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Synthesis and Characterization of Pectin–Chitosan crosslinked of BADGE for Adsorbents Candidate of Textile Dye Waste Water

Budi Hastuti[#], Saptono Hadi[*], Warih Purwendah[#]

[#] Department of Chemistry Education, Faculty of Teacher Training and Education.Universitas Sebelas Maret, Surakarta 57126, Indonesia
E-mail: Budihastuti@staff.uns.ac.id

[*]Department of Pharmacy, Faculty of Mathematics and Natural Sciences.Universitas Sebelas Maret, Surakarta 57126, Indonesia

***Abstract*— The increasing development of the textile industry in Indonesia has resulted in a negative effect on the dyes' wastewater that can pollute the environment. There are several methods developed to reduce the dyestuff levels in water pollution, such as coagulation and flocculation, membrane filtration, adsorption, precipitation, photocatalytic degradation, ion exchange, advanced oxidation, and biological treatment. In order to find out the solution, it is necessary to process liquid dyes waste, which has several advantages, including the relatively low cost and high efficiency in the process of absorbing liquid dyes. Commercial Chitosan and Pectin, Bisphenol A Diglysidyl Ether (BADGE) were purchased from Sigma Aldrich (Germany), Aceton, Acetic Acid 5%, and Aquadest. Mesoporous Pectin-Chitosan crosslinked BADGE (Pec-Chi-BADGE) membrane was successfully synthesized by the coacervation method, by mixing chitosan solution in 5% acetic acid and pectin solution in aqua dest, then added BADGE as a crosslinker to the solution. The structure and surface characteristics of Chi-Pec-BADGE membranes were analysed using Fourier transform infra-red (FTIR) spectroscopy, scanning electron microscopy (SEM), and XRD. Based on the FTIR characterization indicate that pectin chitosan crosslinked BADGE was successfully synthesized. The results showed that Chi-Pec-BADGE membranes could show the shift of peaks characterized by FTIR meant interactions of functional groups carboxyl, amine, and hydrogen. The results of XRD show that the Chi-Pec-BADGE membranes characteristic was amorphous. Furthermore, SEM data shows that the structure of the adsorbent was porous.**

***Keywords*— pectin; chitosan; Pec-Chi-BADGE; membrane; dye wastewater.**

I. INTRODUCTION

The development of the textile industry in Indonesia is increasing rapidly, which absorbs 1.3 million workers is one important issue recently. Improvement of the textile industry will also increase the pollution of dyes waste as a byproduct of the staining process. The dyeing process in the textile industry will produce 10-15% of the dyestuff as waste and discharged to the environment after the dyeing process. Synthetic dyes are used in the textile industry for reasons of cheap, durable, easy to obtain, and easy to use. However, the resulting waste is colorful and difficult to degrade. [1] Most dyes have complex aromatic structures that are stable and non-degradable under light or heat, even in the presence of oxidizing agents [2]. Long-term intake of water containing excessive dyes may be mutagenic and carcinogenic, in more serious, cause severe direct damage to the liver, digestive system, and the central nervous system of human beings [3]. In textile industries, approximately 10–15% of the dyes are discharged to the environment after the dyeing process, giving rise to a highly colored effluent [4].

There are several methods developed to reduce the dyestuff levels in water pollution such as coagulation and flocculation [5], membrane filtration [6], adsorption [7], precipitation [8], photocatalytic degradation [9], ion exchange [10], advanced oxidation and biological treatment [11]–[13]. From some of these methods, adsorption is considered one of the most promising alternatives to remove dyes from aquatic waste due to its ease of operation, high efficiency, and can be regenerated [14]. Because this method can effectively remove both organic and inorganic pollutants [6-8]. Moreover, the adsorbents can be restored and reused easily [15-17].

One of the most used adsorbents is a modification of pectin and chitosan. Organic-based material such as pectin and chitosan produce films with low physical stability, and hence the change of materials is necessary. Pectin is structurally and functionally the most complex polysaccharide in plant cell walls. [18] Chitosan is a compound with the chemical formula of poly- (2-amino-2-

dioxy-β-D-glucose) [19]. Chitosan is obtained from the deacetylation of chitin and is a natural polysaccharide found in shellfish such as shrimp, crab, lobster, and marine industry. Chitosan is an abundant, cationic adsorption method of biopolymer dye, high adsorption capacity, macromolecular structure, and easily modified. The presence of amino and hydroxyl groups in chitosan showed a high potential for dye adsorption [20].

