Synthesis, characterization and adsorption properties of a novel chitosan derivative

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A novel chitosan derivative has been synthesized by the dispersible nano-SiO$_2$ (DNS), succinic anhydride, and chitosan in two steps. The structure and morphology of the new material are characterized by fourier transform infrared spectroscopy and scanning electron microscope. Thermogravimetric studies show improvement in thermal character. The effects of initial $p$H, adsorption time, adsorbent dosage and temperature have also been studied. The adsorption equilibrium data are fitted with the Langmuir isotherm ($R = 0.999$), which reveals that the maximum capacity for monolayer saturation is $3.9108$ mmol·g$^{-1}$. Chitosan derivative shows stronger adsorption than chitosan. The optimal adsorption conditions of chitosan derivative are found to be $p$H 5.0, time 4 h, and adsorbent dose 0.1 g respectively.

Keywords: Adsorption property, Chitosan derivative, Dispersible nano-SiO$_2$, Succinic anhydride

Most of heavy metals in aquatic environments are not considered biodegradable and cause severe damage to biological life. Cadmium is harmful for plants, animals and human beings, and can bioaccumulate in organisms and ecosystems, which has been reported to be a potent carcinogen and teratogen. Treatment of wastewater from industries through adsorption is widely studied. The performance of nano-SiO$_2$ modified by $\gamma$–aminopropyltrimethoxysilane, also known as dispersible nano-SiO$_2$ (DNS), was improved in comparison with that of common nano-silica. Chitosan is a linear polysaccharide, produced usually by deacetylation of chitin, which is the structural element in the exoskeleton of crustaceans (crabs, shrimp, etc.). Due to its special structure containing many functional groups such as aminyl or hydroxyl, chitosan can chelate with heavy metal ion through coordination bond. So, chitosan can be used in wastewater treatment through adsorption on heavy metal ion. Presently, the chemical modification of chitosan has been studied extensively to improve its chemical stability and absorbability. There are lots of papers about modifying chitosan molecule, but the studies on chitosan modified by DNS and the properties of chitosan derivative for cadmium ion adsorption are very few.

In the present work, carbonyl group and aminyl functional group have been introduced into the chitosan and a novel chitosan derivative is synthesized. Chitosan derivative is generated from succinic anhydride, DNS and chitosan, and characterized by fourier transform infrared spectroscopy (FTIR), thermogravimetry (TG), and scanning electron microscopy (SEM). The effects of various factors, such as $p$H value, reaction time, temperature and dosage on the adsorption behavior of cadmium ion has also been investigated.

Experimental Procedure

Materials and equipments

Chitosan (deacetylation degree 96%) was purchased from Jin Hu Hengtai County Crustacean Products Co. Ltd; DNS was purchased from Henan Province Nano Technology Co. Ltd; and other reagents were obtained commercially.

FTIR spectra were recorded on a Bruker spectrometer (Tensor 27, Germany). The morphologies of hybrid materials were taken with a SEM (JSM-6301F, Japan Electronics Co. Ltd). Thermogravimetric study was performed using DSC 6200 with Seiko Instruments, Japan.

Preparation of chitosan derivative

Under vigorous stirring, succinic anhydride (2 g) was added to the suspension of DNS (0.5 g) and acetone (60 mL) at 333 K. After 2 h, the reaction...
mixture was cooled to room temperature, the suspension was filtrated, and finally the carboxyl DNS (a), which is white powdery particles, was obtained after drying in vacuum.

In the solvent of isopropanol, the reaction of carboxyl DNS (a) (0.5 g) with chitosan (0.5 g) was carried out for 7 h at 348 K. After reaction, the chitosan derivative (b) in white solid was obtained through filtration and drying. The reaction scheme is shown in Fig. 1.

Adsorption behavior of cadmium ion
Chitosan and its derivative were added respectively into aqueous solution (40 mL) of cadmium ion and agitated for 4 h at 298 K. The supernatant fluid was popped out after high velocity centrifuge separation. Then EDTA complexometric titration was carried out to determine cadmium ion concentration. Adsorption ratio \( A, \% \) and adsorption quantity \( Q, \text{mmol·g}^{-1} \) were calculated respectively by the following equations:

\[
A = \left( \frac{C_0 - C}{C_0} \right) \times 100\% \quad \cdots (1)
\]

\[
Q = \left( \frac{(C_0 - C)V}{W} \right) \quad \cdots (2)
\]

where \( C_0 \) (mmol·L\(^{-1}\)) and \( C \) (mmol·L\(^{-1}\)) are the respective cadmium ion concentration of solution before and after reaction; \( V \), the volume of cadmium ion solution (L); and \( W \), the dried weight (g).

Effect of pH on cadmium ion adsorption
An amount of 0.1 g chitosan and derivative was added respectively into 40 mL of the cadmium ion solution, at different pH values in the range 1-7. Adsorption quantity and adsorption ratio of cadmium ion were calculated using the Eqs (1) and (2).

