PREPARATION OF BIO-NANOCOMPOSITE MEMBRANE FOR METHYLENE BLUE ADSORPTION

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ABSTRACT

In this study, the bio-nanocomposite composed of chitosan and nanoclay was prepared by solution intercalation method. The membrane was subsequently fabricated by dry/wet phase separation technique. The structure of bio-nanocomposite was characterized by Fourier-transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD) and scanning electron microscope (SEM). The membrane was applied to adsorb methylene blue (MB) for water treatment. The adsorption of MB was monitored through UV-Vis spectroscopy. The results showed that bionanocomposite membrane could adsorb MB up to 97.9% in 150 min. The MB adsorption of bionanocomposite membrane was 234 times as high as the adsorption of the conventional chitosan films that is promising for environmental applications.

Keywords: bio-nanocomposite membrane, methylene blue adsorption, chitosan, nanoclay.

1. INTRODUCTION

Bionanocomposite is a ‘green’ nanocomposite associated with remarkable properties. Therefore, the study on application of bionanocomposite in environmental treatment has been attracted many attentions [1-5]. In this study, we combined two environmental friendly materials that are chitosan (CS) and nanoclay (MMT). These materials are available in Vietnam with relatively low cost and are an effective materials for organic contaminant treatment [2-4]. However, the study of chitosan/nanoclay bionanocomposite as adsorbents for removing organic pollutants such as methylene blue is only a few.

On the other hands, membrane is a material which has been widely used to separate the pollutants. The main technique having been used to fabricate membrane is inverse phase separation or wet phase. The additional drying step before inverse phase separation allows ones adjust the structure of membrane. In this report, bionanocomposite composed of chitosan and nanoclay has been used to fabricate membrane toward MB adsorptions.

2. EXPERIMENTS
2.1. Materials

Chitosan (CS) made from crab shell chitin with degree of deacetylation of 77 % and Mw of 168 kDa originated from Vietnam. Clay obtained from Thuan Hai province, Viet Nam was purified as reported previously [6]. NaOH, Na$_2$CO$_3$ (Xilong, China) and other solvents (China) were used as received.

2.2. Preparation of CS/MMT membrane

Clay has been dropped in the solution of CS in acetic acid (3 wt%) and vigorously stirred for 24 hours. 10 mL of the dispersion were poured in the petri dish, dried at 50 °C at certain time. The samples were then dipped into the solution of NaOH 2 wt% - Na$_2$CO$_3$ 0.05 wt% for 25 hours, dried at 50 °C.

2.3. Adsorption of methylene blue (MB)

0.7 g of membrane was dipped in 25 mL solution of MB 6 ppm. After an interval of time, the concentration of MB was measured using spectrophotometry at 664 nm.

2.4. Characterization

The intercalation of CS in MMT layers was characterized by powder X-ray diffraction (XRD, D8–ADVANCE, Bruker). The morphology of membrane was observed through scanning electron microscopy (SEM, SE4800, Hitachi, Japan). MB concentrations were measured on V-670 UV-Vis spectrophotometer (Jasco, USA).

3. RESULTS AND DISCUSSION

![Figure 1. XRD patterns of MMT and Chitosan/MMT.](image)

The intercalation of CS into MMT layers affords the increase of the basal space between MMT the layers. XRD patterns are presented in Figure 1. The interlayer spaces (d$_{001}$) of MMT layers were calculated by the Bragg equation ($2d \sin \theta = n \lambda$, where $n$ is the progression of diffraction, $d$ is the basal spacing and $\theta$ is the diffraction angle). The MMT basal space is of 10 nm. After the intercalation, this 2 theta peak almost disappeared on XRD pattern which proved...
the intercalation of CS into MMT layers successfully. The driving force for the intercalation process is the cation exchange reaction between initial cation existed in MMT and the amine group on CS chain since CS is cationic polysaccharide.

The bionanocomposite dispersion was then dried at 50 °C for 3, 4 and 5 hours before the inverse phase separation. SEM images were showed in Figure 2. It can be observed on SEM image that many micropores exist in the membrane which increase the overall adsorption surface area of the membrane. The MB adsorption of CS bulk film with and without MMT (Fig. 3a), and CS bulk film with CS membrane (Fig. 3b) and the CS/MMT membrane (Fig. 3c) were presented.

Figure 2. Cross-section image of bionanocomposite membrane dried at 50°C for 5 h before the inverse phase separation.

Figure 3. The MB adsorption of CS bulk film a) with and without MMT, b) with CS membrane, c) with CS/MMT membrane. Inset of Figure c is the digital image of MB solution at the beginning and after 90 min treatment.

It can be concluded that MMT and the membrane structure significantly improved the adsorption of MB as expected. This result supported the porous structure of membrane observed
in Figure 2. However, the adsorption of bulk CS film, CS membrane or CS/MMT bulk film has low MB adsorption (about 70 – 80 % after 150 min). On contrary, the adsorption of CS/MMT membrane has significantly increased (> 80 % after 90 min. Figure 3c). Moreover, the addition of MMT into the CS film improves the rate of adsorption. The effect of drying time has also been observed on Figure 3c. The results showed that the MB adsorption increases proportionally with the drying time. For longer drying time, the membrane becomes brittle and difficult to take out of the petri dish. Therefore, we chose the drying time of 5 hours for further investigation.

We investigated the content of MMT in the CS/MMT membrane, the results showed in Figure 4. It can be observed that the content of MMT does not affect the MB adsorption significantly. After 150 min treatment, the percent of MB adsorbed is 97.9%. These results indicated the potential use of bionanocomposite CS/MMT membranes as ‘green’ material for contaminant treatment toward sustainable developments.

Figure 4. Effect of MMT content in bionanocomposite CS/MMT membrane on the MB adsorption.

4. CONCLUSION

We successfully developed the bionanocomposite membrane from the Vietnamese-rich materials by dry/wet method. The MB adsorption of the bionanocomposite CS/MMT membrane has been improved about 1.2 – 1.3 times higher than the CS, CS/MMT bulk film. The results indicated the advantages of CS/MMT membranes over conventional nanocomposite film. Furthermore, at the drying stage, it was found that the optimal drying time is 5 hours at 50 °C, and the MMT content is of 1 %. The MB adsorption capacity was as high as 97.9 % indicating the potential applications of newly developed materials as adsorbent for environmental treatment.

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REFERENCES


