

Original Research

Preparation of Chitin Composite Hydrogel for Dye-Contaminated Water Treatment

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Abstract

Chitin is the most abundant natural amino polysaccharide. In this study, chitin was dissolved in 8% NaOH/6% urea solution by freezing/thawing method and then was blended with sodium alginate solution, attapulgite powder and epichlorohydrin. This mixture was set aside for 12 hours at 25°C without agitation. By this simple blending and setting aside method, a novel chitin composite hydrogel for dye-contaminated water treatment was prepared. A cross-linked structure was proved by Fourier transform infrared spectroscopy (FTIR). Freeze-dried composite hydrogel exhibited a porous structure and rod-like attapulgite was distributed on the wall of pores, which was observed by scanning electron microscopy (SEM) images. Swelling test showed that sodium alginate significantly enhanced the swelling of chitin-sodium alginate hydrogel compared to the pure chitin hydrogel. Adsorption test to methylene blue solution showed that adsorption capacity of composite hydrogel changed with the content of attapulgite and increased with the increase of initial concentration of methylene blue. The maximum adsorption capacity was 116.6 mg g⁻¹. Adsorption kinetic is best described by pseudo-second order model. Adsorption isotherm agrees well with Freundlich model. Chitin composite hydrogel is a promising adsorption material for dye-contaminated water treatment.

Keywords: chitin attapulgite, sodium alginate, methylene blue, adsorption material, adsorption

Introduction

Chitin, poly[(1→4)-linked N-acetyl-β-D-glucosamine], is the most abundant amino polysaccharide in nature [1]. Chitin existed in the exoskeleton of arthropods, insects, and the cell walls of fungi, yeast [2]. Especially, chitin in the seafood wastes such as waste crab, shrimp, and lobster shells is abundant. This biopolymer is biodegradable, non-toxic and has been

extensively investigated as adsorbents for the removal of hazardous materials from wastewater [3, 4].

Chitin is highly crystalline due to the strong hydrogen bonding in hydroxyl groups and acetamide groups in linear structure [5]. This high crystallinity leads to poor solubility of chitin in common solvents, which limits its application. Recently, NaOH/urea aqueous solution has been reported as a direct solvent that can dissolve chitin via a freezing/thawing method to obtain chitin solution [6]. Using this solvent, chitin was been fabricated to hydrogels to treat dye-contaminated effluents [7]. Hydrogel has cross-linked structure and hydrophilic groups. When immersed

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in dye-contaminated effluents, dry hydrogel swell and absorb a large amount of dye solution [8]. Enhancing the swelling ability of hydrogel is beneficial to the adsorption [9]. The common used method is introducing hydrophilic groups or ionic groups into the structure, such as grafting polymerization of acrylamide [10] or sodium acrylic. Carboxylate anion(-COO⁻) in molecular chain of sodium polyacrylic repel each other via electronic repulsion, which expand the network of hydrogel. This expansion significantly enhances the swelling of hydrogel. But sodium polyacrylic is difficult to be degraded in nature.

Alginate is a nature polysaccharide extracted from marine brown algae [11]. It is a block copolymer of β -D-mannuronic acid and α -L-guluronic acid residues, linked by (1 \rightarrow 4) glycosidic bonds. These two residues all have carboxyl group (-COOH). When extracted in alkaline conditions, carboxyl groups changed to carboxylate anion(-COO⁻) and alginate exists as sodium alginate. Sodium alginate is water-soluble, nontoxic and degradable in nature and widely been used in food and biomaterial. Using sodium alginate to enhance the swelling of chitin hydrogel has never been reported.

To further enhance the adsorption properties of hydrogel, inorganic adsorbents are incorporated into the hydrogel such as laponite [12], sepiolite [13], and halloysite nanotubes [14]. Attapulgite is a kind of hydrated octahedral layered magnesium aluminum silicate whose theoretical formula is $(Al_2Mg_2)Si_8O_{20}(OH)_2(OH_2)_4 \cdot 4H_2O$. Attapulgite has rod-like morphology with diameter of 20 nm and length of several micrometers [15]. Due to this rod-like morphology and nanoscale size, attapulgite has high specific surface area and widely applied in adsorption of pollutants such as heavy metals and dyes from wastewater. Si⁴⁺ in attapulgite can be isomorphic substituted by some ions, such as Al³⁺, forming negatively charged sites (Si-O⁻) [16]. These negative charges are beneficial for adsorbing dye with positive charge [17]. But attapulgite suspends in water, leading to the difficulty of separation from the water after adsorption. Combination of attapulgite with hydrogel to form composite hydrogel to avoid above problem [18, 19]. Chitin-attapulgite hydrogel has never been reported.

