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OPTIMIZATION OF CHITOSAN/PECTIN POLYELECTROLYTE COMPLEX USING GLUTARALDEHYDE-CROSSLINKED AS METHYLENE BLUE ABSORBENT

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ABSTRACT
This study aimed to make a crosslinked chitosan/pectin membrane with glutaraldehyde under conditions of time, pH, and maximum concentration in the adsorption of methylene blue. The first step was to synthesize the chitosan-pectin polyelectrolyte complex membrane which was cross-linked with glutaraldehyde by dissolving pectin in distilled water, then combining chitosan in acetic acid and adding glutaraldehyde and evaporated at 70°C. The second step is to characterize the synthesized membrane using FTIR, and determine the optimum contact time, optimum pH, and maximum concentration of methylene blue in adsorption. The results showed that the optimum mass ratio of 10% glutaraldehyde crosslinked polyelectrolyte membranes of 10% glutaraldehyde at the optimum contact time to adsorb methylene blue was 40 minutes with an adsorption capacity of 7,125 mg/g; The optimum pH is 6; the maximum adsorption concentration of methylene blue was 100 mg/L with the maximum adsorption capacity being 40.244 mg/g and following the Langmuir isotherm, the equilibrium constant (K) was 1.42 × 104 L/mol.
Keywords: Chitosan/Pectin, Crosslinked, Glutaraldehyde, Adsorption, Methylene Blue.
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INTRODUCTION

Dye in the textile, carpet, pulp, and paper industries is an important component that is always used.[1] One of the dyes that are often used is methylene blue. The use of dyes in various industries will produce waste that can cause environmental pollution that will disrupt terrestrial ecosystems, water, and also human health.[2] The resulting waste causes skin irritation, respiratory tract irritation, vomiting, diarrhea, nausea, and cyanosis.[3,4] The adsorption method is rated as one measure to prevent and reduce waste from the use of methylene blue which can harm the environment and health. This method has advantages in addition to being environmentally friendly, safe, simple in design and operation, requiring low energy, non-toxic, and inexpensive.[5] Absorbents that have been widely used in absorbing methylene blue include chitosan[6], pectin[7], and the combination of chitosan/pectin.[8] Chitosan and pectin are natural polymer compounds that are widely used as absorbents because they have good permeability and mechanical strength. Various modifications were made to improve the physical characterization with various compounds made by crosslinking.[9,10] This study modified the absorbent as a methylene blue absorbent, namely a cross-linked chitosan/pectin polyelectrolyte membrane with glutaraldehyde which was determined to optimize absorption based on time, pH, and the maximum concentration of adsorbed methylene blue.

EXPERIMENTAL

Materials

Methylene Blue (base blue 9, CI_{52015}; chemical formula, $C_{16}H_{18}N_3ClS$) (Merck), pectin (UD Yogyakarta, Indonesia), chitosan isolated from crab shells, CH_3COOH (Merck), NaOH, glutaraldehyde (GLA), HCl (Merck), NaCl, FT-$IR_{(KBr)}$ (Shimadzu) and Spectrophotometry UV-Visible (Shimadzhu Prestige21).

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Crosslinked Using Glutaraldehyde Chitosan/Pectin Membrane Preparation

The formation of glutaraldehyde crosslinked chitosan/pectin polyelectrolyte membrane refers to the modified reference.[11,12,13] Pectin 0.6 g was dissolved in 20 mL distilled water, added 1.4g chitosan then stirred rapidly with the addition of 78 mL 0.4 M acetic acid until the solution is homogeneous for 2 hours and 2 mL of 10% glutaraldehyde is added and then stirred for 45 minutes. Crosslinked using glutaraldehyde chitosan-pectin membrane was poured into a Petri dish and dried in an oven for 6 hours at 70°C. Added 2 mL of 1 M NaOH and let stand for 12 hours, then the membrane film was washed with distilled water and dried at room temperature.

