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Ionic interactions between sulfuric acid and chitosan membranes

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Abstract

Treatment of chitosan with crosslinking agents is a common strategy for improving the performance of chitosan membranes in industrial applications. The preparation of sulfuric acid–crosslinked chitosan membranes was studied by infrared spectroscopy, elemental analysis, and X-ray diffraction, to better understand the mechanism of sulfuric acid treatment. The results indicated that first H_2SO_4 protonated the chitosan amine groups, then the SO_4^{2-} anions slowly interacted with chitosan NH_3^+ groups to form ionic bridges between the polymer chains. Kinetic analysis showed that protonation was the rate-limiting factor in the adsorption of sulfuric acid by the membrane. The strong interactions between chitosan NH_3^+ groups and SO_4^{2-} anions were related to changes in membrane crystallinity. Protonation of 10-μm-thick chitosan membranes by 0.01 M sulfuric acid was accomplished within 5 min and complete ionic crosslinking required 30 min. The results of this study suggest better guidelines for treating chitosan membranes with divalent and multivalent acids.

Keywords: Chitosan membrane; Ionic crosslinking; Protonation

1. Introduction

Chitosan (*N*-deacetylated chitin) is a biodegradable, non-toxic, natural polymer with excellent biocompatibility. It can be derivatized easily due to the free amino and hydroxyl groups on the saccharide backbone (Brugnerotto, Desbrieres, Roberts, & Rinaudo, 2001; Kurita, 2001; Sashiwa et al., 2003). Because of its ideal properties, it has been studied as a membrane material for proton exchange (López-Chávez et al., 2005; Mukomaa, Jooste, & Vosloo, 2004a; Mukomaa, Jooste, & Vosloo, 2004b; Soontarapa & Intra, 2006), reverse osmosis (Yeom, Lee, & Lee, 2000), ultrafiltration (Musale, Kumar, & Pleizier, 1999), pervaporation (Devi, Smitha, Sridhar, & Aminabhavi, 2005; Ge, Cui, Yan, & Jiang, 2000; Lee, Nam, & Woo, 1997; Mochizuki, Amiya, Sato, Ogawara, & Yamashita, 1989; Nam & Lee, 1999), gas separation (Krasemann & Tieke, 1999), and lithium batteries (Yahya & Arof, 2003).

Chitosan membranes are often modified by adding bifunctional crosslinking agents, in order to increase swelling and improve mechanical performance in applications. There are two kinds of crosslinking systems: one is chemical crosslinking, using agents such as glutaric dialdehyde and ethylene glycol diglycidyl ether; the other is ionic crosslinking, using sulfuric acid or tripolyphosphate. Chitosan membranes crosslinked with sulfuric acid have been studied as materials for proton exchange and pervaporation. In pervaporation of water–alcohol mixtures, sulfuric acid–crosslinked chitosan membranes exhibited the highest selectivity, with a low permeation flux (Devi et al., 2005; Ge et al., 2000; Lee et al., 1997; Mochizuki et al., 1989; Nam & Lee, 1999). In research on proton exchange membranes, the methanol permeability of crosslinked chitosan membranes was an order of magnitude lower than that of Nafion 117 under the same conditions (Mukomaa et al., 2004a) and the membrane conductivity reached 0.01–0.03 S cm^{-1} at room temperature (Mukomaa et al., 2004b; Soontarapa & Intra, 2006).

Although the structure and properties of sulfuric acid–crosslinked chitosan membranes have been investigated using techniques such as X-ray diffraction, FT-IR spectros-

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copy and NMR spectroscopy, there is little information available about the details of the sulfuric acid–chitosan interaction. To explain why sulfuric acid improves the performance of chitosan membranes in proton exchange and pervaporation applications, and to further develop industrially useful chitosan-based materials, it is important to determine what processes take place when chitosan is exposed to a polyvalent acid. This study investigated the dynamic evolution of the sulfuric acid–chitosan crosslinking reaction, and the results provide new details about both the mechanism and the timescale of the sulfuric acid treatment. By clarifying the molecular changes and optimizing some of the treatment conditions, we provide better guidelines for convenient preparation of crosslinked chitosan membranes.

2. Experimental

2.1. Materials

Chitosan was purchased from Jinan Haidebei Marine Bioengineering Co., Ltd., China ($MW = 6 \times 10^5$, 95% deacetylated). All other reagents and solvents used were analytical reagent grade.

