. However, the major challenge in this field is to select the most promising types of adsorbents. Among many adsorbents developed or reported, polysaccharides, natural or modified, have gained particular attention [1,2]. Chitosan (CTS) is produced commercially by deacetylation of chitin, which is the structural element in the exoskeleton of crustaceans (such as crabs and shrimp). Due to the presence of chemical reactive groups (primary, secondary hydroxyl groups and highly reactive amino groups), CTS, pristine or modified, has been considered to be an attractive adsorbent for removing many kinds of pollutants from the effluents, especially for dyes [3,4], heavy metals [5–7] and organic pollutants [8–10].

Chemical modifications are promising ways to obtain various utilizations of CTS. Of possible modifications, graft copolymerization is anticipated to be quite promising for developing sophisticated functions. Graft copolymerization of synthetic

polymers onto CTS backbone can introduce desired properties and enlarge the field of the potential applications of CTS by choosing various types of side chains. CTS bears two types of reactive groups that can be grafted: one is the free amino groups on deacetylated units and the other is the hydroxyl groups on the C₃ and C₆ carbons on acetylated or deacetylated units [11]. Very recently, graft copolymerization of vinyl monomers onto CTS using free radical initiation has attracted the interests of many scientists. The copolymerization of CTS with vinyl monomers in water in the presence of initiator would yield a three-dimensional cross-linked product [12–14].

This type of product belongs to a family of hydrogels which are slightly cross-linked hydrophilic polymers with excellent three-dimensional structured polymeric networks consisted of flexible chains. These hydrogels are usually prepared from free radical solution polymerization and the resulting products are mainly in the gel-form [15,16], which requires more energy to dry, to smash and to granulate. To overcome this drawback, we select CTS as the backbone to graft poly(acrylic acid) (PAA) due to that CTS bears two types of reactive groups: amino and hydroxyl groups. Furthermore, CTS can be considered as the cationic polymer and acrylic acid can be recognized as the anionic monomer, and accordingly, an anticipated granular hydrogel without drying, smashing and granulating would be formed as the polymerization proceeds [17,18]. Due to its super-hydrophilicity and tailored functionality, the resulting hydrogel shows several advantages over traditional adsorbents: fast adsorption rate, high adsorption capacity, easy

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separation, wide pH application range and mild regeneration, and accordingly, this is a fast-responsive and wide pH-independent adsorbent material for removing pollutants from aqueous solution. However, the pure organic hydrogel shows higher swelling degree which is not beneficial for practical applications, and in recent years, the preparation of organic–inorganic composite hydrogel has attracted a great deal of attention due to their low production cost, higher mechanical resistance and extensive applications [19–21]. The clay incorporation into the hydrogel can not only increase the adsorption capacity but also enhance the adsorption rate, leading the adsorption process to be complete within a few minutes [22].

Based on above background, a composite hydrogel, chitosan grafted poly(acrylic acid)/unexpanded vermiculite (CTS-g-PAA/UVMT), was prepared *via in situ* copolymerization in aqueous solution by introducing UVMT micro-powder into CTS-g-PAA polymeric networks. Vermiculite is a layered aluminium silicate with exchangeable cations and reactive –OH groups on its surface, and after the polymerization, the platelets of vermiculite can be exfoliated and dispersed finely in the polymer matrix, forming a composite hydrogel [15]. The three-dimensional structured hydrophilic networks of the resulting hydrogel would decrease the diffusion resistance and speed the equilibrium for an adsorption system, and the presence of a large number of functional ionized carboxyl groups within the polymeric networks is expected to increase significantly the adsorption capacity for an adsorbate, such as ammonium-nitrogen (NH₄-N) in this study.

NH₄-N is an important member of the group of nitrogen-containing compounds that act as nutrients for aquatic plants and algae. However, if NH₄-N levels in water are too high, they can be toxic to some aquatic organisms, and if enough nutrients are present, eutrophication may occur, which is a serious problem throughout the world and poses a direct threat to public health [23]. Therefore, the total removal or at least a significant reduction of NH₄-N in water is thus obligatory prior to disposal into streams, lakes, seas and land surface. As the convenient and effective approach, natural or modified zeolite [24,25] and molecular sieve [26] have been reported as the adsorbents to remove NH₄-N in water. However, the adsorption capacity is too low to satisfy the effective demand. Yuan and Kusuda used a hydrogel of poly(*N*-isopropylacrylamide-*co*-chlorophyllin) to adsorb NH₄-N and found that in a swollen state, the developed hydrogel had an adsorption capacity of 12.89 μmol/g (0.18 mg/g) for NH₄-N [27]. In our previous studies, two composite hydrogels, i.e. poly(acrylic acid)/biotite (PAA/BT) and polyvinyl alcohol semi-IPN (interpenetrating polymer network) poly(acrylic acid)/tourmaline (PVA semi-IPN PAA/Tm), were prepared and used to remove NH₄-N from aqueous solution. The two composite hydrogels showed high affinity to NH₄-N, rendering that the experimental adsorption capacity was 32.87 mg/g for PAA/BT and 32.06 mg/g for PVA semi-IPN PAA/Tm at an initial NH₄-N concentration of 100 mg/L [21,28]. In current work, we used a composite hydrogel, i.e. CTS-g-PAA/UVMT, to remove NH₄-N in synthetic wastewater. The effects of various experimental parameters, such as vermiculite content, pH, contact time, NH₄-N concentration, co-existing PO₄-P ion and ion strength were investigated. The adsorption isotherms for NH₄-N onto the composite hydrogel, as well as the reusability studies were also investigated.