Effect of reaction time on cadmium ion adsorption
An amount of 0.1 g chitosan and derivative was added respectively into 40 mL of the cadmium ion solution at pH value 5. Cadmium ion concentrations of solution after adsorption were determined at different adsorption time, such as 10, 30, 60, 120 and 240 min.

Effect of absorbent dose on cadmium ion adsorption
Batch experiments were carried out at room temperature (298 K) by separately putting different amounts of chitosan and its derivative, such as 0.05, 0.10, 0.20, 0.25, 0.40 and 0.60 g into the solution. After stirring for 4 h, the cadmium ion concentration of solution was calculated.

Effect of temperature on cadmium ion adsorption and adsorption isotherms
At pH 5.0, chitosan derivative dose 0.1 g, and adsorption time 240 min, the adsorption experiments were carried out at different temperature, such as 293, 298, 303, 313, 323 K. After stirring for 4 h, the cadmium ion concentration of solution was calculated.

At 298 K, pH 5.0, chitosan derivative dose 0.1 g, and adsorption time 240 min, the adsorption isotherms experiment was carried out at the initial Cd\(^{2+}\) concentration of 0.005-0.04 mol·L\(^{-1}\).

Results and Discussion

Infrared spectrum characterization
In infrared spectrum of chitosan, the peaks at around 3437 cm\(^{-1}\) are due to O-H and N-H stretching vibration, at 1622 cm\(^{-1}\) due to -NH\(_2\) characteristic absorption, at around 2923 and 2884 cm\(^{-1}\) due to C-H stretching vibration of methyl and methylene, and at 896 cm\(^{-1}\) due to characteristic peak of β-glycoside linkage.

In infrared spectra of DNS, the peaks at 3424 cm\(^{-1}\) are due to N-H, but C-H stretching vibration of methyl and methylene appear at 2937 cm\(^{-1}\) and 2882 cm\(^{-1}\) respectively. The wide peak at 1102 cm\(^{-1}\) is the characteristic absorption peak of Si-O-Si symmetric stretching vibration.

The FTIR result of carboxyl DNS shows that the characteristic absorption peak of O-H stretching vibration at around 3425 cm\(^{-1}\) is broadened observably than that of the DNS, due to inducting -COOH in molecule\(^{14}\), and peaks at 2945 cm\(^{-1}\) and 2882 cm\(^{-1}\) are strengthened observably than the DNS, which show that the molecule has more -CH\(_2\)-. The strong peak of C=O stretching vibration appears at around 1727 cm\(^{-1}\) and 1643 cm\(^{-1}\). Thus the results of FTIR demonstrate the presence of carboxyl DNS.

In FTIR of chitosan derivative, the peaks of O-H and N-H stretching vibration at around 3428 cm\(^{-1}\) are strengthened and widened observably. The peaks of
C-H stretching vibration of methyl and methylene at around 2918 cm⁻¹ or 2846 cm⁻¹ are strengthened observably, indicating the more alkyl groups -CH₃- introduced into chitosan molecules. The peaks of C=O stretching vibration at around 1644 cm⁻¹ and 1618 cm⁻¹ are strengthened observably than peak of the carboxy DNS which demonstrate more -C=O and N-H groups. The broad peak in the range 1052~1221 cm⁻¹ is the overlap-peak of Si-O-Si symmetric stretching vibration and O-H stretching vibration in chitosan. All the results demonstrate that inorganic DNS is introduced into organic chitosan, and chitosan derivative is generated by the reaction of nucleophilic substitution between nano-size DNS particles and chitosan.

Scanning electron microscope characterization

The difference in structural morphology between DNS and chitosan derivative is further supported by the difference in their SEM images. The SEM images of the surface of DNS and chitosan derivative are shown in Fig. 2, “aggregation” phenomenon takes place in DNS. The rugged structure distributed in the particles of chitosan derivative, and hence some holes and gaps are formed, which are scattered around the surface and interior of chitosan derivative. The structure also indicates that the powerful adsorption capacity of Cd²⁺ of chitosan derivative may arise from such structure and composition, which favors embedding of metal ions into chitosan derivative.

Thermal characterization

Figure 3 shows the TG and DTA curves of chitosan and chitosan derivative respectively. The chitosan shows thermal degradation at two loss stages, one before 108°C and another after 263°C in polymer mass. The thermal degradation of derivative occurs at two different ranges of temperatures, namely before 92°C and after 255°C with different % weight loss respectively. The first one is due to water elimination which is adsorbed physically to the polymer and the second one may be due to the dehydration of the saccharide rings, depolymerization, and decomposition of the polymer. As the intermolecular hydrogen bond becomes weak in chitosan derivative, the thermal decomposition temperature of chitosan derivative
decreases in the first stage. However, the weight loss rate of chitosan derivative becomes slower than chitosan after 336°C, which shows the improvement in thermal stability of derivative.

It can be seen from DTA curve (Fig. 3), that the temperature difference electromotive force of chitosan derivative becomes smaller than that of chitosan after 517°C, indicating that the decomposition rate of chitosan derivative is slower. The results of TGA and DTA reveal that the nano-DNS introduced into chitosan does not affect the degradation mechanism, but thermal stability is improved.