In this study, we demonstrate a simple method to prepare a novel chitin-sodium alginate/attapulgite composite hydrogel under mild conditions. Influences of content of sodium alginate and attapulgite on the swelling degree of composite hydrogel were studied. Adsorption properties of composite hydrogel for methylene blue(MB) were studied. This study may provide a basis for the application of chitin composite hydrogel as adsorbents for dye-contaminated water.

Material and Methods

Materials

NaOH, urea, epichlorohydrin, and methylene blue (methylthionium chloride C₁₆H₁₈N₃SCl) were all A.R. grade. Chitin was provided by Shanghai Aladdin Biochemical Technology Co., Ltd. Sodium alginate was provided by Shanghai Qingxi Chemical Technology Co., Ltd. Attapulgite was provided by Jiangsu dianjinshi Au soil Mining Industry Co., Ltd. Distilled water was used in all experiments.

Preparation of Composite Hydrogel

2 g chitin powder was dispersed in 100 g 8 wt% NaOH/6 wt% urea solutions and then was cooled to -20°C to freeze. Then the ice was thawed at 25°C and was agitated to form chitin solution. 2 g sodium alginate was dissolved in another 8 wt% NaOH/6 wt% urea solution (100 g) at 25°C. The above two solution were blended by certain weight ratio, the total weight is kept at 50 g. 7 mL epichlorohydrin was dispersed into above blend. The resultant mixture was stand at 25°C for 12 h to obtain hydrogel. Hydrogel was freeze-dried after been removed the residual reagent by immersing in distilled water. hydrogels with weight ratio of 5:1, 4:1, 3:1, 2:1, and 1:1 (chitin solution: sodium alginate solution) were coded as CA5-1, CA4-1, CA3-1, CA2-1, and CA1-1, respectively. Pure hydrogel without sodium alginate was coded as C.

Composite hydrogels were prepared based on CA2-1. Attapulgite powder was added into chitin-sodium alginate solution blend whose weight ratio is 2:1. Then 7 mL epichlorohydrin was added. The mixture was set aside at 25°C for 12 h to obtain composite hydrogel. Composite hydrogel was freeze-dried after been removed the residual reagent by immersing in distilled water. The mass of attapulgite were 1, 3, 5, 7, 10 g and the prepared composite hydrogels were coded as CAA-1, CAA-3, CAA-5, CAA-7, CAA-10, respectively.

Characterization

Surface morphology of freeze-dried composite hydrogel was observed by scanning electron microscopy (SEM, JSM-7800, JEOL). The structure of composite hydrogel was detected by Fourier transform infrared spectroscopy (FTIR) spectrometer (Thermo Fisher Nicolet iS10). Wide-angle X-ray diffraction (XRD) measurement was carried out on an XRD diffractometer (D8-Advance, Bruker). The patterns with the Cu K α radiation at 40 kV and 30 mA were recorded in the region of 2 θ from 5° to 70°. Absorbance was measured with UV-Vis spectrophotometer (VARIAN Cary 50).

Swelling Degree Measurement

CA5-1, CA4-1, CA3-1, CA2-1, CA1-1, CAA-1, CAA-3, CAA-5, CAA-7, and CAA-10 were immersed in distilled water, respectively. Each hydrogel was weighted until the weight is not increase. The swelling degree, S , was calculated by the final weight W_f and the initial weight W_0 .

$$S = \frac{W_f - W_0}{W_0} \quad (1)$$

Dye Adsorption Capacity Measurement

0.1 g CAA-1, CAA-3, CAA-5, CAA-7, and CAA-10 were immersed in 50 mL methylene blue (MB) solution of 202.8 mg L^{-1} at 25°C for 72 h. Concentration of final MB solution ($C_e/\text{mg L}^{-1}$) was calculated by absorbance of 664 nm via standard curve of MB. The adsorption capacity, $Q/\text{mg g}^{-1}$, was calculated by Eq. (2).

$$Q = \frac{(C_0 - C_e)V}{m} \quad (2)$$

The initial dye concentration of the solution, $C_0/\text{mg L}^{-1}$, is 202.8 mg L^{-1} . The volume of the solution, V/L , is 0.05 L. The original weight of the sample, m/g , is 0.1 g.