2. Materials and 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, with an degree of deacetylation of 0.90 and average molecular weight of 3.0 × 10⁵, Zhejiang Yuhuan Ocean Biology Co., Ltd., Zhejiang, China) were used as received. Unexpanded vermiculite (UVMT, Longyan Colloidal Co., Ltd., Fujian, China) was milled through a 320-mesh screen prior to use, with a chemical composition of analytical SiO₂ 44.23 wt.%, Al₂O₃ 15.10 wt.%, Fe₂O₃ 14.26 wt.%, MgO 16.69 wt.%, CaO 4.02 wt.%, TiO₂ 0.92 wt.%, MnO 0.13 wt.%, K₂O 3.64 wt.%, Na₂O 0.24 wt.%, and P₂O₅ 0.06 wt.%.

A 1000 mg/L stock standard solution of NH₄-N was prepared by dissolving an appropriate amount of ammonium chloride (dried to constant mass at 100–105 °C) in 1000 mL of distilled water. A series of working standard solutions were prepared by an appropriate dilution of the stock solution. The initial pH value was adjusted by addition of 0.1 and 1.0 mol/L NaOH or HCl solutions to designed value (Mettler Toledo FE20 pH-meter). Other reagents used were all analytical grade and all solutions were prepared with distilled water unless stated otherwise.

2.2. Preparation of CTS-g-PAA/UVMT composite hydrogel

A series of composite hydrogels from CTS, AA, and UVMT were prepared according to the following procedure [29]. 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, 0.15 g MBA and an appropriate amount of UVMT was added. The oil bath was kept at 80 °C for 4 h to complete the polymerization reaction. When the reaction was finished, the resulting product was neutralized with 2.0 mol/L NaOH solution to neutral pH, dehydrated with methanol and dried at room temperature, by which a granular composite hydrogel was formed (Fig. S1, Supporting Information). All adsorbent samples used for test had a particle size in the range of 40–80 mesh.

2.3. Swelling degree and swelling ratio

In 200 mL of distilled water, an accurately weighed composite hydrogel (0.05 g) was immersed and separated from unabsorbed water at set interval or equilibrium (4 h) by filtrating with a 100-mesh stainless screen and hanging up for 10 min. The swelling degree (SD) and swelling ratio (SR) were calculated from the following equations:

$$SD = \frac{m_s - m_d}{m_d} \quad (1)$$

$$SR = \frac{Q}{Q_e} \quad (2)$$

where m_s and m_d were the swollen and dry weight of each composite hydrogel, while Q and Q_e denoted the swelling degree at set interval and at equilibrium, respectively.

2.4. Adsorption experiment

Adsorption measurements were performed in a series of 50 mL conical flasks containing 0.05 g hydrogel adsorbent and 25 mL NH₄-N solution. The mixtures were shaken in a thermostatic shaker (THZ-98A) at 30 °C/120 rpm for a given time, and then the adsorbent was separated by direct filtration. The NH₄-N concentration in the solution was measured according to Nessler's reagent

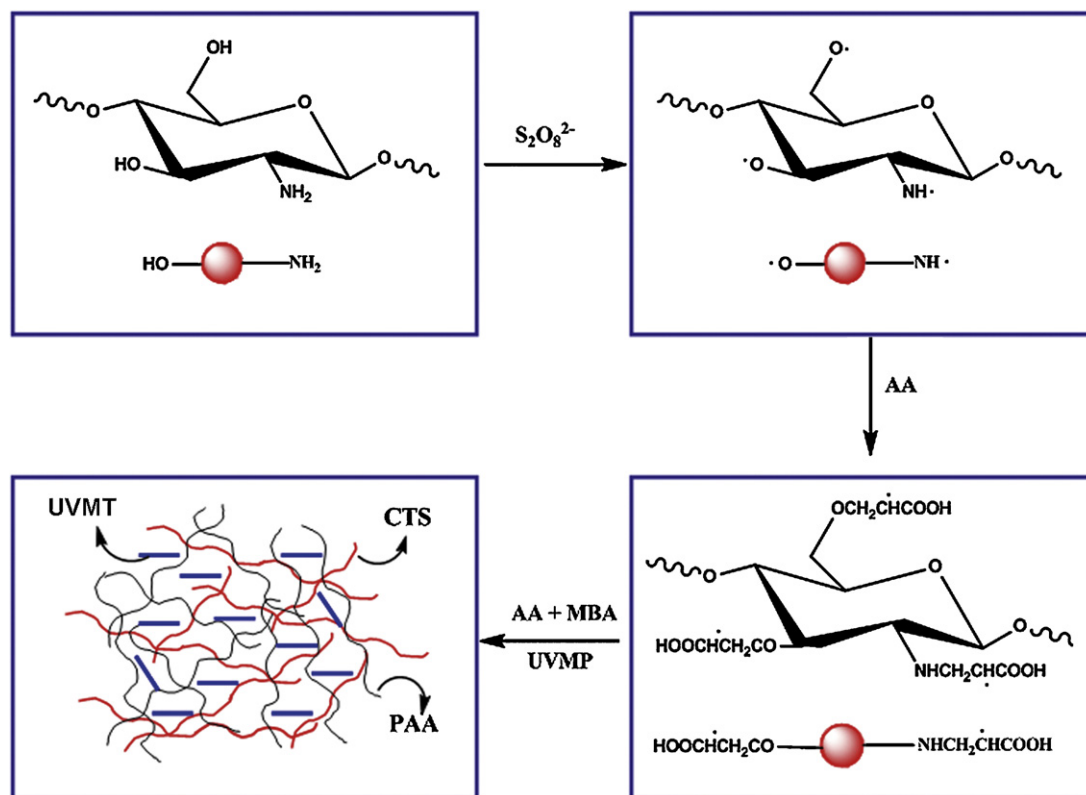


Fig. 1. Schematic preparation of CTS-g-PAA/UVMT composite hydrogel.

colorimetric method. The adsorption capacity of the as-prepared hydrogel for NH_4-N was calculated from the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (3)$$

where q_e is the adsorption capacity of NH_4-N onto adsorbent (mg/g), C_0 is the initial NH_4-N concentration (mg/L), C_e is the equilibrium NH_4-N concentration (mg/L), m is the mass of adsorbent used (mg), and V is the volume of NH_4-N solution used (mL).

