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## RESEARCH ARTICLE

### PROTONATION OF THE NH<sub>2</sub> GROUPS THROUGH CROSSLINKING CHITOSAN MEMBRANES WITH H<sub>2</sub>SO<sub>4</sub>

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#### ABSTRACT

Chitosan a biopolymer membrane prepared by solution casting method was cross-linked with 0.1, 0.5, and 0.7 M H<sub>2</sub>SO<sub>4</sub>. The structural properties were characterized by FTIR and XRD and the results showed protonation of the NH<sub>2</sub> groups by H<sub>2</sub>SO<sub>4</sub> and the cross-linking decreased the crystallinity of the chitosan membrane.

#### Key words:

Chitosan,

H<sub>2</sub>SO<sub>4</sub>,

Cross-linking,

FTIR, XRD,

Protonation

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## INTRODUCTION

Chitosan, a biopolymer is an N-deacetylated product of chitin (Hirano *et al.*, 1984) the second most naturally occurring polysaccharide analogues of cellulose where the hydroxyl groups at carbon-2 have been replaced by the acetamido and amino groups respectively (Krajewska, 2004 and Krajewska, 2001). It consists of one primary amine and two free hydroxyl groups for each monomer with a unit formula of C<sub>6</sub>H<sub>11</sub>O<sub>4</sub>N found in shells of crustaceans, cell walls of fungi and exoskeletons of insects (Tharanathan and Kittur, 2003, Kurita, 2001 and Pangburn, *et al.*, 1984). Chitosan is biocompatible, non-toxic,

biodegradable and physiologically inert (Krajewska, 2004 and Sandford, 1989). They are widely used in industries ranging from health and beauty aids to water purification, biomedical applications, agriculture, biotechnology, nutrition, and treatments in the finishing process of textile fibers.

In its natural state (dry state), a Chitosan membrane is almost non-conductive. However when an appropriately cross-linked Chitosan membrane is fully hydrated, it can have a conductivity close to 10<sup>-3</sup> Scm<sup>-1</sup> (Ying Wan, *et al.*, 2003). It has been found, however if Chitosan is dissolved in acetic acid and resulting solution is cast into thin film, then the H<sup>+</sup>, H<sub>3</sub>O<sup>+</sup> and CHCOO<sup>-</sup>

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ions in the acetylated Chitosan film will be dispersed in the immobilized Chitosan solvent and these ions can be mobilized under the influence of an electric field. If  $H^+$  or  $H_3O^+$  ions are more mobile than the  $CH_3COO^-$  the film becomes a proton conductor. Chitosan in an acidic medium can become a polyelectrolyte membrane through the protonation of the  $NH_2$  groups (Mohamed, *et al.*, 1995). The objectives of the present work are to synthesize the Chitosan from chitin and study its degree of deacetylation from infrared measurements. The synthesized Chitosan is cross-linked and protonated with sulfuric acid and systematically studied the infrared vibrations using FTIR technique and the structural studies using XRD.

## MATERIALS AND METHODS

### Membrane preparation

The Chitosan solutions were prepared by mixing 0.1 g of finely grinded Chitosan powder with 5 ml of acetic acid in a 100 ml glass beaker and stirred for about 1 hour continuously using a Teflon pellet, which was rotated with a help of a magnetic stirrer maintained at room temperature to form a 2 wt % solution. Minor insoluble solids were removed using a syringe filter with a pore size of 1micron. The casting of the films is carried out onto optically plane glass moulds, which has maximum surface smoothness and economical. Film casting technique was employed in the present study for the bio-polymer membrane preparation. The membranes were then kept in an oven at a temperature of  $60^\circ C$  and dried for 24 hours. The dried membranes were neutralized in 2M NaOH for 15 minutes and thoroughly washed with demineralized (DM) water.

