



The Modified Cellulose Through Polyelectrolyte Membrane Techniques as an Adsorbent Candidate for removing of Dyes

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<http://dx.doi.org/10.13005/ojc/340665>

Received: October 25, 2018; Accepted: November 21, 2018)

ABSTRACT

Disposal of dyestuff into rivers or other water can disrupt the aquatic biota ecosystem in it. Thus the pollution of dyes in the aquatic environment needs to be overcome. One effort to reduce the dye content in water is by making adsorbent membranes based of cellulose which are biomaterials of chitosan and alginate. This aims of study was to make polyelectrolyte membranes from chitosan and alginate which will be applied as adsorbents of textile dyestuffs. The research was done by mixing chitosan gel in 2,5% acetic acid solution with alginat gel in water for 3 h stirring. The solution then was printed out into a polypropylene container and dried. The formed membrane was characterized using FTIR to identify functional groups, XRD and SEM to analyze their physical characteristic. The results showed that the Chi-Alg membrane adsorbent had stability and resistance to the acidic environment. Characterization results using FTIR showed that the adsorbent has functional group of amine, carboxyl and hydrogen that identify on wave number 1597 cm⁻¹, 1635 cm⁻¹ and 3000-3700 cm⁻¹ respectively. The results of XRD show that the adsorbent was semi crystalline. Furthermore, SEM data shows a solid structure of the adsorbent.

Keyword: Chitosan, Alginate, Chi-Alg, adsorbent, Dyestuff.

INTRODUCTION

Liquid waste which contains many dyes is produced by several domestic industries such as the textile industry and chemical laboratories. These textile industries produce liquid waste every day from the textile industry production process. Dyestuff waste is toxic, dangerous, stable to light,

heat and oxidizing agents and difficult to degrade due to the complex structure of aromatic molecules (Kyzas *et al.*, 2009). Environmental pollution due to waste disposal of colored substances can inhibit photosynthetic activity (Jing *et al.*, 2013). Dyestuffs if discharged into the aquatic environment without handling beforehand can cause serious pollution to water sources which cause environmental ecology damage and can disrupt human health.



According to Sen and Demirer (2003) textile dyestuffs contain azo (R-N = N-R') compounds with the same or different organic chains and benzene derivatives. Dyes themselves can cause an increase in Biological Oxygen Demand (BOD) and transmit disease through water (Gupta *et al.*, 1988). One of the dyes that become waste in industry and chemical laboratories is methylene blue with the molecular formula $C_{16}H_{18}N_3SCl$. Methylene blue is widely used in industries because methylene blue is a basic dye and has good solubility. In the coloring of the production process in the textile industry, methylene blue is bound to only about 5% while the remaining 95% is wasted as wastewater (Liu *et al.*, 2007). According to Government Regulation No. 22 of 1990, the maximum level of methylene blue in the waters was set at 10 mg L^{-1} . Therefore, special handling of the methylene blue dye in the waters is needed so that its concentration in the waters can be reduced or reduced.

Today, there are many studies on wastewater treatment through the adsorption process using modified polymers in order to absorb wastewater containing heavy metals and wastewater containing harmful dyes. Compared to other methods such as filtration and sedimentation, adsorption is one method of waste treatment that does not require high costs (Gottipati *et al.*, 2010).

One of the biomaterials that are relatively easy to obtain is chitosan. As biodegradable, inexpensive, and sufficient abundance as a biomaterial, chitosan has been used in a variety of applications, including in the medical, agricultural, manufacturing and waste treatment fields. Chitosan has been reported to function as a material capable of reducing the presence of dyes in waste. Chitosan effectively absorbs reactive and acidic dyes, especially in low pH (Tan *et al.*, 2015). Chitosan, by its nature has a high affinity for adsorbing impurities such as heavy metals and dyes through the presence of several active groups available in this material. However, some of its properties such as only dissolving in acidic conditions, low mechanical strength, and small surface area can inhibit its adsorption ability. This makes chitosan requires modification with other materials to improve its nature (Representing *et al.*, 2014). Modifications are needed to improve the hydrophilicity. In this study, pectin was chosen as a biomaterial to modify chitosan. Addition of other materials to chitosan was

carried out to improve mechanical characteristics, swelling capacity and increase the adsorption capacity of dyestuffs (Zhang *et al.*, 2013).