II. Material and Method

A. Materials

Commercial Chitosan and Pectin, Bisphenol A Diglysidyl Ether (BADGE) were purchased from Sigma Aldrich (Germany), Aceton, Acetic Acid 5%, and Aquadest.

B. Procedure

Chitosan (0.2 g) was dissolved in 10 ml of acetic acid (5%) and stirred to the homogenate. In another container, Chitosan (0.2 g) was dissolved in 10 ml of aqua dest and awakened to the homogenate. For the crosslink solution, 0.113 g of crosslinker agent (BADGE) is dissolved in 25 ml of acetone. Furthermore, Pec-Chi-BADGE was synthesized by mixing three solutions in 2:2:1 ratio and then stirred for 3 hours at room temperature. Then, the mixture is printed into a polypropylene container and dried. After drying, the membrane is removed. Pectin-Chitosan crosslinked BADGE (Pec-Chi-BADGE) layer was characterized using FTIR spectroscopy, XRD, and using SEM.

III. Result and Discussion

A. XRD Characterization

The XRD patterns show that pectin (Figure 1) is amorphous.

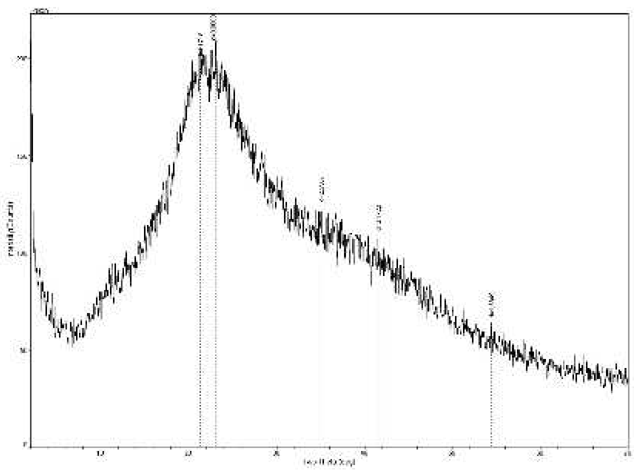

Fig. 1 XRD test result from pectin

It has one broad, sharp peak only at an angle (2Θ) = 21° degree whereas chitosan (Figure 2) is semi-crystalline because it has the height at an edge (2Θ) of 11° and 21°. If we look, Pec-Chi-BADGE (Figure 3) adsorbent shows no peak in the XRD pattern.

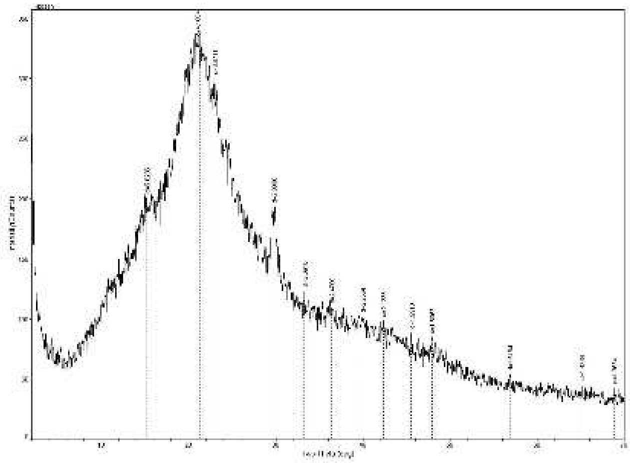

Fig. 2 XRD test result from chitosan

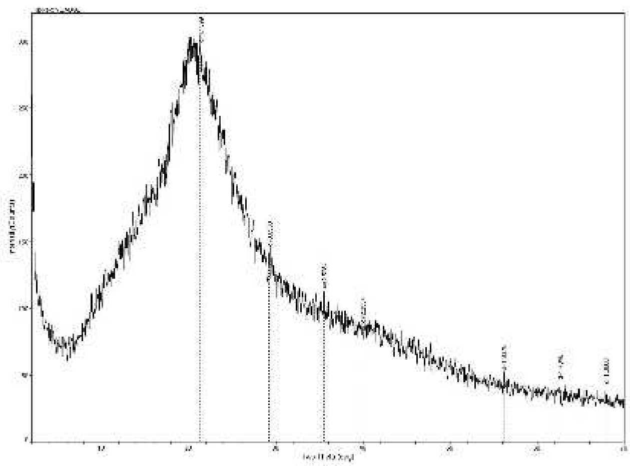

Fig 3. XRD test result from Pec-Chi-BADGE

This fact from all XRD test results (Figure 4) probably indicates the decreased ability of hydrogen bonds because of chemical modification, and therefore, pec-chi-BADGE adsorbent becomes amorphous material and more stable.