2.2. Membrane preparation

The chitosan membranes were prepared as follows: 1 g chitosan flakes was dissolved in 100 ml of 1% acetic acid (w/w). After complete dissolution of the chitosan, the solution was cast on a glass plate and left to dry for 24 h in the ambient air, and then the plate was transferred to an oven and dried at 60 °C for 2 h. The dry membranes were immersed in 2 M NaOH for 30 min to ensure the complete removal of residual acid from the membranes. The membranes were then thoroughly washed with de-ionized water until a neutral pH was obtained.

The membranes were submersed in 0.01 M sulfuric acid at room temperature. Eight membranes were prepared, with the submersion time varying from 10 s to 90 min. These crosslinked membranes are designated as CCS-10 s, CCS-30 s, CCS-1 min, CCS-5 min, CCS-10 min, CCS-30 min, CCS-60 min, and CCS-90 min. All of the crosslinked chitosan membranes (CCSs) were washed with deionized water until a neutral pH was obtained.

2.3. Measurements

CCSs were dried to constant weight before infrared spectra were recorded. The average thickness of the membranes was 10 μm. The spectra were recorded using a Nicolet Avatar 360 operating in the range of 400–4000 cm^{-1}. Each membrane was cut into a suitable size and placed in the sample holder of the spectrophotometer. The elemental content of each CCS was characterized using an EA1112 organic elemental analyzer (Thermo Quest, America). X-ray diffraction patterns were recorded on a Rigaku D/max 2200PC X-ray diffractometer and used a Cu target at 40 kV and 40 mA. Each sample was cut into a suitable size and then placed in the sample holder of the diffractometer. The diffraction angle was varied from 5° to 40°.

3. Results and discussion

Table 1 lists the FT-IR bands of pure chitosan as measured in our work. Fig. 1 shows the IR spectra of each CCS from 500 cm^{-1} to 1850 cm^{-1} for the first 90 min of reaction. After the reaction progressed for 90 min, no further spectral changes were observed. In the first 5 min of reaction, it could be seen that the band characteristic of NH_2 bending vibrations (1587 cm^{-1}, band 1) gradually weakened, and new absorption bands characteristic of NH_3^+ bending vibrations appeared at 1634 cm^{-1} and 1531 cm^{-1}. These results suggest that the NH_2 groups in the chitosan chains were protonated by the H^+ supplied by sulfuric acid, as described by Scheme 1. The degree of protonation can be monitored by comparing the ratio of the peak area at 1634 cm^{-1} (a NH_3^+ vibrational band) to the peak area at 1380 cm^{-1} (which is unaffected by addition of H_2SO_4). The baselines for measuring peak area are shown in Fig. 2a. Fig. 2b shows the degree of protonation (A_{1630}/A_{1380}) at various reaction times. The value increased quickly as the treatment time increased, and reached a steady level after 5 min. In the first 5 min, it can also be seen that the small band at 1150 cm^{-1} (Fig. 1, band 2) became obscured by the broader band at 1100 cm^{-1}, and another band at 610 cm^{-1} became dominant (Fig. 1, band 3). These spectral changes can be attributed to the presence of SO_4^{2-} ions (Bouchet & Siebert, 1999; Goypiron, De Villepin, & Novak, 1975).

The adsorption of sulfuric acid by the chitosan membrane can be accurately determined by elemental analysis (Table 2). As seen in Table 2, the sulfur content and the molar ratio of sulfur to nitrogen (n_S/n_N) increased during the first 5 min of treatment. Fig. 2b shows that the degree of protonation and n_S/n_N increased simultaneously. These results confirm that protonation is related to adsorption of H_2SO_4 by the membrane. From both infrared spectros-

Table 1
Infrared band assignments for chitosan

Assignment	Peak position (cm^{-1})
O—H stretching	3456
N—H_2 symm. stretching	3367
N—H_2 asymm. stretching	3315
C—H symm. stretching	2916
C—H asymm. stretching	2867
Amide I (C=O)	1649
NH_2 deformation	1587
CH_3 symm. deformation	1382
C—O—C vibration	1159