Adsorption Capacity at Different Initial Concentration of MB

0.2 g CAA-3 was immersed into 0.05 L MB solution at 25°C for 72 h at initial concentration of 100, 200,

300, 400, 500 mg L^{-1} , respectively. Adsorption capacity was calculated by Eq. (2).

Results and Discussion

Preparation

Composite hydrogel was prepared by blending and setting aside under mild condition. Chitin is dissolved in 8 wt% NaOH/6 wt% urea solutions by freezing-thawing method and a viscous solution was obtained. At low temperatures, NaOH hydrates bond with chitin by hydrogen bonding, then urea hydrates are attached outside of the NaOH-chitin complex, leading to the chitin dissolution [20].

Sodium alginate can dissolve in 8 wt% NaOH/6 wt% urea solutions at 25°C . This solution was blended with chitin solution at 25°C to get a homogenous solution. Attapulgite powder was added into above solution and was agitated to disperse in solution to enhance the adsorption capacity of hydrogel. Epichlorohydrin was dispersed in above mixture as small droplets. Then the mixture was set aside for 12 hours at 25°C without agitation. In this period, chitin and sodium alginate were cross-linked by epichlorohydrin and hydrogel formed. The prepared composite hydrogel (CAA-3) is shown in Fig. 1. Yellow color comes from the color of attapulgite which has light yellow color.

Polysaccharides reacted with epichlorohydrin to form cross-linked structure is a facile method to prepare hydrogel [7, 21]. The cross-linked structure of composite hydrogel is described in Fig. 1. Epichlorohydrin has one epoxide rings and one chloride in molecular structure. In high alkaline medium (8%NaOH/6% urea solution),

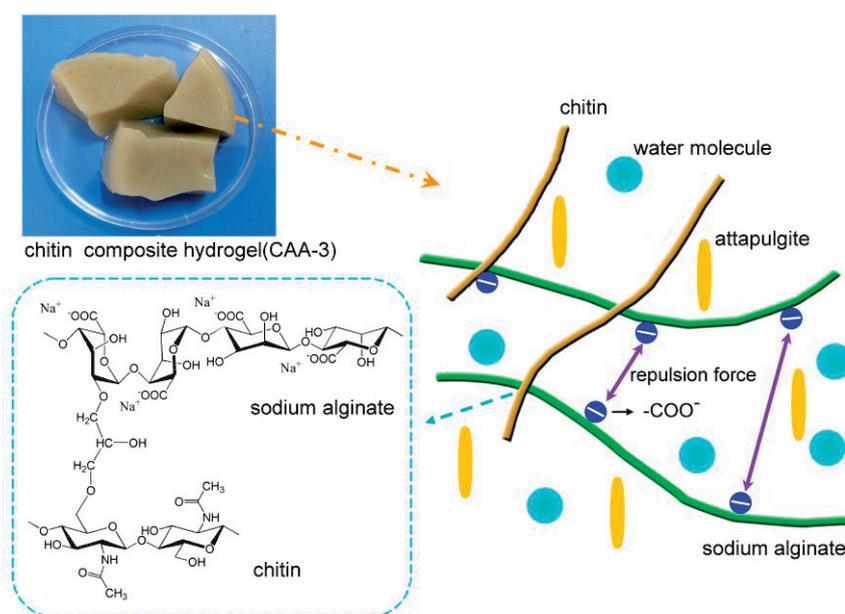


Fig. 1. Schematic depiction of the cross-linking structure of composite hydrogel.