To study the optimum adsorption conditions of the as-prepared adsorbent material, batch adsorption experiments were carried out at different contact times ranged from 0 to 60 min to illustrate the adsorption equilibrium at an initial NH_4-N concentration of 100 mg/L and natural pH. The pH-dependence was performed at different initial pH values (2.0–10.0) with an initial NH_4-N concentration of 100 mg/L and contact time of 30 min. For the adsorption isotherm studies, the initial NH_4-N concentration was kept within 25–1000 mg/L with contact time of 30 min and natural pH. To evaluate the effects of ion strength on NH_4-N removal, the adsorption behaviors were investigated in other water bodies including tap water, well water and lake water.

2.5. Competitive experiment

During the competitive experiment, 0.05 g composite hydrogel was added into the mixing solution containing NH_4-N with fixed concentration of 100 mg/L and PO_4-P with different concentrations. The residual amount of NH_4-N was determined according to Nessler's reagent colorimetric method, and PO_4-P present in the solution was analyzed by ammonium molybdate spectrophotometric method (GB 11893-89, in Chinese).

2.6. Reusability

Reusability was determined according to the following procedures: (i) 0.05 g dried composite adsorbent was immersed in 25 mL NH_4-N solution with the concentration of 100 mg/L and shaken in a thermostatic shaker at 30 °C/120 rpm for a given time, and the adsorbent was separated by direct filtration. The analytical result was recorded as the first adsorption capacity; (ii) the separated NH_4-N -loaded adsorbent was stirred in 25 mL 0.1 mol/L NaOH solution for 10 min. After separation, the adsorbent was eluted with 20 mL distilled water for several times. The regenerated adsorbent was contacted again with 25 mL 100 mg/L NH_4-N solution to obtain the second adsorption capacity; (iii) a similar procedure was repeated and the adsorption capacity for multicycle adsorption–desorption process was then achieved.

2.7. Characterization

FTIR spectra were recorded on a Thermo Nicolet NEXUS TM spectrophotometer using KBr pellets. The surface morphologies of the samples were observed using a JSM-5600 scanning electron microscope (SEM) after coating the samples with gold film. To observe clearly the pores formed, the morphologies of freeze-dried composite hydrogel were also observed with SEM after freeze-drying.

3. Results and discussion

3.1. Description of CTS-g-PAA/UVMT

In this study, CTS-g-PAA/UVMT can be formed in aqueous solution by a synchronous chemical graft of PAA onto CTS backbone and crosslinking reaction of MBA (Fig. 1). A general reaction

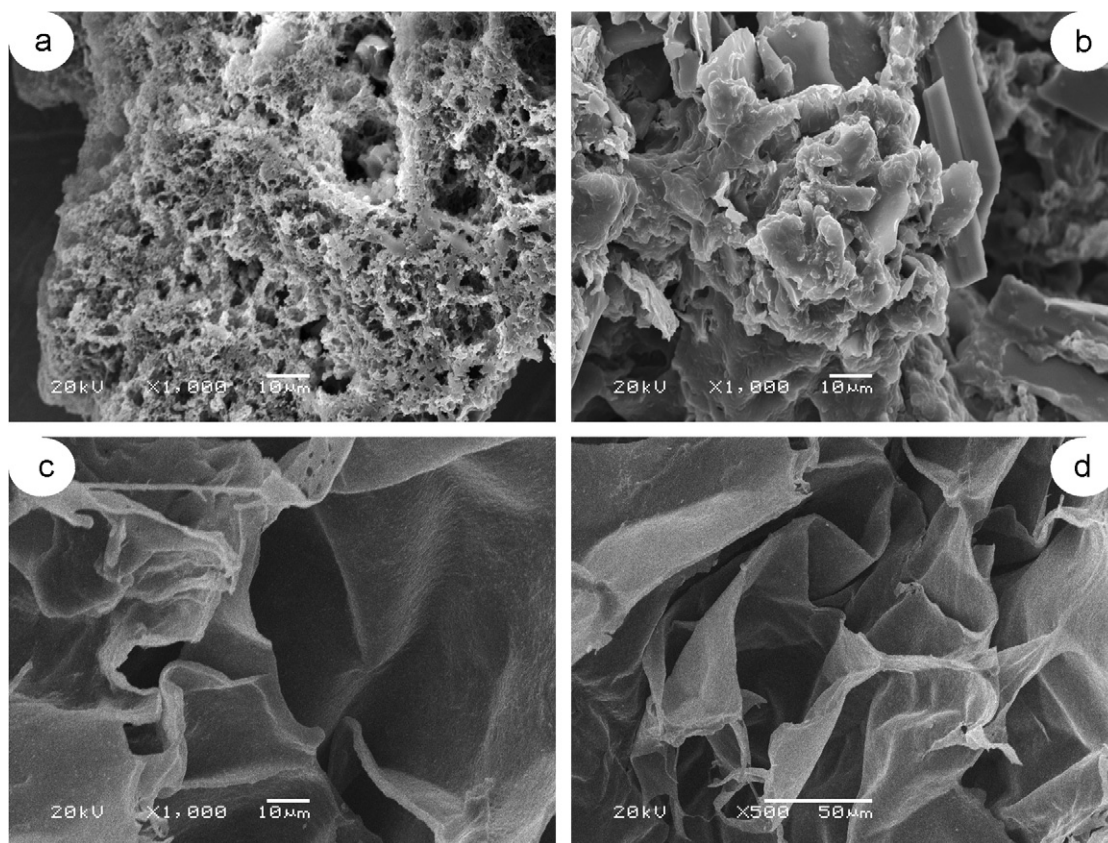


Fig. 2. Scanning electron micrographs of (a) CTS-g-PAA (1000 \times), (b) CTS-g-PAA/UVMT (1000 \times), (c) freeze-dried CTS-g-PAA/UVMT (1000 \times) and (d) freeze-dried CTS-g-PAA/UVMT (500 \times).