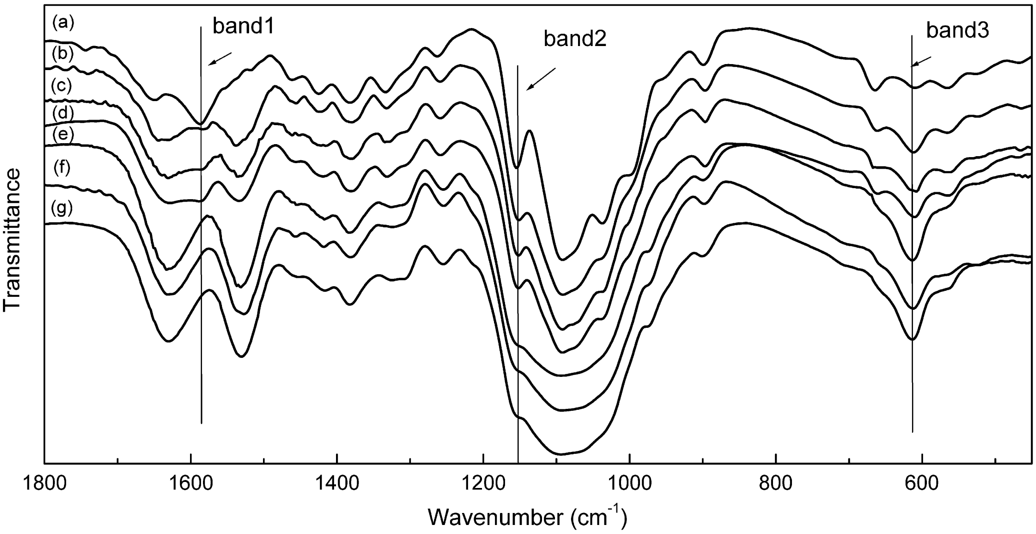
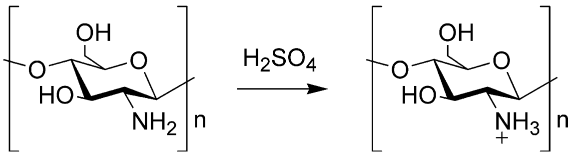


Fig. 1. The infrared spectra of (a) pure chitosan, (b) CCS-10 s, (c) CCS-30 s, (d) CCS-1 min, (e) CCS-5 min, (f) CCS-30 min and (g) CCS-90 min in the range of 500–1800 cm^{-1}.



Scheme 1. Protonation of the chitosan membrane.

copy and elemental analysis, it is clear that 5 min is sufficient for complete protonation of chitosan membranes prepared with 10 μm thickness and submerged in 0.01 M sulfuric acid at room temperature.

By analogy with the adsorption of metal ions by chitosan (Hamdinea, Heuzey, & Bégin, 2005; Lee, Mi, Shen, & Shyu, 2001), the uptake of sulfuric acid might be considered to depend on two processes: diffusion within the chitosan membrane and binding to active sites. However, kinetic analysis shows that sulfuric acid adsorption by chitosan membranes is quite different from the adsorption of metal ions. The latter follows the Fickian law describing a linear relationship between the absorption of metal ions and $t^{0.5}$ (Lee et al., 2001; McKay & Poots, 1980), indicating that diffusion-controlled transport is the limiting factor in metal ion adsorption. In the case of sulfuric acid adsorption, during the first 5 min the linear relationship was between sulfuric acid content in the membrane and log(t), as shown in Fig. 2. Thus, the limiting factor in sulfuric acid adsorption cannot be diffusion-controlled transport, but rather binding to active sites via chemical reaction (protonation). This interpretation is consistent with the parallel trends in degree of protonation and sulfuric acid content in the membrane as reaction time increased (Fig. 2).

After the first 5 min, further IR spectral changes could be seen in the 3500–2500 cm^{-1} region (Fig. 3A). With increasing reaction time, the chitosan O—H and N—H absorption bands gradually became less distinct. A new absorption band appeared near 3200 cm^{-1} and broadened as the reaction progressed. The position of the absorption due to the C—H stretching vibration shifted to higher wavenumbers (from 2911 cm^{-1} to 2934 cm^{-1}), and became stationary after 30 min (Fig. 3B). These changes, which are not synchronous with the protonation process, make it clear that there was an additional interaction between sulfuric acid and the chitosan membrane.