METHODOLOGY

Material

Chitosan, Alginate from Surabaya, Acetic Acid 5%, Aquadest,

Procedure

Preparation of adsorbent

Synthesis of chitosan alginate to make adsorbent. Chitosan 0, 2 g was dispersed in 10 mL of acetic acid 5 % and then stirring until 3 hours. Alginate 0, 2 g was dispersed in 10 mL water and then stirring until 3 hours. After that, Chitosan solution was added to alginate solution and then stirring until homogeny. After all the solution is mixed, the mixture was then printed out into polypropylene container and dried in oven. After dry, the film can be peeled off from the container. The Chitosan-Alginate PEC adsorbent was ready.

Alg-Chi polyelectrolyte membrane, further washed with distilled water and dried at 60°C, and characterized by using an infrared spectrophotometer to show functional groups. Then the membrane analyzed using X-Ray Diffraction (XRD) to determine the stability of the membrane. And the furthermore it analyzed using Scanning Electron Microscopy (SEM) to determine the membrane morphology of the surface and cross section of the membrane.

RESULT AND DISCUSSIONS

FTIR Characterization

-COOH group is the dominant active group in alginate, while the dominant active group of chitosan is $-NH_2$ group. Fourier Transform Infrared (FTIR) Spectroscopy are used to see how interaction between components and the result of synthesis Polyelectrolyte Complex Chi-Alg (PEC) Chi-Alg film. From Fig. 1, it can be seen on three spectra in the region $3000-3700\text{ cm}^{-1}$ that can be observed a broad of hydrogen-bonded OH groups. In this area also can be observed NH group stretching vibrating which overlaps with OH vibration for chitosan spectra. In the area of $1500-1800\text{ cm}^{-1}$ can be observed the stretching vibration of the carbonyl group on the band at 1635 cm^{-1} for alginate (A). While in the chitosan

(B) spectra, in the area of 1597 cm^{-1} show stretching vibration C=O for amide group. In the area around $1600\text{--}1500\text{ cm}^{-1}$ in PEC spectrum induces an amine group that interacts with alginate, that is around 1627 cm^{-1} .

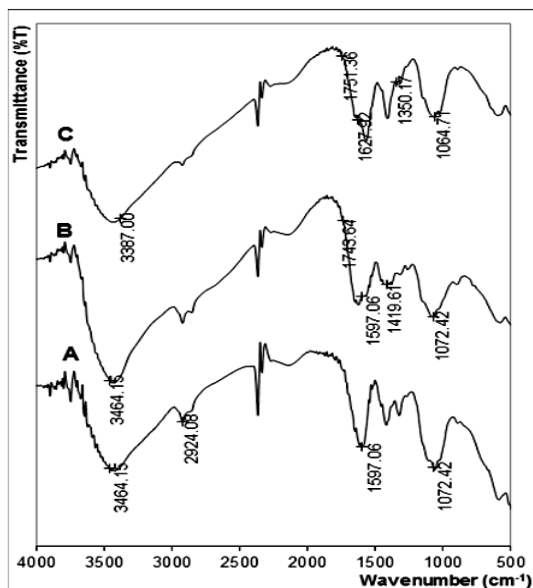


Fig. 1. FTIR spectra from film: A. Alginate; B. Chitosan; C. Alginate-Chitosan

Analysis of Chi-Pec PEC adsorbent by XRD

The phase form of the material from pure film (Alginate, Chitosan) and its modification, the membrane/film was tested using X-Ray Diffraction (XRD). XRD spectra result from alginate showed that the properties of alginate is amorphous, this was characterized by the absence of peaks which appeared anomaly, at peak $2\theta=22^\circ$. The characterized the phase of chitosan from the result of XRD test is semi-crystalline and have peak at $2\theta=22^\circ$ and 29° . In the PEC, between alginate and chitosan, the characteristics of chitosan and alginate is can be seen, it is a combination of chitosan and alginate, it causes the film to become semi-crystalline. This can be explained by the strong interaction like hydrogen bond and ionic interaction between pectin and chitosan with has destroyed the close packing of chitosan molecule for those formation of regular crystalline¹⁰. The presence of alginate in Alg-Chi PEC decreases the crystalline level of chitosan which is seen by the comparison of peak of each spectra.