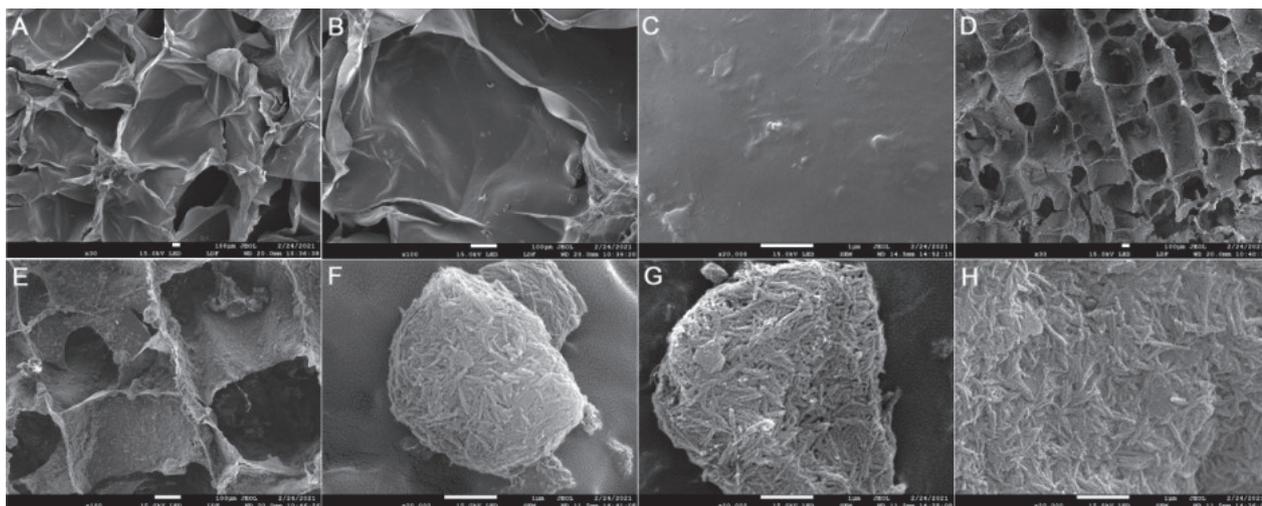


Fig. 2. SEM images of chitin-sodium alginate hydrogel (CA2-1) (A, B, and C) and composite hydrogel (CAA-3) (D, E, F, G, and H).

epoxide rings open up and react with hydroxyl groups of chitin or sodium alginate via etherification. This etherification reaction also occurred between chloride of epichlorohydrin and hydroxyl groups of chitin or sodium alginate. Using this facile blending and setting aside at 25°C method, composite hydrogels were prepared.

Morphology and Structure

Fig. 2 shows SEM images of chitin-sodium alginate hydrogel (CA2-1) (Fig. 2(A-C)) and composite hydrogel (CAA-3) (Fig. 2(D-H)). CA2-1 and CAA-3 all have porous structure (Fig. 2A, D). This porous structure is facile for methylene blue molecules accessing into the interior of composite hydrogel through the porous structure.

Pores in CA2-1 has smooth surface (Fig. 2B, C), which indicates that chitin is dissolved well in 8 wt% NaOH/6 wt% urea solution and no residue of undissolved chitin. Pores in composite hydrogel (CAA-3) exhibits a coarse surface (Fig. 2D), on which large amount of particles located (Fig. 2E). These particles are aggregations of rod-like attapulgite (Fig. 2(F-H)). Size of these particles is 5-20 μm . The average length of the rod-like attapulgite in aggregation is about 1 μm .

FTIR spectra of chitin, sodium alginate, chitin-sodium alginate hydrogel (CA2-1), and composite hydrogel (CAA-3) are shown in Fig. 3. In the spectrum of chitin, the absorption peaks at 1647 cm^{-1} and 1531 cm^{-1} belong to amide band I and amide band II, respectively [22]. In the spectrum of CA2-1, Peaks of 1640 cm^{-1} and 1417 cm^{-1} are anti-symmetric stretch vibration and symmetric stretch vibration of COO^-

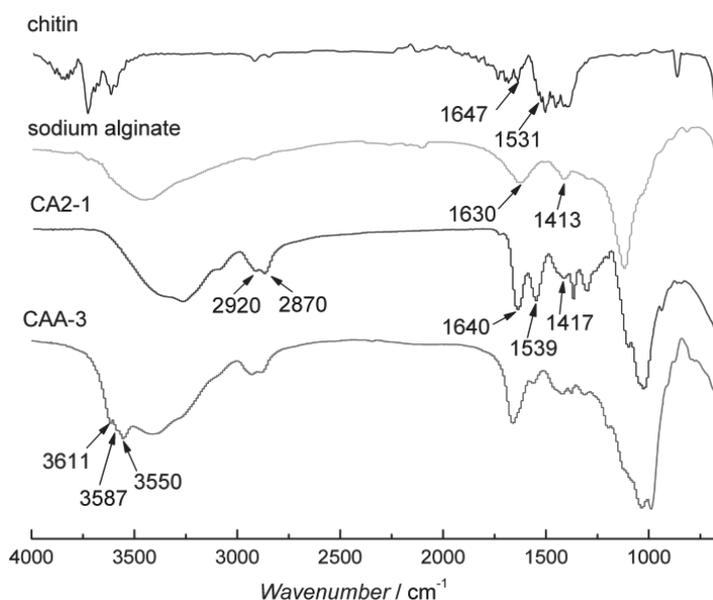


Fig. 3. FTIR spectra of chitin, sodium alginate, CA2-1, and CAA-3.