As shown in Fig. 3A, the broad band near 3200 cm^{-1} became evident after the first 5 min, when the NH_2 groups had already been converted to NH_3^+ groups by protonation. This absorption is assigned to the stretching vibration of N^+—H. This broad band is sensitive to SO_4^{2-} ions, because of the strong interaction between the SO_4^{2-} and NH_3^+ ions. As the reaction time increased, more SO_4^{2-} ions interacted with the NH_3^+ groups, so the band at 3200 cm^{-1} continued to broaden. Crosslinking of the membrane occurs when a SO_4^{2-} anion interacts with two NH_3^+ groups by ionic bonding, as depicted in Scheme 2.

It is known that the rigid crystalline structure of pure chitosan is stabilized mainly by intra- and intermolecular hydrogen bonds (Roberts, 1992; Wan, Creber, Peppley, & Bui, 2004). When glucosamine units in chitosan membranes are protonated, hydrogen bonding involving the NH_2 groups is disrupted, so the rigid crystalline structure weakens. Furthermore, ionic crosslinking, which increases packing of the chitosan chains, can deform the crystalline regions (Lee et al., 2001). Thus, the interactions we detected in this work should contribute to decreased membrane crystallinity, and changes in crystallinity can be used to monitor the progress of the crosslinking reaction.

For chitosan with varying degrees of deacetylation, it has been reported that infrared C—H stretching bands shift to lower wavenumbers and become sharper as crystallinity increases (Mima, Miya, Iwamoto, & Yoshikawa, 1983). Fig. 3B shows that the C—H stretching band in our study

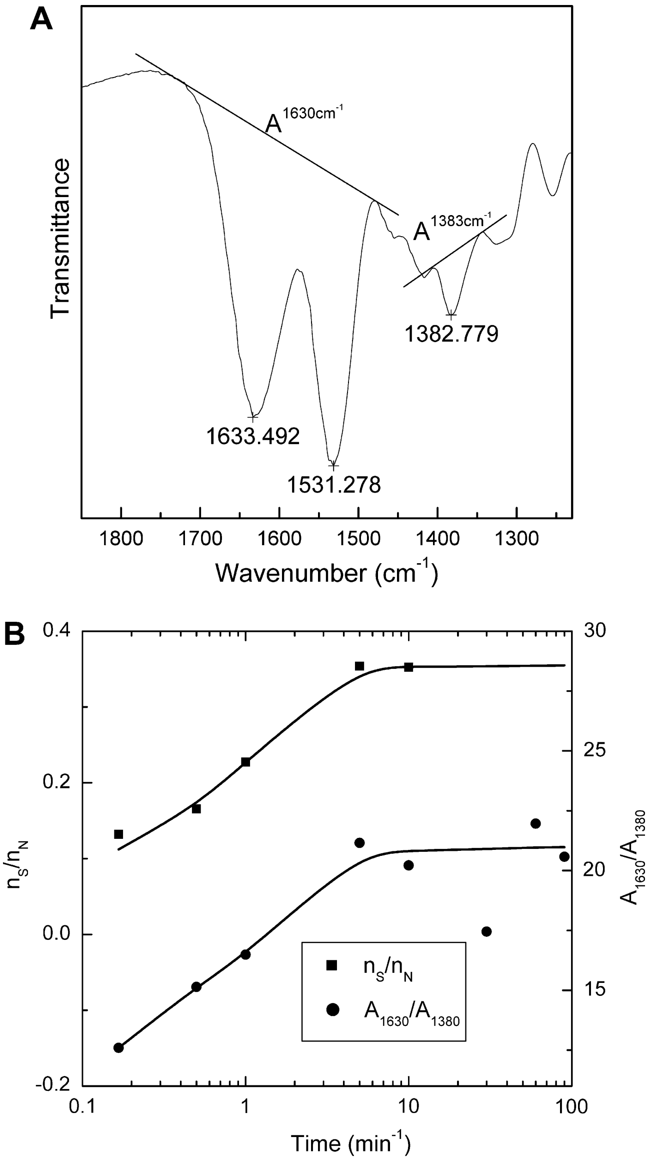


Fig. 2. (a) The infrared spectrum of CCS-5 min and (b) Plots of n_S/n_N and A_{1630}/A_{1380} vs. the crosslinking time.

