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Superadsorption of LiOH solution on chitosan as a new type of solvent for chitosan by freezing/blasting

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ABSTRACT

The adsorption behavior and mechanism of chitosan in aqueous LiOH solution was studied systemically. The results showed that the adsorption of chitosan was mainly due to the breakage of its hydrogen bonds, which were destroyed by the reaction of LiOH with the acetyl and the hydroxyl groups of chitosan. Low temperature also played a crucial role in the adsorption of chitosan. The adsorption of chitosan decreased with increased DD. The adsorption ratio of LiOH to chitosan ($n_{\mathrm{LiOH}}/n_{\mathrm{CS}}$) increased linearly while the adsorption ratio of water to chitosan ($n_{\mathrm{H_2O}}/n_{\mathrm{CS}}$) decreased with the increased DD. All chitosans reached their maximal swelling degree when the concentration of LiOH was 4.8 wt%. Chitosan was stable in LiOH aqueous solution. The LiOH solution may be a potential favorable solvent for chitosan.

1. Introduction

It has been a long term effort to seek appropriate solvents for chitosan ever since its discovery (Austin, Brine, Castle, & Zikakis, 1981). Dilute acids have been chosen as the solvents for chitosan for decades (Muzzarelli et al., 2012; Wang, Turhan, & Gunasekaran, 2004). However, chitosan is unstable in acid. Its hydrolysis is accompanied with the cleavage of glycosidic-bonds, which results in decreased molecular weights and higher dispersivity (Aiba, 1991; Muzzarelli, 2012).

Recently, novel chitin products with good mechanical properties have been successfully prepared from aqueous chitin/alkali solution (Goycoolea et al., 2007; Hu et al., 2007; Rinaudo, 2008). And plenty of works concerning the system of chitin and alkali solution have been carried out (Feng, Liu, & Hu, 2004; Liu, Liu, Pan, & Wu, 2008; Noishiki et al., 2003). Moreover, it is proved that the β-(1→4) glycosidic-bonds of chitin and cellulose are stable in alkali at a temperature lower than 170 °C (Knill & Kennedy, 2003), which contributes to the good mechanical properties of the products.

Chitosan is chemically similar to chitin, so it is possible for it to dissolve or swell in alkali aqueous solution with high stability, and to be processed into products with good mechanical properties (Muzzarelli, Tosi, Francescangeli, & Muzzarelli, 2003). However, few works have been carried out in this field (Fan & Hu, 2009; Fan, Hu, & Shen, 2009).

In our current work, chitosans with high molecular weight ($M_\eta \geq 1.5 \times 10^6$) and different DD were prepared by a modified two-step deacetylation process. And they were used to study the adsorption behavior of chitosan in LiOH aqueous solutions.

This work focused on acquiring basic understanding of the adsorption behavior of chitosan in LiOH aqueous solution and providing guidance for the further development of this new-type solvent for chitosan.

2. Materials and methods

2.1. Materials

α-Chitin and α-Chitosan (shrimp shell, powders) supplied by Zhejiang Golden-shell Biochemical Co. Ltd. (China) were used without further treatment.

$LiOH \cdot H_2O$, NaOH, HCl, CH_3COOH, and CH_3COONa were obtained from Sinopharm Chemical Reagent Co. Ltd. (China). All the reagents were of analytical grade, and used without further purification.

2.2. Preparation of partially N-deacetylated chitosan

N-deacetylated chitosan was prepared heterogeneously under the preparing conditions by a modified two-step deacetylation

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process shown as below. 10 g dried α-chitin powder was stirred with 300 mL NaOH in a flask for a certain time. Then the mixture was cooled by the addition of 1000 ml deionized water. After standing at room temperature for 12 h, the solid was washed to neutral with deionized water, and then dried at 60 °C in the oven for 24 h. The prepared N-deacetylated chitosans were coded as CS65, CS70, CS75 and CS80, for the DD of them were 64.2%, 71.9%, 76.7% and 81.4% respectively. And the preparation conditions are as follows:

CS65–90 °C, 50% NaOH and stirred for 1 h;
CS70–80 °C, 55% NaOH and stirred for 2 h;
CS75–85 °C, 50% NaOH and stirred for 2 h;
CS80–90 °C, 55% NaOH and stirred for 4 h.