SEM Analysis

Morphology of the PEC Alg-Chi adsorbent

film, it can be seen using SEM test, both from the surface and cross section. From the result of SEM for surface appearance with 500X magnification both chitosan and alginate have small and homogeneous pores (Fig. 3 A and B). Fig. 4 show image of Alg-Chi film from the surface in figure 4A and crosssection in figure 4B. It show that PEC film give a different pattern compared to the original compounds namely alginate and chitosan. Alg-Chi PEC film more porous and high complexity. The PEC Alg-Chi adsorbent has large pores surface and more rough, thus this adsorbent has potential to be applied as a super adsorbent to bind dyes in the waters. So it implies that PEC membrane was potential used as an adsorbent candidate for dyestuffs.

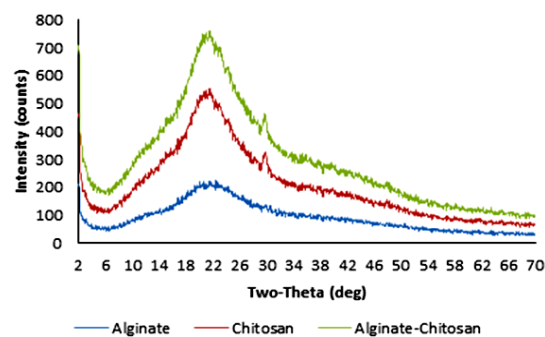


Fig. 2. XRD spectra of the film: A. Alginate; B. Chitosan; C. Alg-Chi

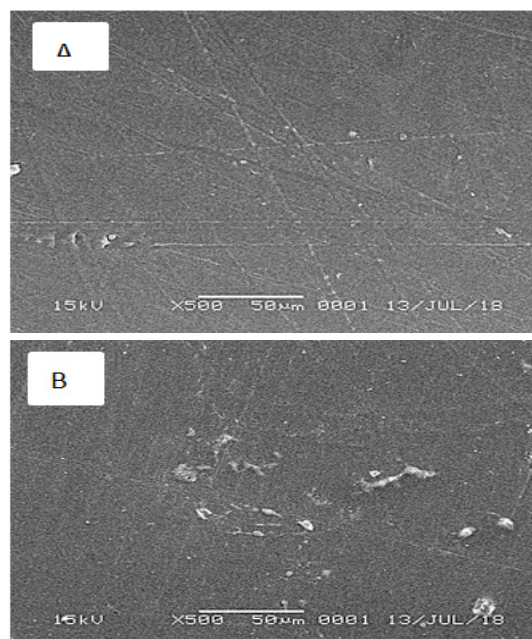


Fig. 3. Surface of the film by SEM with 500x magnification : A: Alginate, B:Chitosan

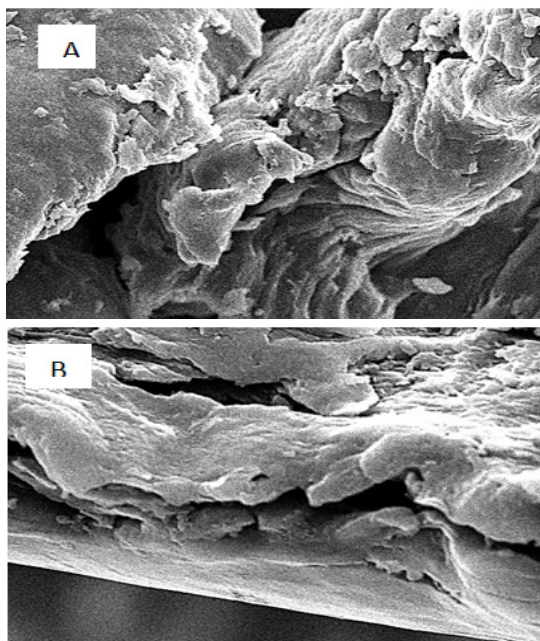


Fig. 4. The image of film by SEM with magnification 3000 x: A. Alg-Chi surface; B. Alg-Chi crosssection

CONCLUSION

Alginate-Chitosan polyelectrolyte complex (Alg-Chi PEC) were prepared by combine both polysaccharides Alginate and Chitosan. Based on FTIR spectroscopy, the adsorbent have active group comprise and interaction of carboxylate and amine groups. The result of characterization using XRD, show that the Alg-Chi PEC adsorbent is semi-crystalline. Based on SEM analysis, the film adsorbent has large pores with a high complexity.

ACKNOWLEDGEMENT

The authors express gratitude to the Indonesian Ministry of Research and Technology Directorate of Higher Education and Universitas Sebelas Maret for funding this research via shceme Hibah Mandatory.

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