mechanism for forming the three-dimensional networks is proposed as follows. Under heating, the initiator APS is decomposed to generate a sulfate anion radical. Then, the resulting anion radical abstracts hydrogen from one of the functional groups ($-\text{NH}_2$ or $-\text{OH}$) on CTS backbone to form the corresponding radical. Consequently, these macro-radicals initiate the grafting of vinyl monomers AA onto CTS backbone. During the polymerization, the sheets of vermiculite would be exfoliated and dispersed in the polymer matrix, and simultaneously, the crosslinking reaction occurs in the presence of MBA, forming thus a composite hydrogel with three-dimensional networks. Our previous studies proved that the reactive functional groups of CTS, such as $-\text{NH}_2$ and $-\text{OH}$, had taken part in the grafting reaction by which PAA was grafted onto CTS backbone [14].

As shown in SEM images (Fig. 2a and b), the composite hydrogel CTS-g-PAA/UVMT shows a similar coarse and porous surface with that of sample without UVMT. SEM micrographs of porous structures prepared by freeze-drying process are displayed in Fig. 2c and d. From the freeze-dried sample, we can observe the interconnected open channels, i.e. three-dimensional networks with thin pore walls. One can speculate that this coarse and porous surface would increase the surface area for water permeation, making the water easily diffuse into the composite hydrogel [30]. That is to say, $\text{NH}_4\text{-N}$ ions are easily accessible to the active adsorption sites within the three-dimensional polymeric networks, and accordingly, the adsorption system would reach its equilibrium in a very short time. To demonstrate the process of rapid water diffusion into the polymeric networks, the swelling data at 5 min and 4 h (swelling equilibrium) had been determined (Fig. S2, Supporting Information). The results indicate that at 5 min, the swelling ratio SR can reach 79.43% and 84.28% for CTS-g-PAA and CTS-g-PAA/UVMT (40 wt.%), respectively.

3.2. Effect of UVMT content on adsorption capacity

With increasing the UVMT content in the adsorbent, a monotonic decrease in the adsorption capacity was observed (Fig. S3, Supporting Information). It seems that the adsorption capacity of the as-prepared hydrogel adsorbent is correlated with the number of carboxylate groups in the adsorbent. That is, the adsorption is credited to the presence of $-\text{COO}^-$ groups within the polymeric networks and adsorption of $\text{NH}_4\text{-N}$ onto this type of adsorbent is mainly controlled by the electrostatic attraction between the negative charged adsorption site of the adsorbent ($-\text{COO}^-$) and the positive charged adsorbate (NH_4^+). Generally, clays are natural, abundant, and inexpensive materials that have high mechanical strength and chemical resistance. Vermiculite is a member of the phyllosilicate group of minerals, resembling mica in appearance. During the polymerization process of the as-prepared composite hydrogel, vermiculite can be exfoliated into small sheets and then dispersed finely in the polymeric networks [29]. The clay sheets embedded within the polymeric networks can improve the gel strength, and the immobilization of clay sheets within the hydrogel can also prevent coagulation of dispersed clay sheets [31]. The UVMT does not cause an increase in the adsorption capacity for $\text{NH}_4\text{-N}$ because the adsorption capacity of UVMT is determined as 7.0 mg/g, quite lower compared to the pure organic hydrogel CTS-g-PAA (26.9 mg/g). Due to lower adsorption capacity of UVMT, a decrease was observed in the adsorption capacity for hydrogel adsorbent having higher clay ratio. Nevertheless, the adsorption capacity was higher than the physical mixture of UVMT and CTS-g-PAA, and the difference in the adsorption capacity increased with increasing the UVMT content. Furthermore, the addition of UVMT is expected to provide the following properties: (i) can reduce the production cost as UVMT is abundant and inexpensive, (ii) can

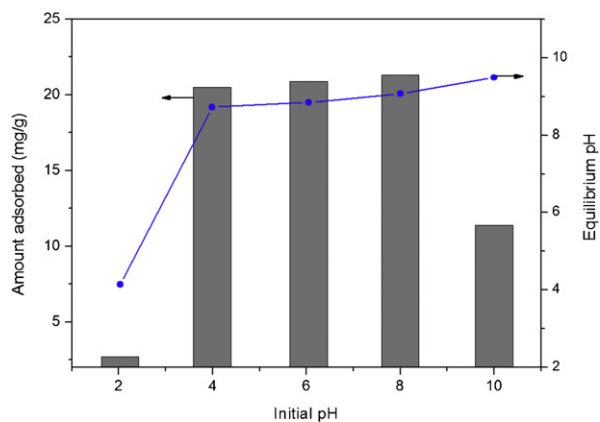


Fig. 3. Adsorption capacity as a function of pH values. Adsorption conditions: contact time, 30 min; 120 rpm; 30 °C; initial $\text{NH}_4\text{-N}$ concentration, 100 mg/L.

enhance the hydrogel strength as more UVMT particles will serve as physical fillers in the polymeric networks, (iii) even more importantly, can reduce the swelling degree, as lower swelling degree is more beneficial for an adsorption process. Compared with CTS-g-PAA, the as-prepared composite hydrogel CTS-g-PAA/UVMT shows a decreasing swelling degree (Fig. S2, Supporting Information), with the decrease percentage of 9.97% at 5 min and 15.16% at swelling equilibrium. Here, it should be mentioned that when 40 wt.% UVMT was involved in the hydrogel adsorbent, the adsorption capacity of the as-prepared composite adsorbent can still reach to 21.7 mg/g, and thus, CTS-g-PAA/UVMT (40 wt.%) was selected as the adsorbent for further study.