2.3. The adsorption experiment of chitosan

2.3.1. The adsorption experiment at room temperature

0.500 g chitosan powders were soaked in 100 g LiOH aqueous solution with different concentration ranging from 1.2 wt% to 6.0 wt%. After standing at room temperature for 4 h and adsorbing fully, the sample was filtered with a 60 mesh nylon net and its surface water was removed by a ashless quantitative filter paper with a pore size of 30 μm. The mass of resulted sample was measured precisely and recorded as m_1.

2.3.2. The adsorption experiment with the treatment of freezing–blasting

0.500 g chitosan powders were soaked in 100 g LiOH aqueous solution with different concentration ranging from 1.2 wt% to 6.0 wt%. After standing for 4 h and frozen for 5 h at −60 °C, the sample was taken out from the freeze-dryer and thawed at the low temperature (0–5 °C). The obtained sample was filtered with a 60 mesh nylon net and the mass was recorded as m_2 after precise measurement.

The adsorption of sample was calculated from Eq. (1):

$$A = \frac{m - 0.500}{0.500} \times 100\% \tag{1}$$

where m is the mass of the swollen samples.

For each sample, three parallel experiments were carried out and the average values were taken.

2.4. Measurement

The amount of LiOH and water adsorbed in samples could be determined by conductometric titrations, using a conductivity meter DDS-307 equipped with a Pt electrode. After the adsorption experiment, 5 ml resultant LiOH solution was took and put into a beaker, diluted with 50 ml deionized water, and then titrated with 1.0 M HCl. A curve of the conductivity against the volume of HCl with two inflectional points was obtained. The volume difference of these two points corresponded to the remaining LiOH in the solution after the adsorption. Then the concentration of LiOH after adsorption could be calculated. The amount of LiOH and water adsorbed in samples were calculated according to Eqs. (2) and (3).

$$\text{Adsorbance}_{\text{LiOH}} = C_{\text{LiOH}} \times 100 - \frac{1.0 \times V_{\text{HCl}} \times 24 \times V_{\text{LiOH}}}{5.0} \tag{2}$$

$$\text{Adsorbance}_{\text{H}_2\text{O}} = m_2 - \text{adsorbance}_{\text{LiOH}} \tag{3}$$

For each sample, three parallel experiments were carried out and the average values were taken.

The DD was determined by conductometric titrations according to Raymond, Morin, and Marchessault (1993).

The M_η of prepared samples was calculated from the classical Mark–Houwink relationship,

$$[\eta] = kM^{\alpha} \tag{4}$$

where $[\eta]$ is the intrinsic viscosity, $\alpha = -1.02 \times 10^{-2} \times \text{DD} + 1.82$, $k = 1.64 \times 10^{-30} \times \text{DD}^{14}\ \text{cm}^3\ \text{g}^{-1}$ (Fan et al., 2009). The intrinsic viscosity was measured with an Ubbelonde viscometer at 30 °C using 0.2 M CH_3COOH–0.1 M CH_3COONa as solvent. The solutions were filtered through a P30 glass filter before determining $[\eta]$.

The stability of chitosan in LiOH aqueous solution was evaluated by DD and M_η of the swollen chitosan after adsorption for 1, 3, 5, and 7 days.

In order to characterize the composition of the prepared chitosan, solubility of the prepared chitosan in acid was evaluated by the transmittance of their solution in 0.2 M acetic acid by a UV–vis spectrophotometer (UV-2550, Shimadzu) with a quartz cell and an optical path length of 1000–600 nm. The sample concentration was 5 mg ml^{-1} (Kubota, Tatsumoto, Sano, & Toya, 2000).