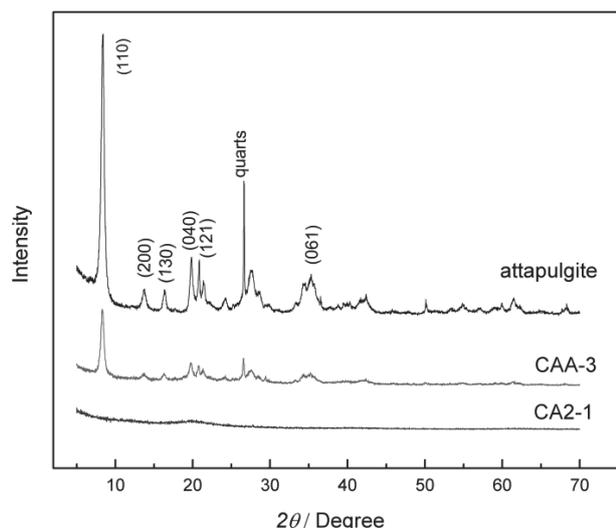


Fig. 4. XRD spectra of attapulgite, CAA-3, and CA2-1.

of sodium alginate, respectively [9]. 1539 cm^{-1} is attributed to amide band I of chitin. 2920 cm^{-1} and 2870 cm^{-1} is attributed to the stretch vibration of $-\text{CH}_2-$. These two peaks strengthened compared to chitin and sodium alginate, meaning the increase of $-\text{CH}_2-$ content. Epichlorohydrin is a chlorinated epoxy compound with $-\text{CH}_2-$ in molecule structure. The cross-linking reaction of chitin and sodium alginate by epichlorohydrin increased the number of $-\text{CH}_2-$ groups in CA2-1 structure. These results indicate that cross-linking of chitin with sodium alginate was successful.

In spectrum of CAA-3, peaks of attapulgite appeared. 3611 cm^{-1} is attributed to the stretching mode of hydroxyls coordinated with the magnesium in attapulgite. 3587 cm^{-1} and 3550 cm^{-1} are attributed to the anti-symmetric and symmetric stretching mode of molecular water coordinated with the magnesium at the edges of the channels of attapulgite [23]. These peaks reveal that attapulgite was successfully incorporated into the hydrogel.

Fig. 4 shows the XRD peaks of attapulgite, CA2-1, and CAA-3. Peak of 8.48° attributes to the (110) crystal face of attapulgite. Other diffraction peaks are assigned as: d(200), d(130), d(040), d(121) and d(061) [24].

These peaks also appeared in CAA-3 in same position, indicates that the crystal structure of attapulgite keep constant during preparation. CA2-1 absence diffraction peaks, indicating the amorphous state of CA2-1.

Swelling Behavior

Fig. 5a) shows the effect of sodium alginate content on swelling degree of chitin-sodium alginate hydrogels (without attapulgite). High sodium alginate content is beneficial to the swelling degree. CA2-1 has largest swelling degree. Swelling degree is an important factor which influences the dye adsorption. Dry hydrogel absorbs dye solution to swell. High swelling degree mean more dye solution was been absorbed into hydrogel. Sodium alginate has carboxylic groups (COO^-) in mannuronic acid and glucuronic acid segments. These negative charged carboxylic groups repel each other due to the static electrical repulsion [25]. This repulsion expand network of chitin and sodium alginate (Fig. 1). With the increase of content of COO^- , expansion of network increased, which increases the swelling degree. Due to the largest swelling degree of CA2-1, composite hydrogels with attapulgite were prepared based on CA2-1.

Fig. 5b) shows the effect of attapulgite content on swelling degree of composite hydrogels (attapulgite inside). Increasing of attapulgite content leads to the decrease of swelling degree. Attapulgite in structure impedes the diffusion of water into the composite hydrogel, leading to a decrease of swelling degree.

Dye Adsorption Capacity

Adsorption capacities of composite hydrogels with different content of attapulgite are shown in Fig. 6. All the composite hydrogel have larger adsorption capacities than hydrogel without attapulgite (CA2-1). attapulgite in hydrogel effectively enhances the adsorption capacity to MB. Increasing attapulgite content, adsorption capacity of composite hydrogel first increases and then decreases.

Attapulgite has nanosized rod-like morphology. Its diameter is 20 nm and length of several micrometers.