Table 2
Elemental analysis of selected crosslinked chitosan membranes

Reaction time	Elemental content (wt.%)				n_S/n_N
	N	S	C	H	
10 s	6.38	1.93	35.99	6.54	0.13
30 s	6.05	2.29	34.71	6.89	0.17
1 min	5.20	2.70	31.79	6.59	0.23
5 min	4.79	3.88	30.91	6.45	0.35
10 min	4.79	3.86	30.27	6.28	0.35

shifted to higher wavenumbers, from 2911 cm^{-1} to 2934 cm^{-1} within 30 min. Therefore, this shift is consistent with decreasing crystallinity as the reaction progressed. This was confirmed by X-ray diffraction. Fig. 4 shows the X-ray diffractograms of chitosan membranes prepared with different sulfuric acid treatment times. The diffractograms exhibit three major crystalline peaks (2θ) around 10°, 15° and 20°, in agreement with previously reported results (Wan, Creber, Pepply, & Bui, 2003). The peaks at 10° and 20° are characteristic of chitosan membrane crystallinity (Samuels, 1981). Their intensity decreases markedly, showing that the crystallinity of the membranes decreases with increased exposure to sulfuric acid. From infrared and X-ray diffraction measurements, changes in crystallinity were essentially complete after 30 min. This suggests that 30 min is sufficient time for complete ionic crosslinking of 10-μm-thick membranes treated with 0.01 M H_2SO_4. In previous reports where 0.5 M sulfuric acid was used to prepare crosslinked membranes, 24 h reaction time was allowed for the crosslinking reaction (Ge et al., 2000; Muk-

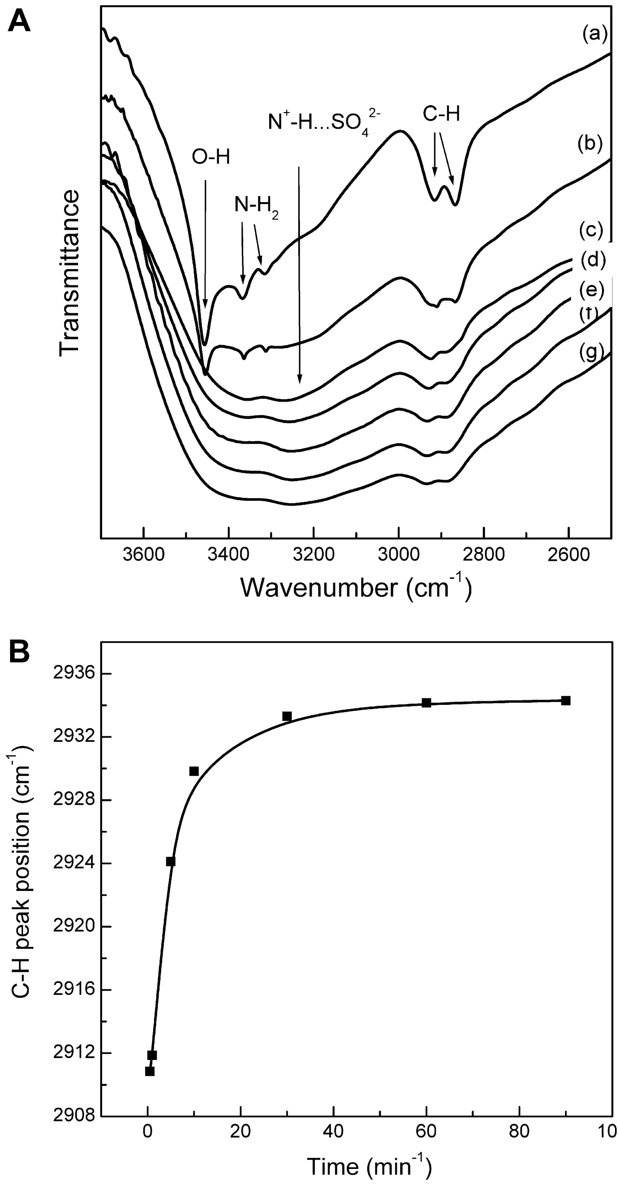
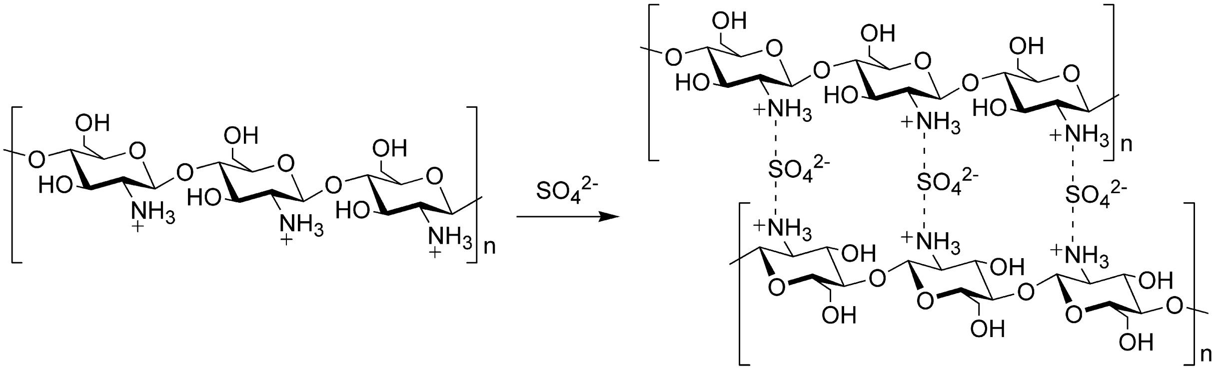