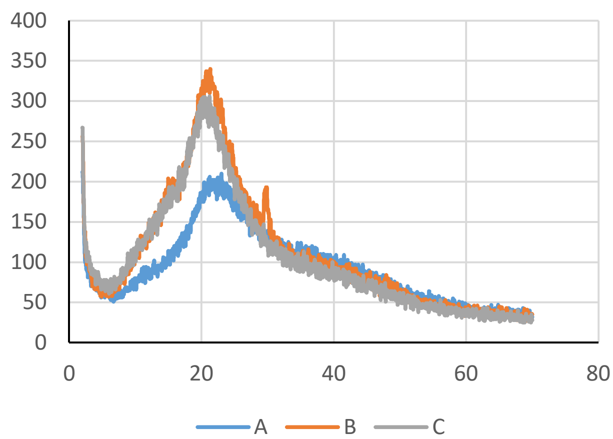

Fig. 4 XRD test result from Pec-Chi-BADGE

B. SEM Characterization

From SEM test result of pectin in figure 5 and 8, it shows that the surface appearance with 500x magnification has small pores and homogeneous. The image in Figures 6 and 9 is the SEM test result from chitosan that appearance with 500x magnification. It shows that chitosan has small pores and homogeneous. After crosslinking with BADGE in the Pec-Chi-BADGE membrane in figure 7, the surface very porous and structurally, the porous is coarser (Figure 10). The SEM image test result clearly shows that Pec-Chi-BADGE exhibit many pores with different shapes and sizes. So, it shows the porous beads have a high surface area and potential to the adsorbent. Because there is a direct relationship between the surface area of adsorbent and the efficiency of adsorption [21]. This shows that the substance can be used for adsorbent, one of which is the adsorbent of dyes.