X-ray diffraction patterns of powdered samples were obtained by a Bruker AXS D8 Advance X-ray diffractometer, 40 kV and 34 mA with Cu Kα radiation at k 1.5406 Å. The relative intensity was recorded in the scattering range (2θ) of 5–60° with steps of 0.1° s^{-1}. The crystalline index (CrI) was determined by the Hermans–Weidinger equation (Zhang, Haga, Sekiguchi, & Hirano, 2000).

FT-IR spectra were measured on a Vector 22 spectrometer (Bruker) in KBr pellets at ambient temperature. All spectra were recorded with an accumulation of 32 scans and a resolution of 4 cm^{-1} in the range from 4000 cm^{-1} to 500 cm^{-1}.

3. Results and discussion

By dispersing CS65 in the LiOH aqueous solution and freezing–blasting afterward in a covered bottle, CS65 can adsorb large amount of aqueous LiOH and swell highly in the LiOH aqueous solution, with the particles turning into transparent hydrogel.

3.1. Effect of the structure of chitosan

3.1.1. Structural change during the two-step deacetylation

The adsorption behavior of chitosan is closely related to its structure. The structure parameters of prepared chitosan with different DD are shown in Table 1. All the four chitosan can dissolve in 0.2 M acetic acid completely, indicating that the original chitin deacetylates quite homogeneously by our two-step deacetylation process, and the composition of the obtained product is totally chitosan. Generally, with the increase of DD, the molecular weight of chitosan decreases gradually, the crystallinity decreases at first and then increases, and the *d*-spacing increases at first and then decreases except for CS75. This fact indicates the structure of the prepared chitosan is loose at first and then becomes relatively denser with the increase of DD. However, due to their different preparing conditions, CS75 has exceptional looser structure.

3.1.2. Influence of structure on the adsorption

As expected, the adsorption behavior of chitosan prepared by the two-step method shows dependency on the DD. Moreover, by data fitting, the relationship among swelling degree, DD and the concentration of LiOH can be expressed as follows:

$$A = 7346.834 + 60851.79 \times C_{\text{LiOH}} - 7782.139 \times \text{DD}$$
$$(R = 0.874, F = 33.99) \tag{5}$$

The adsorption capacities of CS65, CS70, CS75, and CS80 in water ($C_{\text{LiOH}} = 0$ wt%) are 676%, 675%, 675% and 626%, respectively, which

Table 1
Characteristics of original and N-deacetylated chitosan.

Sample	Solubility in acid by transmittance (%)	DD (%)	M_η (Da)	CrI (%)	d (Å)	
					020	110
Chitin	–	–	–	79.3	9.70	4.79
CS65	98.4	64.2	5.6×10^5	44.4	12.18	4.74
CS70	98.2	71.9	5.3×10^5	59.4	10.92	4.67
CS75	99.0	76.7	4.8×10^5	30.2	12.04	4.71
CS80	98.5	81.4	4.4×10^5	57.9	7.93	4.80

do not have significant differences until the addition of LiOH. Generally, the adsorption decreases as the DD increases. The structure of chitosan is loose at first and then becomes denser with the increased DD. Moreover, the loose structure can facilitate the diffuseness and penetration of hydrated LiOH. Therefore, the swelling ability of chitosan decreases with the increase of DD.

In addition, the adsorption behavior of chitosan toward LiOH and water has inseparable relationship with the DD. By the quantitative determination of the adsorption mass of LiOH and water by the conductometric titrations method, the adsorption behavior of chitosan with different DD is studied in this work.