The aim of crosslinking is to improve the physical and chemical properties of the Chitosan. In this work, the membranes were crosslinked and protonated by submersion in different concentrations such as 0.1M, 0.5 M and 0.9M  $H_2SO_4$  for 30 minutes. They were washed thoroughly with DM water and again kept in an oven at a temperature of  $60^\circ C$  and dried for 24

hours. Then the as such synthesized samples were kept under dry condition.

## RESULTS AND DISCUSSION

### Infrared absorption analysis of Cross-linked Chitosan

The analyses were carried out in the two regions ( $1700 - 1100\text{ cm}^{-1}$  and  $3600 - 2800\text{ cm}^{-1}$ ) of the spectra (fig 1.) It is seen from the first region of the spectra ( $1700 - 1100\text{ cm}^{-1}$ ) the band characteristic of  $NH_2$  bending vibrations ( $1584\text{ cm}^{-1}$ ) disappears even for the 0.1M concentration of  $H_2SO_4$  and new absorption band characteristic of  $NH_3^+$  bending vibrations appeared at  $1635\text{ cm}^{-1}$  and  $1532\text{ cm}^{-1}$ . These results suggest that the  $NH_2$  groups in the Chitosan chains were protonated by the  $H^+$  supplied by sulfuric acid, as described by Fig.1. The degree of protonation can be monitored by comparing the ratio of the peak area at  $1635\text{ cm}^{-1}$  ( $NH_3^+$  vibrational band) to the peak area at  $1377\text{ cm}^{-1}$  (which is unaffected by addition of  $H_2SO_4$ ). The degree of protonation ( $A_{1635}/A_{1377}$ ) at various concentration shows that the value increases with concentration and reaches maximum even for 0.5M and remain almost constant. It is also seen that the small band at  $1151\text{ cm}^{-1}$  became obscured by the broader band at  $1100\text{ cm}^{-1}$  can be attributed to the presence of  $SO_4^{2-}$  ion (Bouchet, and Siebert, 1999 and Goypiro, *et al.*, 1975).