3.3. Effect of pH on adsorption capacity

For an adsorption process, pH is one of the most important parameters affecting the adsorption capacity. As shown in Fig. 3, the adsorption capacity for $\text{NH}_4\text{-N}$ onto CTS-g-PAA/UVMT kept roughly constant in the pH range of 4.0–8.0. However, as the pH was lowered to the strongly acid region or increased to the strongly basic region, a sudden decrease in the adsorption capacity was observed. Owing to a small amount of CTS used in the preparation of adsorbent and also, most of the active amino groups of CTS have participated in the copolymerization, the number of $-\text{COOH}$ and $-\text{COO}^-$ groups (as a function of pH) within the polymeric networks plays a vital role in controlling the nature of the composite hydrogel, and accordingly, the adsorption capacity will be affected. The pK_a of PAA is about 4.7 [32,33], then the $-\text{COOH}$ groups can be easily ionized above pH 4.7. Furthermore, when the pH value is larger than 5.7, the $-\text{COOH}$ groups in the PAA chain can be completely dissociated, i.e. all the $-\text{COOH}$ groups can be ionized when $\text{pH} > 5.7$ [32,34].

During the adsorption process, the final pH (the solution pH after the adsorption equilibrium) is even more important for affecting the adsorption capacity for $\text{NH}_4\text{-N}$. It is the final equilibrium pH (not the initial pH) that will dominate the ionization of $-\text{COOH}$ groups. When the initial pH in this study was fixed from 2.0 to 10.0, the equilibrium pH was measured to be within the range of 4.1–9.5 (Fig. 3). Obviously, the equilibrium pH is larger than 5.7 when the initial pH is investigated from 4.0 to 8.0. That is to say, the $-\text{COOH}$ groups in the PAA chain have been completely dissociated (ionized) in this range. Furthermore, after the adsorption, the equilibrium pH values keep almost a constant within pH range of 4.0–8.0. Based on above information, a pH plateau for $\text{NH}_4\text{-N}$ adsorption will be anticipated in the pH range of 4.0–8.0. At lower pH value (such as initial pH 2.0), partial $-\text{COO}^-$ groups will be protonated, and accordingly, the electrostatic attraction between adsorbent and adsorbate

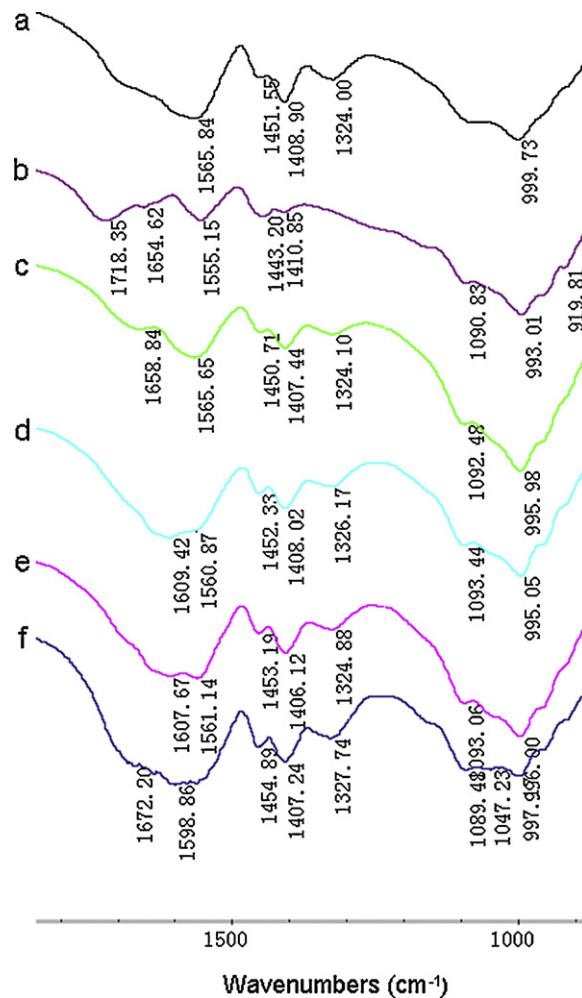


Fig. 4. FTIR spectra of CTS-g-PAA/UVMT before (a) and after the adsorption (b–f): (b) pH 2.0, (c) pH 4.0, (d) pH 6.0, (e) pH 8.0, and (f) pH 10.0.

will be diminished, which is responsible for the decreased adsorption capacity for $\text{NH}_4\text{-N}$ [21,28,35]. At higher pH values (such as initial pH 10.0), $\text{NH}_4\text{-N}$ is neutralized by hydroxyl ion rendering it uncharged [36] and the ion strength of $\text{NH}_4\text{-N}$ solution is increased, resulting in also a decrease in the adsorption capacity. Even then, the as-prepared composite hydrogel is proved to be a viable adsorbent for $\text{NH}_4\text{-N}$ removal due to its pH-independence within pH range of 4.0–8.0.

The changes in the characteristic $-\text{COOH}$ and $-\text{COO}^-$ groups within the polymeric networks can be reflected from the FTIR spectra before and after the adsorption at different pH values. As shown in Fig. 4, we have found the characteristic asymmetric and symmetric vibration absorption bands lying respectively at 1566 and 1409 cm^{-1} in the spectrum of original composite hydrogel. After the adsorption at pH 2.0, the characteristic absorption bands of $-\text{COO}^-$ groups get weakened, and meanwhile, a new absorption band at 1718 cm^{-1} ascribed to $-\text{COOH}$ group is observed, suggesting the transform of partial $-\text{COO}^-$ to $-\text{COOH}$ groups. With increasing pH from 2.0 to 4.0, the stretching vibration of $-\text{COOH}$ groups get weakened and the intensities of asymmetric/symmetric vibration absorption bands of $-\text{COO}^-$ groups show a gradual increase. Afterwards, no obvious changes are observed in the FTIR spectra. From FTIR spectra, it is clearly observed that the $-\text{COOH}$ groups can be almost completely dissociated at initial pH 4.0, when equilibrium pH is determined to be higher than 5.7, a pH value all $-\text{COOH}$ groups have been ionized. The results from FTIR