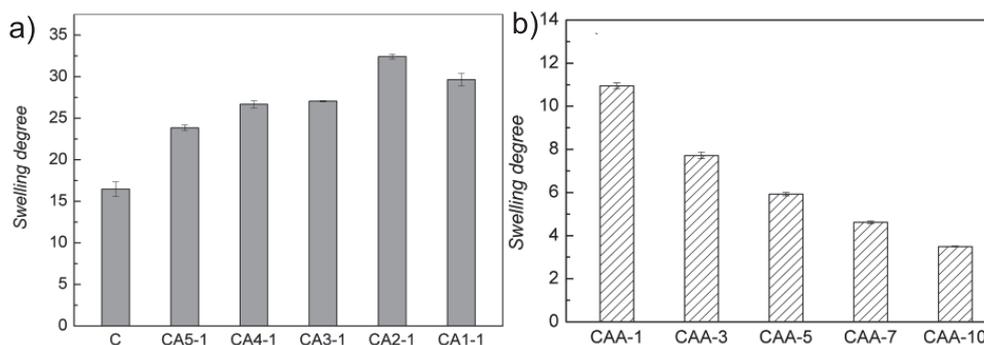


Fig. 5. a) Swelling degrees of chitin-sodium alginate hydrogels; b) composite hydrogels.

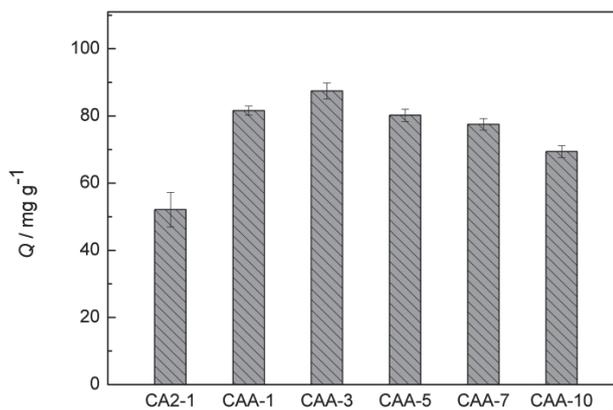


Fig. 6. Adsorption capacities of composite hydrogels with different content of attapulgite.

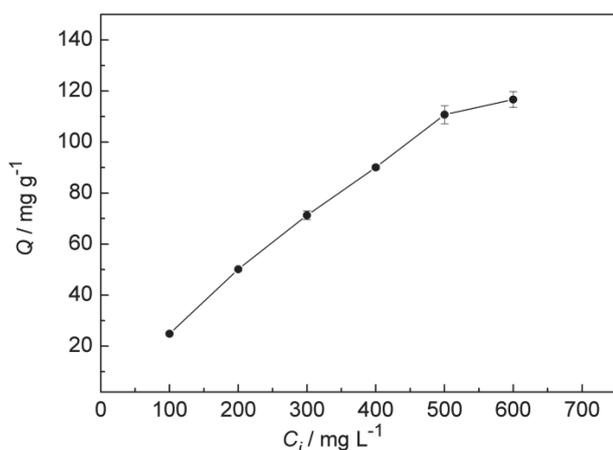


Fig. 7. Effect of initial concentration of methylene blue on the adsorption capacity of CAA-3.

This nanosized rod-like morphology leads to high specific surface area of attapulgite, which is beneficial to contact with more MB molecules. Attapulgite is a

magnesium aluminum silicate with negative charges. Attapulgite adsorbs cationic dyes such as methylene blue via electrostatic attraction. Therefore, high content of attapulgite is beneficial to increase the adsorption capacity. But adsorption capacity correlate to another factor: swelling degree of composite hydrogel. High swelling degree is beneficial for the adsorption of MB as discussed in section of swelling behavior. But increasing content of attapulgite decreases the swelling degree of composite hydrogel as discussed in section of swelling behavior. Due to the competition of two factors, CAA-3 with moderate content of attapulgite has the largest adsorption capacity.

Effects of Initial Concentration of MB on Adsorption Capacity

Fig. 7 shows the effect of initial concentration of MB (C_i) on the adsorption capacity (Q) of CAA-3. With the increase of C_i , Q increases to 116.6 mg L⁻¹ at C_i of 600 mg L⁻¹. This result indicates that adsorption capacity was highly correlated to initial concentration of MB. High MB concentration increases the driving force of concentration gradient, which accelerate the diffusion of MB molecules into the composite hydrogel. As a result, adsorption capacity increases with the increase of initial concentration of MB. This result is similar to the reported study [26].