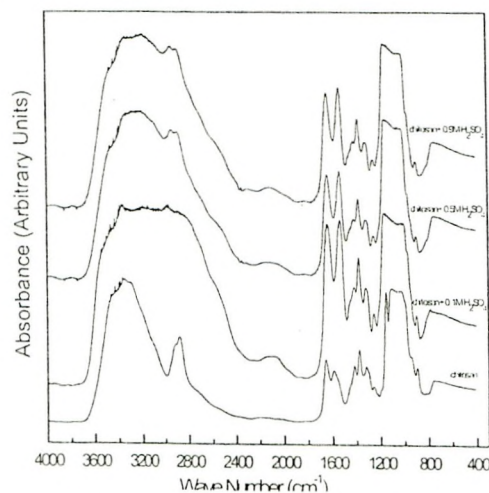


Fig. 1. IR spectra of pure and cross-linked Chitosan films

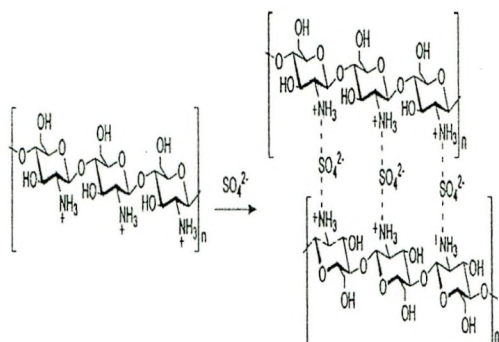


Fig. 2. Ionic cross-linking of Chitosan membrane

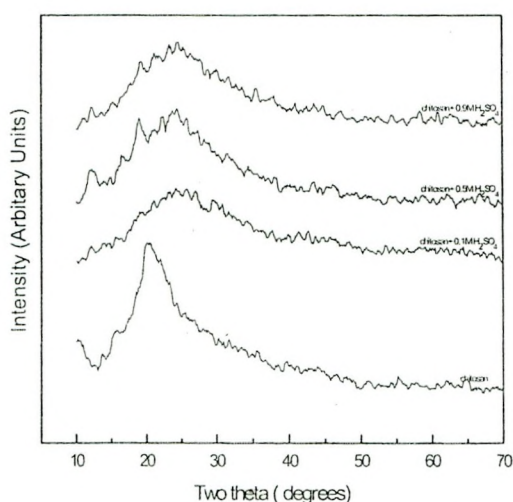


Fig. 3. X-ray diffractograms

In the second region of the spectra ( $3600 - 2800 \text{ cm}^{-1}$ ), the Chitosan O-H and N-H absorption bands gradually became less distinct and a new absorption band appeared near  $3200 \text{ cm}^{-1}$ . The broad band near  $3200 \text{ cm}^{-1}$ , even for the concentration of  $0.1 \text{ M}$  sulfuric acid, confirms the conversion of  $\text{NH}_2$  groups into  $\text{NH}_3^+$  groups by the protonation. This broad band is sensitive to  $\text{SO}_4^{2-}$  ion, because of the strong interaction between the  $\text{SO}_4^{2-}$  ion and  $\text{NH}_3^+$  ions. As the concentration increased, more  $\text{SO}_4^{2-}$  ion interacted with the  $\text{NH}_3^+$  ions, so band at  $3200 \text{ cm}^{-1}$  continued to broaden. Cross-linking of the membrane occurs when a  $\text{SO}_4^{2-}$  anion interacts with two  $\text{NH}_3^+$  groups by

ionic bonding, as presented in Fig. 2. Crystallinity index was determined by IR spectroscopy from absorbance ratio  $A_{1423 \text{ cm}^{-1}} / A_{897 \text{ cm}^{-1}}$ , where  $A_{1423 \text{ cm}^{-1}}$  and  $A_{897 \text{ cm}^{-1}}$  corresponds to the crystalline and amorphous parts respectively (Ferruz and Pages, 1977). It is clear from the IR spectra the area under the crystalline peak diminishes and the area under amorphous peak improves gradually as the concentration of sulfuric acid increases. This result was confirmed with X-ray diffraction studies.

#### XRD pattern of crosslinked Chitosan

X-ray diffraction is a proven tool to study crystal lattice arrangements and yields very useful information on degree of sample Crystallinity. X-ray diffractograms of Chitosan membranes cross-linked with different concentration of sulfuric acid is shown in Fig.3. The diffractograms exhibit two major crystalline peaks ( $2\theta$ ) around  $10^\circ$ ,  $15^\circ$  and  $20^\circ$ . The characteristic peaks of Chitosan disappear for the concentrations of  $0.1 \text{ M}$  sulfuric acid and an amorphous hump is seen around  $25^\circ$ . The same observation is seen in all the concentration of sulfuric acid. From XRD spectroscopy measurements, change in crystallinity even for the small ( $0.1 \text{ M}$ ) concentration of sulfuric acid. This suggests that  $0.1 \text{ M}$  is sufficient for complete ionic cross-linking of  $25 \mu\text{m}$  thick membranes treated for  $30 \text{ min}$ .

It is well known that the rigid crystalline structure of pure Chitosan is stabilized mainly by intra and intermolecular Hydrogen bonds (Ying Wan *et al.*, 2004). When glucosamine units in Chitosan membranes are protonated hydrogen bonding involving the  $\text{NH}_2$  groups is disrupted, so the rigid crystalline structure weakens. Further, ionic cross-linking, which increases packing of the Chitosan chains, can deform the crystalline regions (Lee *et al.*, 2001). Thus the interaction detected in this work decreases the membrane crystallinity, and changes in crystallinity can be used to monitor the progress of the cross-linking reaction.

#### CONCLUSION

The Chitosan membrane was prepared by the solution casting method and it was cross-linked with sulfuric acid. This cross-linked membrane was

characterized by FTIR, XRD. Protonation was confirmed from IR spectra. Cross-linking of chitosan influence the membrane crystallinity was observed from the XRD studies.

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