Fig. 3. (A) The infrared spectra of (a) pure chitosan, (b) CCS-30 s, (c) CCS-5 min, (d) CCS-10 min, (e) CCS-30 min, (f) CCS-60 min and (g) CCS-90 min in the range of 2500–3500 cm^{-1}. (B) The position of the absorption due to the C—H stretching vibration vs. the crosslinking time.



Scheme 2. Ionic crosslinking of the chitosan membrane.

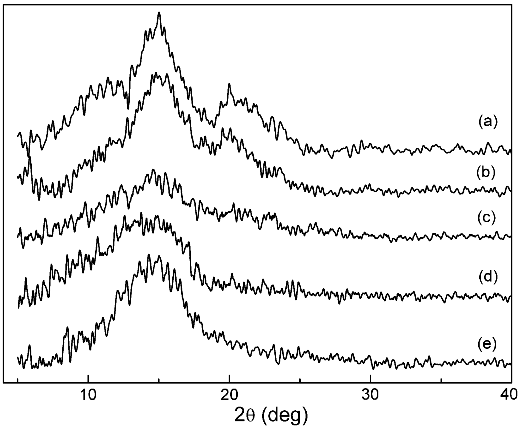


Fig. 4. X-ray diffractograms of the chitosan membranes at different crosslinking times: (a) pure chitosan, (b) CCS-10 s, (c) CCS-10 min, (d) CCS-30 min and (e) CCS-90 min.

omaa et al., 2004b). While the membrane thickness was not reported in those studies, from the results of our work it appears that such a long reaction time would be unnecessary for typical membranes.

It can be seen that the increase of sulfuric acid content in the chitosan membrane was synchronous with protonation and much quicker than ionic crosslinking. This suggests that not all of the SO_4^{2-} ions absorbed by the membrane during protonation were crosslinking agents; only those located between two NH_3^+ groups on the chitosan chains resulted in ionic crosslinking. As the reaction time increased, more SO_4^{2-} ions diffused to locations bridging two NH_3^+ groups, increasing the degree of ionic crosslinking. Therefore, ionic crosslinking is dependent on the mobility of SO_4^{2-} ions in the membrane.

4. Conclusions

Using FT-IR, X-ray diffraction, and elemental analysis to study the interactions between sulfuric acid and chitosan membranes over time, we found distinct protonation, sulfuric acid adsorption, and ionic crosslinking processes. Protonation is the limiting factor in adsorption of sulfuric acid and the prerequisite for ionic crosslinking. This sequence may be a model for other ionic crosslinking reagents such as tripolyphosphate. We have shown that protonation of 10-μm-thick chitosan membranes by 0.01 M sulfuric acid can be accomplished within 5 min and complete crosslinking requires 30 min.

A convenient method for monitoring the interaction of ionic acid and chitosan was established. With increased knowledge of the reactivity of sulfuric acid in CCSs, it may be possible to predict the suitability of other ionic acids for preparing crosslinked chitosan membranes having industrially useful properties.

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