Maximum adsorption capacities (Q_m) of reported adsorption materials fabricated by nature polymers are summarized in Table 1. Chitin composite hydrogel in this work has moderate adsorption capacity.

Adsorption Kinetic

Adsorption capacity results showed that the CAA-3 has the largest adsorption capacity among the composite hydrogels. Therefore, we chose CAA-3 to investigate its adsorption kinetic and adsorption isotherm. Fig. 8 shows the influence of contact time on adsorption

Table 1. Comparison of maximum adsorption capacities of adsorbents for methylene blue.

Adsorption materials	Q_m / mg g ⁻¹	References
Macroporous composite IPN hydrogels based on poly(acrylamide) and chitosan	749.7	[27]
Chitin/clay microsphere	156.7	[28]
Starch-humic acid composite hydrogel	110	[29]
Magnetic β -cyclodextrin-chitosan/grapheme oxide	84.32	[30]
PAMPS/chitosan hydrogel	74	[31]
Attapulgite	51	[32]
G-Fe ₃ O ₄ /alginate	37.05	[33]
Xylan-gelatin cross-linked reusable hydrogel	26.04	[8]
Cellulose-attapulgite nanocomposite hydrogel	24.3	[9]
Chitin composite hydrogel	116.6	This work

Table 2. Adsorption kinetic parameters of CAA-3 for methylene blue.

Model		Parameters	Value
Pseudo-first order	Linear fitting	k_1/min^{-1}	0.0807
		R^2	0.9441
	Nonlinear fitting	k_1/min^{-1}	0.1742
		χ^2	18.7532
Pseudo-second order	Linear fitting	$k_2/\text{g mg}^{-1} \text{min}^{-1}$	-0.1428
		R^2	0.9794
	Nonlinear fitting	$k_2/\text{g mg}^{-1} \text{min}^{-1}$	0.00721
		R^2	0.9822
		χ^2	2.4691

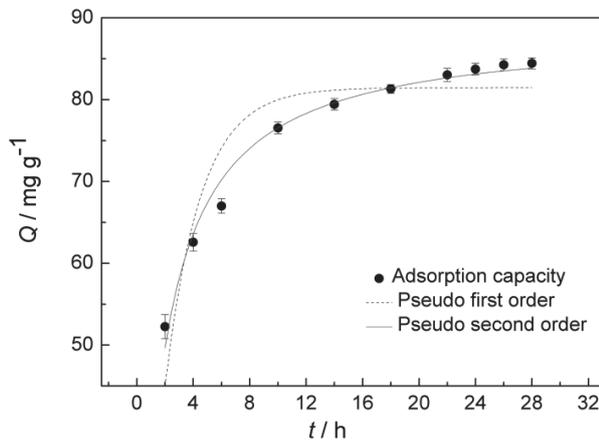


Fig. 8. Effect of contact time on the adsorption capacity of CAA-3.

capacity of composite hydrogel at 25°C. In the initial 10 h, Adsorption capacity increased rapidly. Then adsorption capacity increased slowly and was nearly

constant after 24 h. Experimental data was analyzed by Pseudo-first order model (Eq. (3)) and pseudo-second order model (Eq. (4)).

$$\log(Q_{eq} - Q_t) = \log Q_{eq} - k_1 t \quad (3)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_{eq}^2} + \frac{1}{Q_{eq}} t \quad (4)$$

In these models: k_1/min^{-1} is the first-order rate constant; $Q_{eq}/\text{mg g}^{-1}$ is the amount of dye adsorbed at equilibrium; $Q_t/\text{mg g}^{-1}$ is the amount of dye adsorbed at any time t/min ; $k_2/\text{g mg}^{-1} \text{min}^{-1}$ is the second-order rate constant.

Fig. 8 also shows the non-linear fitting of pseudo-first order and pseudo-second order models. Pseudo-second order model reveals high fitness to the experimental data. The high value of the correlation coefficient (R^2) also proves the fine fitness of pseudo-second order model (Table 2). Pseudo second-order model assumes that the rate-limiting step of adsorption is chemical sorption [34]. This is coordinate with the adsorption behavior of CAA-3. The initial adsorption is relatively rapid, and then the adsorption increases slowly until equilibrium reached. Rapid stage indicates the strong electrostatic interaction between the cationic MB and negatively charged attapulgite. A similar tendency has been reported by other researchers [35].