Fig. 5 SEM test result of the surface from membrane pectin

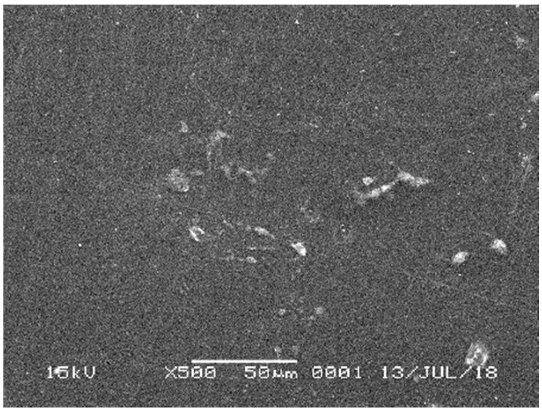

Fig. 6 SEM test result of the surface from membrane chitosan

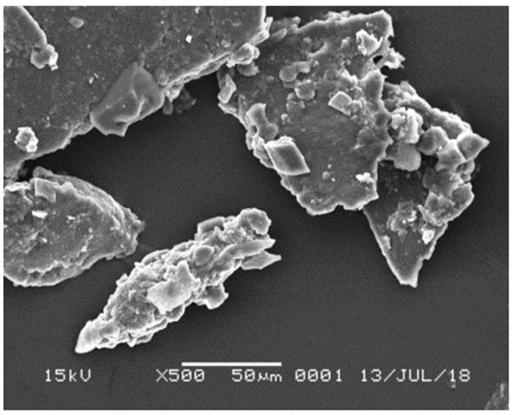

Fig. 7 SEM test result of the surface from membrane Pec-Chi-BADGE

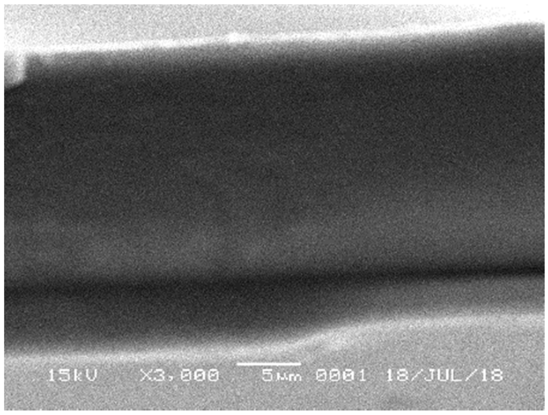

Fig. 8 SEM test result of a cross-section from membrane pectin

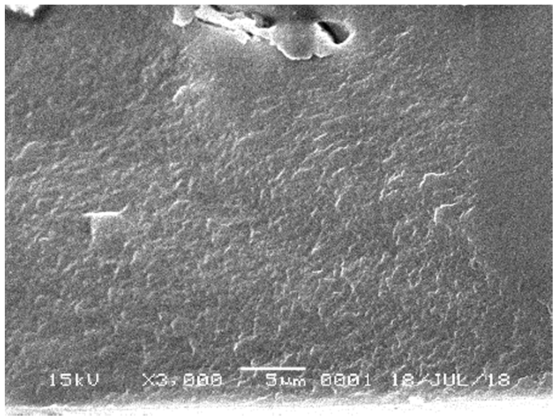

Fig. 9 SEM test result of a cross-section from membrane chitosan

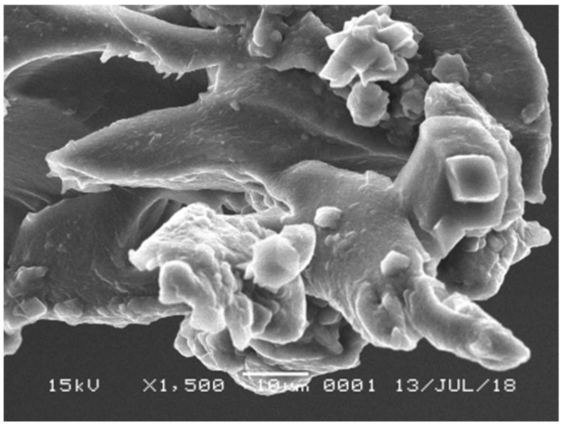

Fig. 10 SEM test result of a cross-section from membrane Pec-Chi-BADGE

C. FTIR Analysis

The FT-IR spectrum of chitosan (Figure 11A) shows absorption peaks at 3425 $cm^{-1,}$ which correspond to the hydroxyl group (-OH group) and N-H stretching vibration, at 1597 cm^{-1} which correspond to $-NH_2$. The peak at 2924 cm−1 is attributed to the stretching vibration of the C-H bond of methylene present in Chitosan beads. The overlap probably causes the Expansion and shift of -OH peak with that of -NH of the amine. The absorption band at 2854 cm^{-1} is a stretching vibration of C-H group methylene and at 1080 cm^{-1} is belongs to the C-O group. Another band of chitosan is observed at 1651 cm^{-1}, indicating the presence of amide groups (-NHCO). The peak at 3448 cm−1 is corresponding to the hydroxyl group (-OH group) of Pectin Beads (Figure 11B). The height at 1064 cm^{-1} is the stretching vibration of -

CO. Absorption at 1604 cm^{-1} is a specific absorption for -COOH group.

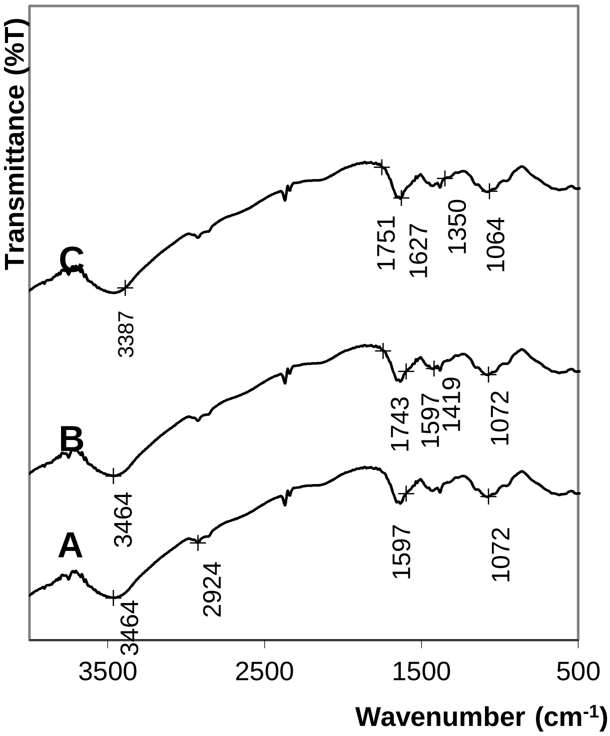

Fig. 11 FTIR test result from membrane: A. Chitosan; B. Pectin; C. Pectin-Chitosan-BADGE