Crosslinked Using Glutaraldehyde Chitosan/Pectin Membrane Characterization

Characterization of membrane films using spectrophotometer FTIR, and membrane stability at various pH.[12,14] The manufacture of crosslinked using glutaraldehyde chitosan-pectin membranes was carried out by varying the mass of chitosan: pectin: glutaraldehyde can be seen in Table-1.

Table-1: Mass Ratio Variations of Chitosan, Pectin, and Glutaraldehyde

No	Mass ration Chitosan: Pectin	Mass of Chitosan (g)	Mass of Pectin (g)	Volume of GLA (mL)
1	70% : 30%	1.4	0.6	2
2	80% : 20%	1.6	0.4	2
3	90% : 10%	1.8	0.2	2

Optimization of Time and Membrane pH Against Methylene Blue Adsorption

The adsorption process for methylene blue was carried out with variations in contact time, pH, and concentration of methylene blue.[12] Variations in contact time used were 5, 10, 15, 20, 25, 30, 40, 50, 60 and 90 minutes. While the variations in pH used were 3, 4, 5, 6, 7, 8, and 9. The concentration variations of methylene blue used were 25 mg/L, 50 mg/L, 100 mg/L, 150 mg/L, and 200 mg/L. Analysis of the adsorbed methylene blue was observed and determined using spectrophotometry UV-Vis.

RESULTS AND DISCUSSION

Membrane Analysis with FT-IR(KBr)

This study used chitosan/pectin as an adsorbent material crosslinked with glutaraldehyde. Chitosan has an active amine group and pectin has a carboxylic group and interaction is formed between chitosan/pectin by involving the -NH active group with a carboxylate (-COOH) to form $-NH_3^+$ ions to form a complex polyelectrolyte membrane that can adsorb cationic dyes by utilizing the hydroxyl group (-OH) on the membrane. The chitosan/pectin membrane forms a stable polyelectrolyte complex.[15,16] The resulting chitosan/pectin membrane is unstable at a pH below five so the glutaraldehyde aldehyde group cross-links with the -NH group of chitosan to form a Schiff base, so the membrane is stiffer than its original nature. Crosslinked using glutaraldehyde chitosan/pectin membranes were characterized using an $FT\text{-}IR_{(KBr)}$ spectrophotometer. The $FT\text{-}IR_{(KBr)}$ spectrum of chitosan (Fig.-1a) shows the absorption peak of the OH group at a wave number of 3425.58 cm^{-1}, the absorption of the methylene CH group at a wave number of 2877.79 cm^{-1}, and a wave number of 1080.14 cm^{-1}. shows the absorption of the CO group. The wide absorption of the -OH group is due to overlapping with the absorption of the -NH group. Another absorption occurred in the area of 1651.07 cm^{-1} indicating the presence of a -NHCO.[14,16,17] group. The $FT\text{-}IR_{(Kbr)}$ spectrum of pectin at a wave number of 3387.00 cm^{-1} (-OH group); 2939.52 cm^{-1}(aliphatic C-H group); 1064.71 cm^{-1} (-CO group) and 1627 cm^{-1} (-COOH group)[12,14] are shown in Fig.-2. The characteristics of crosslinked using glutaraldehyde chitosan/pectin membrane indicated absorption peaks at wave numbers 3343 cm^{-1} (-OH group) and 1604.77 cm^{-1} indicating the formation of interactions between chitosan-pectin and crosslinked using glutaraldehyde.

Optimization of Crosslinked Using Glutaraldehyde Chitosan/Pectin Membrane

Determination of the optimization of the adsorbent membrane aimed to determine the optimum time required for the adsorbent to adsorb methylene blue optimally. The time variations of the adsorbent used were 5, 10, 20, 25, 30, 40, 60, and 90 minutes. The 10% glutaraldehyde crosslinked chitosan/pectin membrane obtained the optimum time at 40 minutes for 70:30 membranes with an adsorption capacity of

7.125 mg/g; 80:20 membrane with adsorption capacity of 6.914 mg/g; and 90:10 membrane, the optimum time was obtained in the 30th minute with an adsorption capacity of 6.015 mg/g. After 40 minutes there was a decrease due to desorption, the methylene blue adsorbent released methylene blue. The graph of the relationship between methylene blue contact time and adsorption capacity with crosslinked using glutaraldehyde chitosan/pectin membranes is shown in Fig.-2.