Adsorption Isotherm

Adsorption isotherm of composite hydrogel was analyzed by Langmuir model and Freundlich model. Langmuir isotherm model assumes the adsorption is monolayer adsorption and can be expressed by Eq. (5)

$$\frac{C_e}{Q_{eq}} = \frac{C_e}{Q_{max}} + \frac{1}{Q_{max} b} \quad (5)$$

Freundlich model describe adsorption occurring on a heterogeneous surface and can be expressed by Eq. (6).

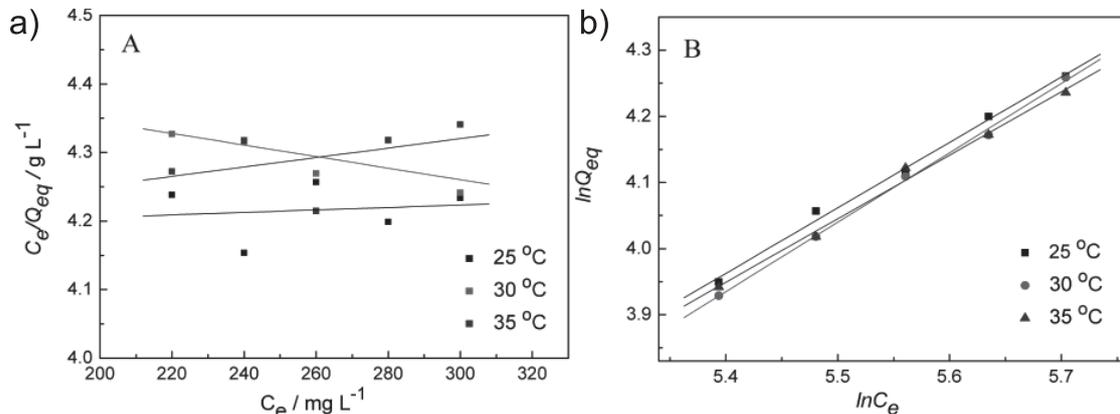


Fig. 9. Fitting curves of isotherm models of CAA-3: a) Langmuir model; b) Freundlich model.

Table 3. Isotherm parameters for methylene blue adsorbed onto CAA-3.

T/°C	Langmuir model			Freundlich model		
	$Q_{\max}/\text{mg g}^{-1}$	$b/L \text{ mg}^{-1}$	R^2	$1/n$	$K_F/\text{mg g}^{-1}$	R^2
25	5571.0306	4.305×10^{-5}	0.01941	0.9897	0.2512	0.9938
30	-1184.1326	-1.8710×10^{-4}	0.5178	1.0501	0.1763	0.9978
35	1452.4328	1.6737×10^{-4}	0.1874	0.9604	0.2904	0.9918

$$\ln Q_{eq} = \frac{1}{n} \ln C_e + \ln K_F \quad (6)$$

$Q_{\max}/\text{mg g}^{-1}$ is the maximum adsorption capacity; $b/L \text{ mg}^{-1}$ is the Langmuir adsorption equilibrium constant. K_F is the Freundlich adsorption capacity parameter, and $1/n$ (dimensionless) is the Freundlich adsorption intensity parameter. Fitting curves of Langmuir and Freundlich isotherm model are shown in Fig. 9(a-b), respectively. Freundlich model fitted well with experiment adsorption data. High value of R^2 of Freundlich model (Table 3) also indicates Freundlich model is a suitable model to describe adsorption isotherm of composite hydrogel. Freundlich model indicates that the adsorption occurring on a heterogeneous surface, which means that methylene blue first be adsorbed by attapulgite on out pores and then diffused into the inner pores of hydrogel and be adsorbed.

Conclusions

Composite hydrogel based on chitin, sodium alginate and attapulgite was fabricated by a simple blending and setting aside method at 25°C. Freeze-dried chitin composite hydrogel has porous structure and rod-like attapulgite locate on the pore surface. Sodium alginate significantly enhanced the swelling degree of hydrogel compared to neat chitin hydrogel. Attapulgite effectively enhanced the adsorption capacity of hydrogel which reached 116.6 mg g^{-1} for methylene blue. Adsorption kinetic and isotherm can be described by pseudo-second order equation and Freundlich equation, respectively. Due to the facile preparation method and the mild preparation condition, chitin-sodium alginate/attapulgite composite hydrogel is a promising material using for removal of methylene blue from water.

Acknowledgments

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Conflict of Interest

The authors declare no conflict of interest.

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