Furthermore, the FTIR spectra for Pec-Chi-BADGE (Figure 11C) shows that this material has a hydroxyl group (-OH group), which indicated by the presence of a peak at wavenumbers of 3425 cm^{-1} and an active carboxylic group (-COOH) at 1581 cm^{-1}. The bands related to C=O stretching of the ester could also be observed at 1851 cm^{-1} [22-24]. The Peak is on 833 cm^{-1} is corresponding to para-substituted C-H on the benzene ring. The result indicates that BADGE has been cross-linked [25], and Pec-Chi-BADGE has been successfully synthesized.

D. Effect of pH

In this study, the impact of pH of the solution was studied using 10 mL of 10 ppm methylene blue solution, which was interacted with 10 mg adsorbent membrane at pH variation of 2, 3, 4, 5, 6, 7, and 8. The solution was then shaken for 60 min, and at certain times the solution samples were taken. The concentration of methylene blue in the solution was measured based on its absorbance using a UV-Vis spectrophotometer at a maximum wavelength of 660 nm.

Pec-Chi-BADGE membranes contain carboxyl groups from pectin and amino groups from chitosan. In this study, the pH range of 4 to 8 was chosen as at pH <4 pectin-chitosan membrane was slightly fragile because the $–NH_2$ group of chitosan was protonated to $–NH_3^+$. This was indicated by the presence of some material that was released from the Pec-Chi-BADGE membrane that led the solution to become cloudy. At pH <4, the amount of –COO group of pectin was very small, so the interactions that occur between $–NH_3^+$ from chitosan and –COO from pectin were limited.

It was found that the optimum pH for the Pec-Chi-BADGE membrane was pH 5. At pH 5, the high percentage of adsorption could be affected by the presence of many $–NH_2$ groups from chitosan, causing interaction with the carboxyl group on the pectin decreasing. This results in the increasing number of –COO groups in the pectin, which can interact with methylene blue. Besides, it was assumed that the chitosan-pectin and Pec-Chi-BADGE membrane pores were matched, which resulted in greater methylene blue adsorption.

The plot of methylene blue adsorption by the Pec-Chi-BADGE membrane are presented in the figure below.

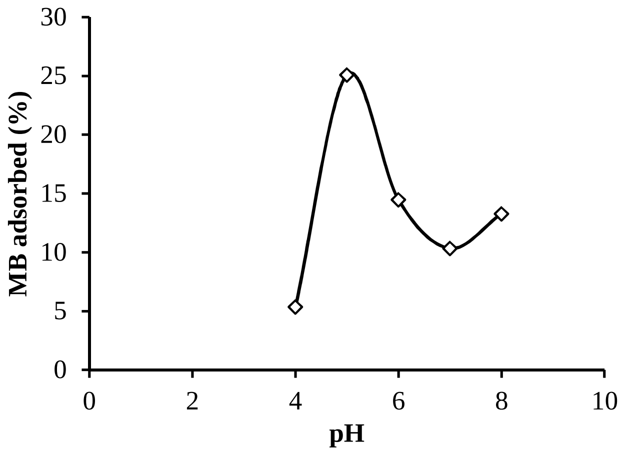

Fig. 12 The methylene blue adsorption by Pec-Chi-BADGE membrane

IV. CONCLUSIONS

The Pec-Chi-BADGE layer is made by a concertation method to combine pectin and chitosan in order to get excellent adsorbent to reduce dyes concentrate in wastewater and resistance on acidic condition. Based on the XRD characterization of Pec-Chi-BADGE, the structure of the membrane is amorphous and leed to give stable properties. Based on the FTIR characterization indicate that pectin chitosan crosslinked BADGE was successfully synthesized. Peak appearance at 833 cm^{-1} shows phenyl groups in BADGE material. The presence of carboxylic and amine active groups leed to the membrane was potentially be used as strong adsorbents. Based on SEM characterization, the structure of Pec-Chi-BADGE is very porous with a rough pore structure. This shows that the membrane can be used as an adsorbent; one of them is dyes adsorbent.

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