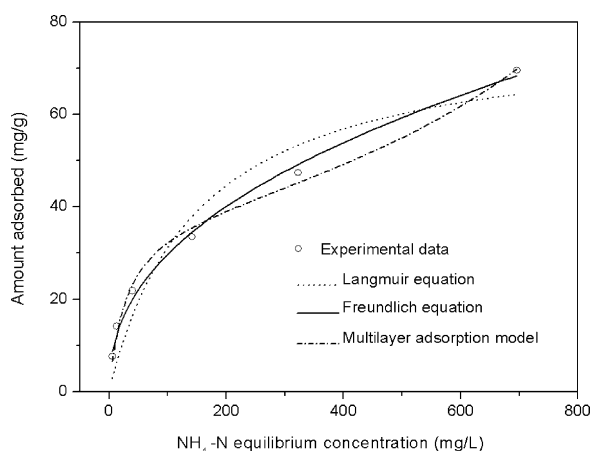


Fig. 5. The change of adsorption capacity as a function of equilibrium $\text{NH}_4\text{-N}$ concentration. Adsorption conditions: contact time, 30 min; 120 rpm; 30°C ; natural pH.

analysis are consistent with those obtained from pH effects, confirming that the electrostatic attraction between -COO^- groups and $\text{NH}_4\text{-N}$ dominates the whole adsorption process. Also, FTIR analysis can demonstrate the pH plateau for $\text{NH}_4\text{-N}$ removal within pH range of 4.0–8.0.

3.4. Effect of contact time on adsorption capacity

It is clearly observed that the maximum adsorption capacity was achieved within a few minutes (Fig. S4, Supporting Information), meaning its faster adsorption kinetics for $\text{NH}_4\text{-N}$ removal. The as-prepared CTS-g-PAA/UVMT possesses super-hydrophilic characteristics which make the size of polymeric networks increase when contacting with water, leading thus an expansion in the size of three-dimensional networks as a result of stronger electrostatic repulsion generated by the ionization of PAA chains. The size expansion of the three-dimensional networks can increase its porosity and diminish the diffusion resistance for an adsorbate, permitting the adsorption system to attain equilibrium within a few minutes. When the adsorption equilibrium is achieved, the adsorption capacity is found to be 21.7 mg per gram of adsorbent.

3.5. Adsorption isotherms

The adsorption of $\text{NH}_4\text{-N}$ onto CTS-g-PAA/UVMT was studied at different initial $\text{NH}_4\text{-N}$ concentration to determine the adsorption isotherms. It is observed from Fig. 5 that the amount adsorbed for $\text{NH}_4\text{-N}$ increased gradually by increasing $\text{NH}_4\text{-N}$ concentration, as a result of increasing driving force of concentration gradient.

Analysis of the adsorption equilibrium data is important to optimize the adsorption process and to illustrate the adsorption mechanism. In this study, three most common isotherm equations namely, Langmuir, Freundlich and Multilayer adsorption models were employed.

Langmuir's model of adsorption predicts the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent. The isotherm equation assumes that the adsorption takes place at specific homogeneous sites within the adsorbent,

which implies that all adsorption sites are identical and energetically equivalent. Langmuir equation can be expressed as following [37]:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (4)$$

where q_e is the equilibrium adsorption capacity of $\text{NH}_4\text{-N}$ on adsorbent (mg/g), C_e is the equilibrium $\text{NH}_4\text{-N}$ concentration (mg/L), and the definition of q_e and C_e is the same thereafter. q_m is the monolayer adsorption capacity of the adsorbent (mg/g) and b is the Langmuir adsorption constant (L/mg). These parameters can be determined by non-linear regression of the experimental data.

Freundlich isotherm endorses the heterogeneity of the surface and assumes that the adsorption occurs at sites with different adsorption energies, which varies as a function of surface coverage. Freundlich isotherm is represented as following [38]

$$q_e = K C_e^{1/n} \quad (5)$$

where K is a constant related to the adsorption capacity and $1/n$ is an empirical parameter related to the adsorption intensity, which varies with the heterogeneity of the adsorption material.

Multilayer adsorption model considers that the adsorption takes place in a multilayer equilibrium on a homogenous surface, and the total multilayer adsorption capacity (q_e , mg/g) can be expressed by the following equation [39]:

$$q_e = \frac{q_m K_1 C_e}{(1 - K_2 C_e)[1 + (K_1 - K_2)C_e]} \quad (6)$$

where q_m is the monolayer adsorption capacity (mg/g), K_1 and K_2 are the equilibrium adsorption constants of the first and second layers, respectively (L/mg). It can be seen that for an ideal monolayer adsorption, K_2 will have a value of zero, and then Eq. (6) will be reduced to the monolayer Langmuir isotherm of Eq. (4).

Data obtained from $\text{NH}_4\text{-N}$ adsorption are fitted against Langmuir, Freundlich, and Multilayer adsorption model, as shown in Fig. 5. The isotherm parameters and corresponding coefficient R^2 are summarized in Table 1. The results indicate that the adsorption data can be described by Freundlich isotherm or Multilayer adsorption isotherm. The composite hydrogel used in this study has an interconnected three-dimensional network with thin pore walls and functional anionic carboxylate groups are distributed uniformly along the polymeric networks. Then, the adsorption sites are speculated to be identical. Apparently, the adsorption may reveal the heterogeneity of the adsorption surface, but this is attributable to the fact that the swollen three-dimensional polymeric networks can also "capture" and "immobilize" some $\text{NH}_4\text{-N}$ ions.

