Adsorption of Methylene Blue Dyes Using Pectin Membrane

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Abstract: Environmental pollution caused by methylene blue textile dyes is very dangerous for the aquatic environment and human health. To overcome this problem, various adsorbents have been developed for the processing of methylene blue liquid waste. This aim of this research is to know the ability of pectin membrane toward methylene blue dyes. Pectin is a biomaterial isolated from the plant cell walls. Pectin is an anionic polymer, many contain active groups which able to bind positive ions of methylene blue. This method of this research is an experimental method in the laboratory. Pectin adsorbent membrane was made by dissolving of pectin into a 5% acetic acid solution. The optimal condition of the adsorption of methylene blue by pectin membrane was determined. The functional groups of pectin membranes were analyzed by infra red spectroscopy. The adsorption of methylene blue was analysis by using Ultraviolet-Visible Spectroscopy. The characterization of FTIR showed that pectin membranes have carboxyl and hydroxyl active groups. The results showed that the optimum condition of the adsorption process of methylene blue dye was within pH 4 with adsorption capacity of 0.75 mg/g and 60 minutes of contact time with adsorption capacity 17.64 mg/g. The optimum adsorption capacity of pectin membranes in adsorbing methylene blue was 19.39 mg/g

Keyword: pectin membrane, methylene blue, carboxyl group, hydroxyl group

1. Introduction
In an industrial process, dyes are often used, both in the textile, paper, cosmetics, plastic, food and cigarette industries. The biggest use of dyes is in the textile industry in the coloring process (dyeing). Waste from the textile industry in the form of water-soluble dyes. The development of the textile industry in Indonesia continues to increase, thereby also increasing liquid dye waste which is increasingly polluting the environment. The polluted environment will disturb the balance of the ecosystem.

There are 3 types of dyes in the textile industry, namely anionic, cationic and non-ionic [1]. One of the most widely used dyes is methylene blue (C₁₆H₁₈CIN₃S) which is a cationic dye [2]. Methylene blue can be toxic to the environment and humans. In the environment, the concentrated methylene blue content can inhibit the penetration of sunlight into the waters so that it disturbs the ecosystem. In humans can interfere with health [3].

To overcome these problems, it is necessary to liquid dye waste treatment. Various methods have been carried out to remove dyes including Chemical methods such as indirect electrochemical oxidation [4], advanced oxidation process [5]; biological methods using ligninolytic enzyme from fungi [6], activated sludge microorganisms [7]; As well as the physical methods through filtration membranes [8] and adsorption with activated carbon[9]. Among these methods, the adsorption
process is one of the effective methods for removing dyes from wastewater [10]. The adsorption method is a simple economical and environmentally friendly method for removing dyes [11]. Adsorption by using an adsorption membrane can adsorb metal ions [12]. Adsorption using a membrane gets better adsorption capacity and a relatively faster time than granular form [13].

Pectin is a complex polysaccharide compound found in plant walls and is acidic. Pectin compounds are derived from the word pectos, which means thickener. The constituent of pectin compounds is carbohydrates and polygalacuronic acid, where there are carboxyl groups that can be partially esterified [14]. Pectin is a natural polysaccharide that is water-soluble and has a carboxyl methylate group [15]. The adsorption process occurs because methylene blue which is positively charged dyes will be attracted by pectin which is a negatively charged polysaccharide. This study uses pectin which is then made into a membrane. Pectin membranes are prepared by dissolving pectin powder into 5% acetic acid. Furthermore, the pectin membrane was characterized and its adsorption ability was tested against the methylene blue dye. The importance of this research is because it is easy to do and effective in reducing methylene blue but does not require expensive costs. The novelty of this study compared with research from other researchers is to make a membrane from a biopolymer material namely pectin as an adsorbent membrane to adsorb methylene blue dyes.

2. Procedure

2.1. Preparation of adsorbent.

Synthesis of pectin membrane to make adsorbent. Pectin 0.2 grams was dispersed in 10 mL of acetic acid 5% and then stirring until 1 hour to form a gel. Pectin gel was then poured into a membrane mold (polypropylene container) and dried. After drying, pectin membranes are formed, then characterized using FTIR to analyze functional groups, testing the membrane crystallinity using XRD and testing surface morphology and cross-section using SEM.

2.2. Application of absorbent membrane.

2.2.1 The effect of acidity (pH) of the solution on dye adsorption. Pectin membrane 20 mg was immersed in a 20 mL methylene blue solution 50 ppm which has been varied pH 2, 3, 4, 5, 6 and 7 with 0.1 M NaOH, 1 M NaOH and 0.1 M HNO₃ solution. The mixture is stirred for 2 hours at a speed of 50 rpm. Then the mixture is filtered. The filtrate and the blank solution were diluted with distilled water and then analyzed by Ultraviolet-visible Spectroscopy (UV-Vis).