The results are shown in Fig. 1, from which we can conclude that the adsorption of LiOH on chitosan increases with the increase of DD while the adsorption of water decreases. The amount ratio of absorbed LiOH to chitosan ($n_{\mathrm{LiOH}}/n_{\mathrm{CS}}$) has an approximately linear increase relation with the DD while the amount ratio of absorbed water to chitosan ($n_{\mathrm{H_2O}}/n_{\mathrm{CS}}$) has an approximately linear decrease relation with the DD. The amount ratio of LiOH to water ($n_{\mathrm{LiOH}}/n_{\mathrm{H_2O}}$) also decreases linearly with the increase of DD. When the DD is 65% and 80%, the amount ratio of LiOH to water absorbed by chitosan is around 1:9, 1:6, respectively, which means chitosan with low DD can absorb more water than chitosan with high DD.

In fact, the results of former researches usually showed that chitosan with higher DD could adsorb more water and the reason was with the increase of DD, the content of free amino group increased, as well as the hydrophilicity of chitosan. However, we observed opposite result and CS65, CS70, CS75 and CS80 showed abnormal adsorption behavior in LiOH aqueous solution. This phenomenon may attribute to the following two aspects. The main motivation of the swelling of chitosan in aqueous LiOH solution is the destruction effect of hydrogen bonds in chitosan acted by LiOH. On the one hand, chitosan with high DD has denser structure and stronger hydrogen bonds, making it less vulnerable to the destruction effect acted by LiOH. Therefore, it needs more LiOH to destroy the structure of chitosan and break its intra- and inter-molecular hydrogen bonds. As a result, chitosan with high DD adsorb more LiOH. On the other hand, the structure of chitosan with high DD is too dense for LiOH to destroy completely, so the hydrophilicity of it is restrained and less water can be absorbed. CS65 has looser structure than CS80. That is why CS65 adsorbs more water than CS80.

3.2. Effect of LiOH

Chitosans with four different DD can only swell in water slightly with a swelling degree about 650%, and are still presented as dispersed particles. However, with the addition of LiOH, the adsorption increases significantly and chitosan turns from dispersed particles to gel, with the increasing trend of the adsorption growing flat as the concentration of LiOH increases. When the concentration of LiOH increases from 0 wt% to 1.2 wt%, the adsorption of CS65 increases by six times, from 670% to 4300%. When the concentration of LiOH increases to 4.8 wt%, the adsorption of CS65 reaches the