Based on above-mentioned discussions, the adsorption mechanism of $\text{NH}_4\text{-N}$ onto CTS-g-PAA/UVMT is mainly due to the electrostatic attraction between positively charged $\text{NH}_4\text{-N}$ and negative charged -COO^- groups. When the adsorbent is immersed in an aqueous solution, the water molecules penetrate quickly into the composite hydrogel and dissociate -COOH groups to -COO^- groups, resulting in a dimensional increase of polymeric networks as a result of the repulsion between negative charges on carboxylate groups. And then, $\text{NH}_4\text{-N}$ ions are diffused and trapped within the polymeric networks due to the ionic interaction. The schematic illustration of electrostatic attraction between $\text{NH}_4\text{-N}$ and CTS-g-PAA/UVMT is shown in Fig. 6.

Table 1
Isotherm constants for $\text{NH}_4\text{-N}$ adsorption onto CTS-g-PAA/UVMT composite hydrogel.

Langmuir model			Freundlich model			Multilayer adsorption model			
q_m	b	R^2	K	n	R^2	q_m	K_1	K_2	R^2
78.23	6.64×10^{-3}	0.9281	4.13	2.33	0.9956	37.65	3.65×10^{-2}	6.80×10^{-4}	0.9947

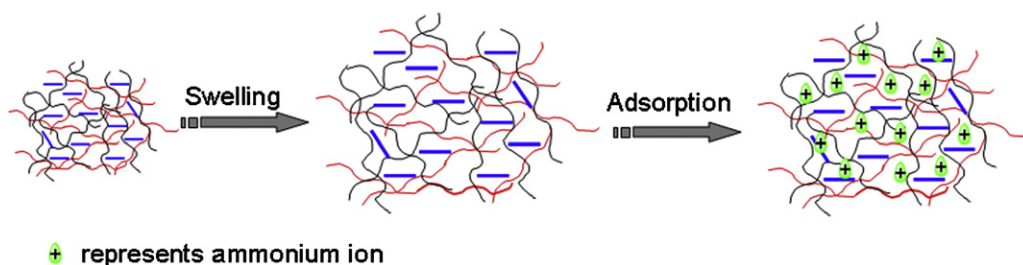


Fig. 6. Model scheme for the adsorption of $\text{NH}_4\text{-N}$ onto CTS-g-PAA/UVMT.

Table 2

The amount adsorbed for $\text{NH}_4\text{-N}$ onto different adsorbents.

Adsorbent	Adsorption conditions			Monolayer adsorption capacity (mg/g)	Reference
	$\text{NH}_4\text{-N}$ concentration (mg/L)	Contact time	pH		
Natural zeolite	5–120	8 h	5.0	6.30	[40]
Zeolite	0–200	4 h	6.5	23.83	[41]
Zeolite	10–300	75 min	8.0	28.65	[42]
Clinoptilolite	11.12–115.16	1.5–2.5 h	6.0	1.74	[43]
Clinoptilolite	25–150	40 min	/	5.166–8.121	[44]
Sepiolite	150–7000	6 h	/	25.49	[45]
Volcanic tuff	20–300	3 h	7.5	13.64	[46]
AS-SBA-15 ^a	50–700	1 h	3.0–7.0	25.4–52.4	[47]
PAA/BT ^b	10–2000	30 min	4.0–9.0	344.47	[21]
PVA/PAA/Tm ^c	13–130	30 min	3.0–8.0	33.78–42.74	[28]
CTS-g-PAA/UVMT	25–1000	30 min	4.0–8.0	78.23	This study

^a Arene-sulphonic acid-SBA-15.

^b Poly(acrylic acid)/biotite.

^c Polyvinyl alcohol semi-IPN poly(acrylic acid)/tourmaline.

To compare the adsorption capacity of the as-prepared composite hydrogel with other adsorbents reported in the literature, the monolayer adsorption capacity (i.e. q_m) calculated from Langmuir equation was used. As one of the most important parameters, q_m can predict the adsorption limit when all the adsorption sites have been occupied, and thus can be utilized as a reasonable data for comparing the adsorption capacities. As listed in Table 2, the hydrogel adsorbents exhibit several advantages over other adsorbents, including high adsorption capacity, fast adsorption rate, and wide pH-independence. As the hydrogel material, CTS-g-PAA/UVMT is prepared with a granular form, while PAA/BT and PVA/PAA/Tm are present in gel form which requires more energy to dry, to smash and to granulate. All the results give an indication that the as-prepared composite hydrogel is a potential and reliable adsorbent for $\text{NH}_4\text{-N}$ removal from aqueous solution.

3.6. Effects of co-existing $\text{PO}_4\text{-P}$ and ion strength on adsorption capacity

Generally, $\text{PO}_4\text{-P}$ would coexist with $\text{NH}_4\text{-N}$ in a eutrophicated water body. Then in this section, the effect of co-existing $\text{PO}_4\text{-P}$ on adsorption capacity was firstly investigated in a mixed solution containing $\text{NH}_4\text{-N}$ and $\text{PO}_4\text{-P}$. Fig. 7 shows the variation of amount adsorbed for $\text{NH}_4\text{-N}$ in a series of solutions containing $\text{PO}_4\text{-P}$ with different concentrations. It is observed that the adsorption capacity decreased with increasing $\text{PO}_4\text{-P}$ concentration. Nevertheless, the adsorption capacity was observed to be as high as 20 mg/g even when 25 mg/L $\text{PO}_4\text{-P}$ was present in the solution. However, the residual $\text{PO}_4\text{-P}$ concentration in the solution was linear to the initial $\text{PO}_4\text{-P}$ concentration with the expression of $y = x + 0.17$ (regression coefficient $R = 1$) where y and x denotes the residual and initial $\text{PO}_4\text{-P}$ concentration, respectively (inset in Fig. 7). That is to say, in the mixed solution containing $\text{NH}_4\text{-N}$ and $\text{PO}_4\text{-P}$, CTS-g-PAA/UVMT can exclusively adsorb $\text{NH}_4\text{-N}$ while $\text{PO}_4\text{-P}$ is remained, a strong

evidence that the electrostatic attraction is the main adsorption mechanism for the adsorption of $\text{NH}_4\text{-N}$ onto CTS-g-PAA/UVMT.