2.2.2 The effect of contact time of the solution on dye adsorption. Pectin membrane 20 mg was immersed in a 20 mL methylene blue solution 50 ppm which has been adjusted to the optimum pH then is stirred with different time variations with variations in contact time was 15, 30, 45, 60, 75, 180, 360, 720 and 1440 minute. Then the mixture is filtered. The filtrate and the blank solution were diluted with distilled water and then analyzed by Ultraviolet-visible Spectroscopy (UV-Vis).

2.2.3 The effect of concentration of the solution on dye adsorption. Pectin membrane 20 mg was immersed in a 20 mL methylene blue solution which has been adjusted to the optimum pH then is stirred with different concentration variations with variations in concentration was 10, 20, 30, 40, 50, 60, and 70 ppm. Then the mixture is stirred for 2 hours. After that, the mixture is filtered. The filtrate and the blank solution were diluted with distilled water and then analyzed by Ultraviolet-visible Spectroscopy (UV-Vis).

3. Result and Discussions

3.1. FTIR Spectrum of Membrane

How to see the interaction between components of pectin in membrane is used Fourier Transform Infrared (FTIR) Spectroscopy. From figure 1, it can be seen on spectra in the region 3000-3700 cm⁻¹
can be observe a broad of hydrogen-bonded OH groups. In pectin, the dominant active group is -COOH group, which is can see in area 1500-1800 cm\(^{-1}\). The band at 1643 cm\(^{-1}\) can be observed the stretching vibration of the carbonyl group. Based on pectin spectra, at 1380 cm\(^{-1}\) are C-H bending and at 1300-1000 cm\(^{-1}\) are C=O stretching.

**Figure 1.** FTIR test result from pectin membrane

3.2. **XRD Characterization**

X-Ray Diffraction (XRD) are used to analysis the phase form of the material from pectin membrane. The result of XRD spectra showed that the properties of pectin is amorphous. This characterized can be seen in the absence of peaks which appeared anomaly, at peak \(2\theta=20^\circ\). If the peak at \(2\theta=20^\circ\) emerge, the membrane will have semi-crystalline or crystalline properties.

**Figure 2.** XRD test result from pectin membrane.

3.3. **SEM Characterization**

Scanning Electron Microscope (SEM) is used to view morphology of pectin membrane. Its can see both forms the surface and cross section of membrane. In the 500X magnification for surface appearance pectin have small and homogeneous pores (figure 3). And from a cross-section view (figure 4), the pores are smoother and smaller. So that if it is made into an adsorbent it can absorb more dyestuffs.
3.4 Adsorption test The effect of acidity (pH) on dye adsorption.

The contact between the pectin membrane and the methylene blue solution varies in pH solution from 2 to 8. This is to see the pH at which the optimum methylene blue solution can be absorbed. From the results of contacting the pH variation of the methylene blue solution with the pectin membrane, it was found that methylene blue can be absorbed in optimum at pH 4 with an adsorption capacity of 700 μg / g. From Figure 5, it can be seen that after pH 4, the absorption results in a decrease in the capacity of methylene blue adsorption.

3.5 The effect of contact time on dye adsorption.

From the contacting process between the pectin and methylene blue membranes using different time variations, it was found that the pectin membrane can absorb the optimum methylene blue at the 60 minute with a percent of adsorbed about 70.5%. From Figure 6, it can be seen that after the 60th minute, absorption has decreased. This happens because at the optimum time (60 minutes), the active site on the membrane is still widely available. But after passing the optimum time, the membrane begins to saturate and the active surface of the membrane is covered by methylene blue so that the membrane's absorption ability decreases.
3.6 The effect of concentration of the solution on dye adsorption.

From Figure 8, it can be seen that the absorption of methylene blue by the pectin membrane has increased with increasing concentration of methylene blue. This is possible that in low concentration condition, the amount of methylene blue contained is also low so that the active sites of the pectin membrane are still large. The optimum adsorption capacity of pectin membranes in adsorbing methylene blue was 19.39 mg/g which corresponds to 70.5% of initial concentration.

This result is comparable to other previous studies. For example, study on adsorption of brilliant blue R dyes using biomaterials of activated sludge microorganisms reported adsorption capacity of 60% [7]. Another result of congo red adsorption by activated carbon from *Mucuna pruriens* seed shells obtained adsorption capacity of 60% [9]. This shows that pectin membrane which is a biosorbent is quite potential to be used as an absorbent to remove dyes from waste water from the environment.
4. Conclusion

Pectin membrane has hydroxyl and carboxyl active groups, and forms a microporous membrane. Pectin membrane can adsorb the methylene blue optimum on pH 4 with adsorption capacity is 0.75 mg/g. Pectin membrane can adsorb the methylene blue optimum on with contacting time on 60 minute with percent is absorbed of methylene blue is 70.5%. The adsorption of pectin membrane toward methylene blue has increased with increasing concentration of methylene blue.

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