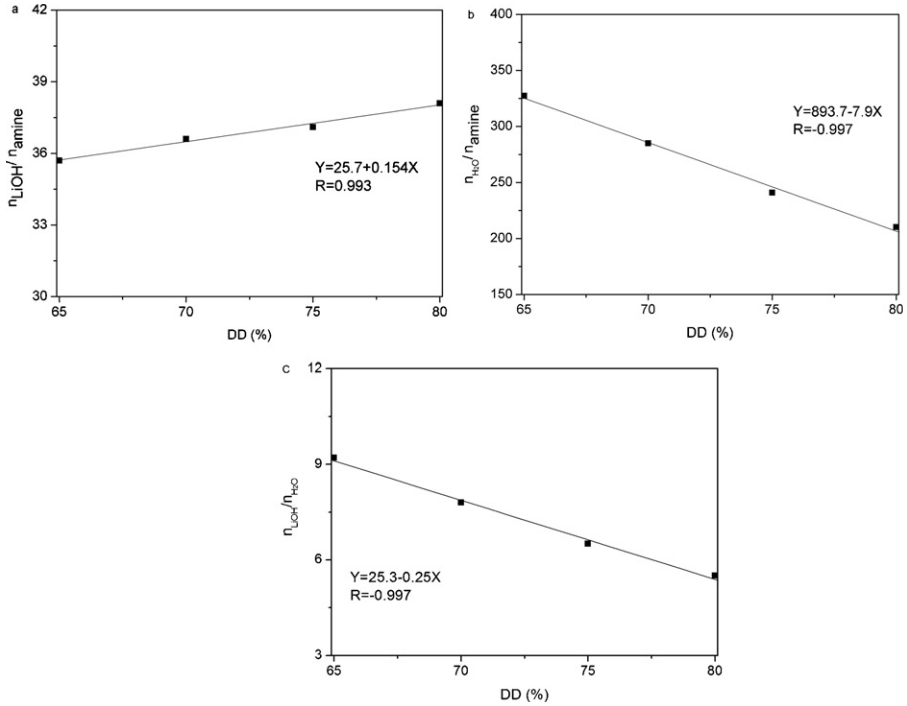

Fig. 1. Dependence of the freezing–blasting adsorption behavior of chitosan to LiOH and water as a function of the DD. (a) $n_{\mathrm{LiOH}}/n_{\mathrm{cs}}$ vs DD; (b) $n_{\mathrm{H_2O}}/n_{\mathrm{CS}}$ vs DD; (c) $n_{\mathrm{LiOH}}/n_{\mathrm{H_2O}}$ vs DD.

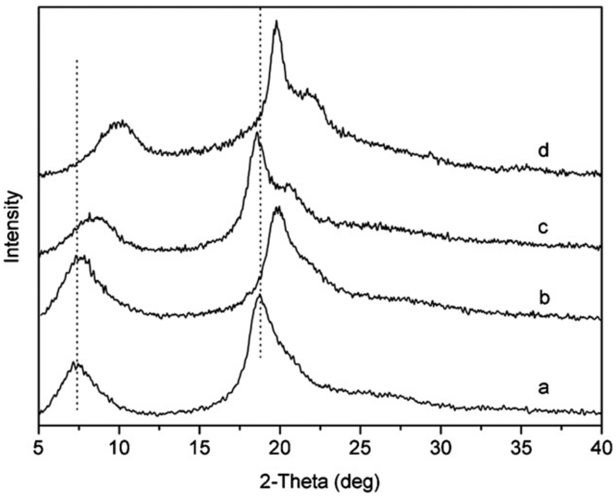

Fig. 2. X-ray diffraction patterns of power of LiOH, CS65, and the freeze-dried swollen sample of CS65 in different solvents. (a) LiOH, (b) CS65, (c) swollen CS65 in 1.2 wt% LiOH aqueous solution and (d) swollen CS65 in 4.8 wt% LiOH aqueous solution.

maximum value of 5560%. Thereafter, the adsorption of CS65 experiences a decrease as the concentration of LiOH increases further. CS70, CS75, CS80 exhibit similar adsorption behaviors as CS65.

LiOH exists in form of $[\mathrm{Li(H_2O)}]_m{}^+$ and $[\mathrm{OH(H_2O)}_n]^-$ in water (Hunt & Friedman, 1983; Rempe et al., 2000). When the concentration of LiOH is low, many water molecules can be bonded by Li^+ and OH^- and the ions are too large in size to enter into the chitosan structure. As the concentration of LiOH increases, the hydrated ions reduce to smaller sizes and can diffuse and penetrate into chitosan more easily, so the adsorption of chitosan increases. However, with the concentration of LiOH increasing further, the water molecules bonded by Li^+ and OH^- become much fewer, resulting in the decrease of adsorption degree instead.

There are large amount of O, H, and N atoms in chitosan molecules, which form very strong hydrogen bonds between each other. Blackwell reported that the intramolecular and intermolecular hydrogen bonds in chitosan form the stacks of hydrogen bonds between parallel chains and the interstack hydrogen bonds. Both the intrastack and interstack hydrogen bonds characterize the special properties of chitin (Minke & Blackwell, 1978). Thus chitosan cannot dissolve in most solvents, although it is hydrophilic. The reason of the swelling of chitosan in the LiOH aqueous solution may be that LiOH can destroy the intra- and inter-molecular hydrogen bonds in chitosan. As a result, the hydrophilic effect of chitosan takes the domination, making it swell in LiOH/H_2O mixture.

Compared with CS70, CS75 and CS80, CS65 has the best adsorbing ability. Therefore, CS65 was chosen to study the effect of freezing–blasting treatment on the adsorption behavior of chitosan, as well as the adsorption mechanism.