In order to study the effect of ion strength on adsorption capacity, the efficacy of the as-prepared composite hydrogel in different water bodies, including tap water, well water and lake water, was assessed and compared with that in distilled water, as summarized in Table 3. Tap water, well water and lake water were collected from Lanzhou, Xuyi county (Jiangsu) and Taihu Lake in Jiangsu. The results indicate that the adsorption capacity shows a decreasing tendency in the order of distilled water, tap water, lake water and well water. Obviously, pH cannot produce some negative effects on the adsorption capacity for that the as-prepared composite hydrogel has a wide pH application range (Fig. 3). Then, the decrease in the

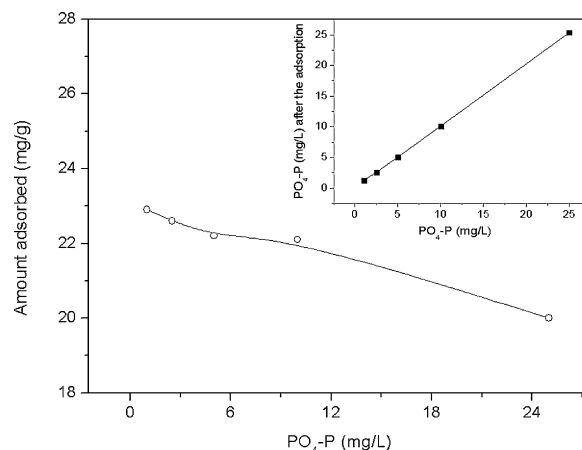


Fig. 7. The variation of amount adsorbed for $\text{NH}_4\text{-N}$ in a series of solutions containing $\text{PO}_4\text{-P}$ with different concentrations. Adsorption conditions: contact time, 30 min; 120 rpm; 30 °C; initial $\text{NH}_4\text{-N}$ concentration, 100 mg/L; natural pH. The inset shows equilibrium $\text{PO}_4\text{-P}$ concentration against initial $\text{PO}_4\text{-P}$ concentration.

Table 3
Adsorption capacities in different water bodies.

Water body	pH	Conductivity ($\mu\text{S}/\text{cm}$, 25 °C)	Adsorption capacity (mg/g)
Distilled water	6.22	18.0	21.7
Tap water	7.97	476	16.2
Well water	7.70	661	4.87
Lake water	8.09	588	12.8

Adsorption conditions: contact time, 30 min; 120 rpm; 30 °C; initial $\text{NH}_4\text{-N}$ concentration, 100 mg/L.

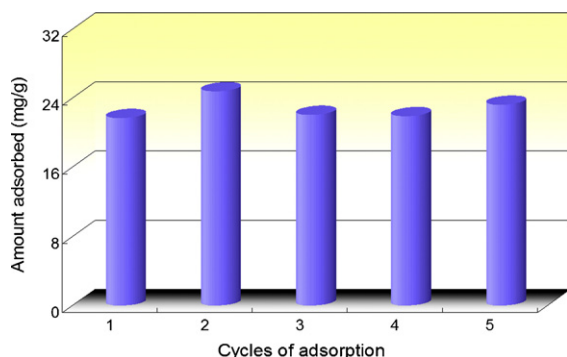


Fig. 8. The amount adsorbed for $\text{NH}_4\text{-N}$ as a function of cycles of adsorption. Adsorption conditions: contact time, 30 min; 120 rpm; 30 °C; initial $\text{NH}_4\text{-N}$ concentration, 100 mg/L; natural pH. Desorption conditions: 25 mL 0.1 mol/L NaOH/10 min, 20 mL distilled water/5 min/twice.

adsorption capacity arises from the ion strength in different water bodies, and as reflected in conductivity, the adsorption capacity is in inverse proportional to the ion strength. Nevertheless, the results from the effects of co-existing $\text{PO}_4\text{-P}$ and ion strength indicate that the as-prepared composite hydrogel shows high affinity to $\text{NH}_4\text{-N}$.

3.7. Reusability

The regeneration of an adsorbent may be crucially important for keeping the process costs down and to open the possibility of recovering the pollutant extracted from the solution. For this purpose, it is desirable to desorb the adsorbed pollutants and to regenerate the spent adsorbent material for another cycle of application. In this study, the preliminary experiments have proved that $\text{NH}_4\text{-N}$ adsorbed on the composite hydrogel can be effectively desorbed with 0.1 mol/L NaOH solution within 10 min. As shown in Fig. 8, no noticeable changes in the adsorption capacity are observed after five cycles of adsorption–desorption process, confirming the reusability of developing composite hydrogel and demonstrating that the as-prepared composite hydrogel is amenable to efficient regeneration and reusable for multicycle adsorption.

4. Conclusion

Adsorption studies were investigated for $\text{NH}_4\text{-N}$ removal from aqueous solution onto a composite hydrogel, CTS-*g*-PAA/UVMT. The results indicate that the as-prepared composite hydrogel shows good affinity to $\text{NH}_4\text{-N}$, with the adsorption capacity of 21.7 mg/g even if 40 wt.% UVMT is incorporated. The adsorption system can reach equilibrium within a few minutes and shows pH-independence in a wide pH range (4.0–8.0). The as-prepared composite hydrogel can exclusively absorb $\text{NH}_4\text{-N}$ in the mixed solution containing $\text{NH}_4\text{-N}$ and $\text{PO}_4\text{-P}$, and can be easily regenerated with no conspicuous losses in the adsorption capacity. Electrostatic attraction is predominant during the adsorption process. Besides the advantages over traditional adsorbents, including fast adsorption rate, high adsorption capacity, easy separation,

wide pH application range and mild regeneration, the composite hydrogel can be prepared with granular form, and is more beneficial as an efficient adsorbent material for $\text{NH}_4\text{-N}$ removal from aqueous solution.

Acknowledgement

This work is supported by the National Natural Science Foundation of China (No. 21107116).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cej.2011.10.064.

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