**Cadmium ion adsorption performance**

*Effect of pH on cadmium ion adsorption*

In the adsorption process, the solution pH is one of the important parameters. As shown in Fig. 4, the adsorptive capacity of chitosan and its derivative is very low at pH 1-2. At pH 7.0 and more than 7.0, the solution shows obvious precipitate. As pH is increased, their adsorptive capacity to cadmium ion enhances. There are a large number of aminyl and carbonyl in chitosan derivative, they can form complex with cadmium ion through coordination bond, such as oxygen-cadmium bond and nitrogen-cadmium bond. Therefore, the adsorption rate and quantity after modification are greatly improved. Chitosan derivative chelated with cadmium ion is mainly through active sites such as -C=O, -NH-, -OH, etc. The value of pH can affect the complexation of active sites. In the acidic solution, the conversion of -NH- to -NH$_2$- and the activity of –C=O decreases significantly, which results in the decrease in adsorption to Cd$^{2+}$. With the increase in alkalescence, the adsorbance to Cd$^{2+}$ increases because of increasing active sites. The adsorption capacity decreases after pH value of 5. When pH value is 5, the adsorption effect of cadmium ion is found to be the best, so this is considered as the best adsorption condition.

*Effect of reaction time on cadmium ion adsorption capacity*

As shown in Fig. 5, the adsorption capacity of chitosan and chitosan derivative to cadmium ion is powerful. The adsorption is jumped up rapidly after
10 min, and then up to 120 min, the adsorption quantity and ratio are 3.7480 mmol·g\(^{-1}\) and 78.98\% respectively. This may be due to the presence of many grooves, hydroxyl, carbonyl and aminyl functional groups. Chitosan derivative has high adsorption rate to cadmium ion, which would be useful. When the outer layer of chitosan derivative reaches the saturated adsorption, the Cd\(^{2+}\) ions diffuse into the micropore and subsequently are adsorbed onto the inner hools and gaps of chitosan derivative. With decrease in diffusion rate, adsorption rate slows consequently. Adsorption quantity and ratio are found to be 3.7898 mmol·g\(^{-1}\) and 79.12\% respectively after 4 h. This indicates that the longer the adsorption time, the stronger is the adsorption capacity.

**Effect of absorbent dosage on cadmium ion adsorption**

Figure 6 shows that the adsorption ratio of chitosan derivative is higher than that of chitosan although the adsorption ratio of both enhances with the increase in amount of absorbent. The Cd\(^{2+}\) adsorption ratio onto chitosan derivative is found to be 5.9565 mmol·g\(^{-1}\) with an adsorption rate of 65.67\%. With increasing adsorbent dose, adsorption ratio increases and corresponding adsorption quantity decreases. The best dosage is found to be 0.1 g.

**Effect of temperature on cadmium ion adsorption and adsorption isotherms**

As shown in Fig. 7, the adsorption capacity of the cadmium ions increases with the increase in temperature, which indicates that the adsorption is mainly chemical adsorption. The adsorption quantity of the cadmium ions by chitosan derivative is larger than by chitosan at the same temperature.

Figure 8 indicates that the cadmium ions adsorption quantity on chitosan derivative increases with the initial Cd\(^{2+}\) concentration. But up to a certain level, equilibrium adsorption quantity does not change, which demonstrates the adsorption saturation of adsorbent.
The Langmuir model shows that the adsorbent surface has sites of identical energy and that each adsorbate molecule is assumed to be located on a single site; hence, it predicts the formation of a monolayer of the adsorbate on the adsorbent surface. Figure 9 shows the equilibrium amount of Cd (II) ions adsorbed on the chitosan derivative surface, as well as the equilibrium concentration of this ions. The experimental adsorption data are fitted according to the Langmuir isotherm models. According to equation

\[ \frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{K_L \times Q_m} \]

... (3)

the plot of \( \frac{C_e}{Q_e} \) versus \( C_e \) is obtained in (Fig. 10). From the intercept and the slope, correlation coefficient values (R=0.999) and \( K_L \) (1.7501 L·mmol\(^{-1}\)) can be calculated. The Langmuir isotherm is chosen to interpret the adsorption. The value for the maximum adsorption capacity (\( Q_m \)) is found to be 3.9108 mmol·g\(^{-1}\), which is close to experimental value (\( Q_e = 3.8236 \) mmol·g\(^{-1}\)). Hence, the adsorption of cadmium ions on chitosan derivative is monolayer adsorption.

**Conclusion**

Chitosan derivative has been synthesized by modified DNS and chitosan and then characterized with FTIR, SEM and TG. The effects of solution pH value, reaction time, adsorption dosage and temperature on Cd\(^{2+}\) adsorption capacity are investigated. The adsorption equilibrium data are fitted with the Langmuir isotherm. The results show that chitosan derivative is a good adsorbent of cadmium ion, which provides a new way for removal of heavy metal ion.

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**References**