Fig. 2 illustrates the X-ray powder diffraction patterns of LiOH, and the freeze-dried samples of CS65 swollen in LiOH aqueous solutions with different concentration. The major peaks at $2\theta = 33.5^\circ$, 36.8°, 31.8° and 29.9° are observed for $LiOH{\cdot}H_2O$ in Fig. 2a (Vasanthan, Shin, & Tonelli, 1996). CS65 has two characteristic diffraction peaks located at $2\theta = 7.3^\circ$ and 18.7° (Fig. 2b).

The swollen and freeze-dried sample of CS65 in 1.2 wt% LiOH aqueous solution (Fig. 2c) has the characteristic diffraction peaks of CS65 and $LiOH{\cdot}H_2O$ at the same time. The diffraction pattern is similar to the superposition of the diffraction patterns of CS65 and $LiOH{\cdot}H_2O$, but the diffraction peaks belonging to CS65 become broader and weaker. When CS65 swells in 4.8 wt% LiOH aqueous solution, its XRD pattern (Fig. 2d) resembles that of $LiOH{\cdot}H_2O$ more and the characteristic diffraction peaks of CS65 almost disappear.

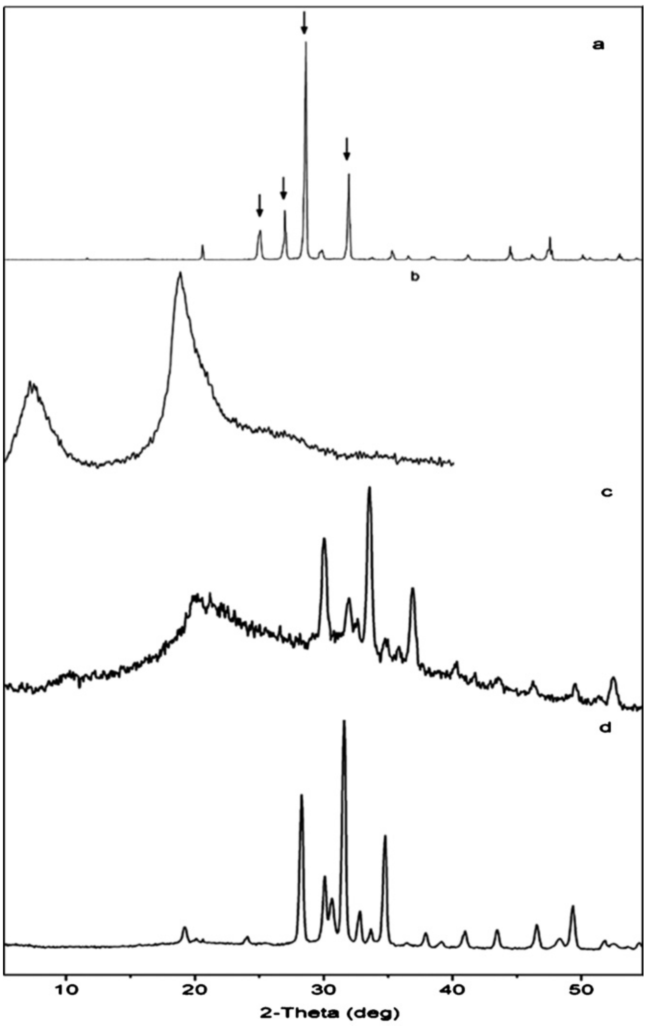

Fig. 3. X-ray diffraction patterns of powder of CS65 and swollen CS65. (a) CS65; (b) CS65 swollen in water at room temperature; (c) CS65 swollen in water by freezing–blasting; (d) regenerated CS65 swollen in 4.8 wt% LiOH solution by freezing-blasting.

These studies indicate that the adsorption behavior of CS65 in LiOH aqueous solution takes place at the amorphous region with a loose structure at first, and then proceeds to the crystal region with a relatively denser structure. Similar results were obtained by Ng too (Ng, Hein, Ogawa, Chandrkrachang, & Stevens, 2007). When the concentration of LiOH is low, the crystals of CS65 cannot be fully destroyed, so parts of the crystal structure of CS65 are maintained in the swollen sample. With the increase of the LiOH concentration, the crystal structure of CS65 is continuously damaged and fully destroyed in the end. At this moment, with the hydrophilic effect taking advantage, CS65 adsorbs large amount of water and swells highly. The interaction between chitosan and LiOH has a high resemblance to the behavior of chitin in NaOH aqueous solution (Liang, Zhang, & Xu, 2007; Rinaudo, 2008).

3.3. Effect of freeze-blasting

CS65 can only swell in LiOH aqueous solution quite slightly at room temperature, while the adsorption of CS65 in LiOH solution experiences a significant increase after the freeze-blasting treatment.

Fig. 3 shows the X-ray powder diffraction patterns of sample a, b, c, and d, which refer to CS65, swollen sample of CS65

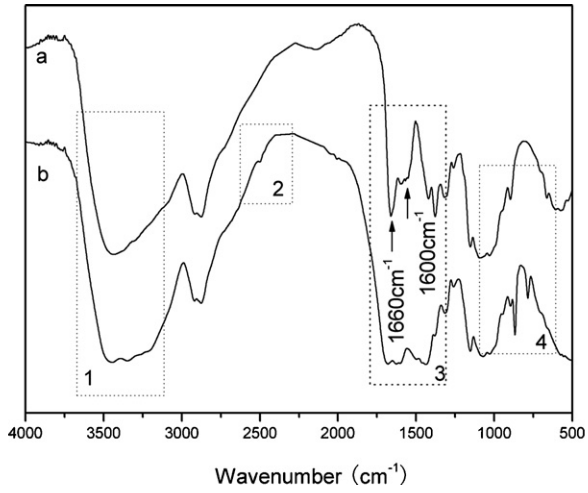

Fig. 4. FT-IR spectra of power of CS65 (a) and freeze-dried swelling. CS65/LiOH gel (b).

in water at room temperature, swollen sample of CS65 in water after freezing–blasting treatment and the regenerated swollen sample of CS65 in 4.8 wt% LiOH treated by freezing–blasting respectively.

The adsorption of water on CS65 almost has no effect on its crystal structure and the swelling only takes place at the amorphous region. In contrast, the sample treated by freezing–blasting experiences a changed crystal structure. This fact indicates that the adsorption starts to proceed to the crystal region and low temperature plays a key role in destruction of the crystal structure of chitosan and the penetration of small molecules into the crystals of chitosan.

LiOH exists in water in the form of $[Li(H_2O)]_m^+$ and $[OH(H_2O)_n]^-$, and protons (H^+) and hydroxide ions (OH^-) have abnormal high activity in the solution (Tuckerman, Marx, & Parrinello, 2002). At room temperature, the rapid exchange between bulk water and coordinated water leads to the unstable structures of $[OH(H_2O)_n]^-$ and $[Li(H_2O)_m]^+$. However, at low temperature, this exchange becomes slow enough that the hydrated ions can maintain its structure, which has an apparent important effect on the diffusion and permeation of the hydrated ions into chitosan. Moreover, it has been proved that chitosan can absorb some water, which exists as bonding-water, intermediate-water and free-water. And the free water can freeze under freezing temperature. With the volume of water increasing, the structure of chitosan can be expanded and the hydrogen bonds of chitosan can be destroyed. In this work, the sample is frozen at first and then thaws slowly at low temperature. During this process, the structure of chitosan was distracted, with the effective diffusion and permeation of $[Li(H_2O)]_m^+$ and $[OH(H_2O)_n]^-$ in chitosan under low temperature, enabling chitosan to swell highly in LiOH aqueous solution. So the freezing–blasting treatment has a great impact on the shift of hydrogen bonds between chitosan and LiOH hydrate, contributing to the superadsorption of aqueous LiOH on chitosan (Lv, Hu, & Shen, 2006).

3.4. Presumable mechanism of adsorption of chitosan in LiOH

Fig. 4 illustrates the FT-IR spectra of the powders of CS65 (a) and the freeze-dried swelling CS65/LiOH gel (b). There are significant differences between spectrum a and b, which are marked with boxes. The absorbance peaks of chitosan which appear at 1660 and 1600 cm^{-1} in spectrum a can be ascribed to the amide I and amide II groups. Compared to spectrum a, the peak of the amide I group in spectrum b weakens remarkably and almost disappears, indicating that LiOH has reacted with the acetyl amino group of CS65. Moreover, the peak at 3450 cm^{-1} in spectrum b which can be ascribed to secondary amine group and hydroxyl group significantly widens and has the trends to break into several small peaks, indicating there may be some reactions on the two groups. According to the references, the hydroxyl groups of chitosan are active and can react with concentrated alkali, thus we can presume that the hydroxyl group of chitosan has reacted with LiOH and the new peaks appearing at 2500 and 785 cm^{-1} probably can be attributed to the replacement reaction between Li$^+$ and the hydrogen in the hydroxyl group of chitosan (Saito, Okano, Gaill, Chanzy, & Putaux, 2000).

Table 2
Structural parameter of CS65 before and after swelling.

Sample	DD (%)	M_η (Da)
D_0	64.2	5.1×10^5
D_1	64.7	4.8×10^5
D_3	66.6	4.6×10^5
D_5	67.8	4.5×10^5
D_7	69.5	4.5×10^5

According to the above analysis, it can be concluded that in the adsorption process of LiOH aqueous solution on chitosan, LiOH not only reacts with the hydroxyl group of CS65, but also reacts with the acetyl amino group of CS65, leading to the weakening of the amide I peak ascribed to acetyl amino group. So LiOH can destroy the hydrogen bonds of chitosan effectively and make chitosan highly swell or even dissolve in the solution of LiOH.

3.5. Stability of chitosan in LiOH aqueous solution

One of the reasons that restrict the development of chitosan is the poor stability of its solution. Chitosan hydrolyzes badly in acid, resulting in the decrease of molecular weight and polydispersity, as well as the poor mechanical properties of its products. Researchers have been devoted to exploring appropriate mild solvents for chitosan for decades.

Table 2 shows the DD and M_η of CS65 and CS65 regenerated in 4.0 wt% H_2SO_4 after swelling in 4.8 wt% LiOH solution for 1, 3, 5, and 7 d, and the samples are coded as CS0, CS1, CS3, CS5, and CS7, respectively. A slow deacetylation occurred during the storage of the CS65/LiOH swelling gel with an increase of the DD, and the molecular weight of CS65 only decreased slightly. The results indicate that CS65 is stable in this LiOH aqueous solution. Therefore, LiOH aqueous solution may be a potential favorable solvent for chitosan.

4. Conclusion

The adsorption behaviors of chitosan with four different DD and molecular weight in the LiOH aqueous solution were investigated. The results indicated that the adsorption increased with increasing concentration of LiOH, and reached the maximum at the concentration of 4.8 wt%. The adsorption of LiOH and H_2O on chitosan was closely related to its DD. n_{H_2O}/n_{LiOH} had a linear decrease relation with the DD of chitosan. XRD patterns indicated that the adsorption of LiOH aqueous solution on chitosan proceeded from amorphous region to crystal region and LiOH destroyed the hydrogen bonds and crystal structure of chitosan. When the concentration of LiOH was 4.8 wt%, the crystal structure of chitosan was completely destroyed. The treatment of freezing–blasting played a key role in the adsorption behavior of chitosan. Chitosan was stable in LiOH aqueous solution. Therefore, LiOH aqueous solution may be a potential favorable solvent for chitosan.

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