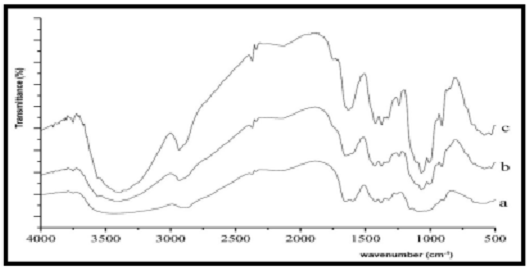

Fig.-1: FTIR Spectrum of the Membrane (a) Chitosan; (b) Pectin; and (c) Cross-linked Using Glutaraldehyde Chitosan/Pectin

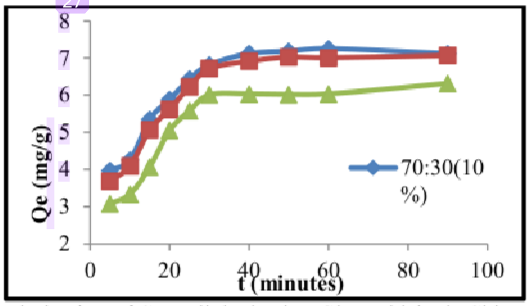

Fig.-2: Optimization of Cross-linked using Glutaraldehyde Chitosan/Pectin

Optimizing the pH of Cross-linked using Glutaraldehyde Chitosan/Pectin

The degree of acidity or pH of the solution is one of the parameters that determine the adsorbent in the adsorption process. A pH value that is too low or too high makes the adsorbent not work optimally. Determination of the optimum pH was carried out at pH variations of 3 to 9 (Fig.-3). The results showed that pH 3 had an adsorption capacity of 7.606 mg/g and increased at pH 4 and pH 6 was the optimum condition with an adsorption capacity of 8.22 mg/g. Furthermore, the adsorption capacity decreased to pH 9, this was due to the high pH conditions containing more -OH ions in the solution, resulting in an interaction between OH- ions and methylene blue. Methylene blue has a strong interaction with OH- from the solvent so the interaction between methylene blue and the active site of the membrane is getting smaller.

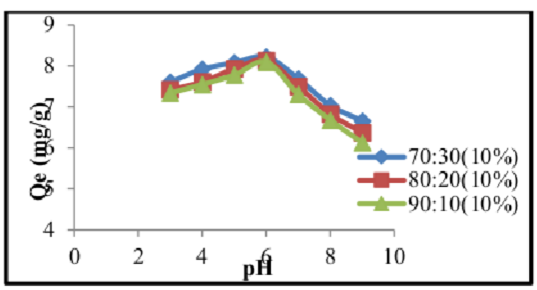

Fig.-3: pH Optimization of Cross-linked Using Glutaraldehyde Chitosan/Pectin Membranes

Maximum Absorption Analysis of Cross-linked using Glutaraldehyde Chitosan/Pectin

Determination of the effect of methylene blue concentration on adsorption crosslinked using glutaraldehyde chitosan/pectin membrane aims to determine the maximum absorption capacity of methylene blue. The analyzed concentrations of methylene blue were 25 mg/L, 50 mg/L, 100 mg/L, 150 mg/L, and 200 mg/L at the optimum pH and absorption time. Determination of the maximum absorption of various concentrations was measured using UV-Visible spectrophotometry at a maximum wavelength of 664 nm. The relationship between the absorption capacity of the membrane and the concentration of methylene blue is shown in Fig.-4.

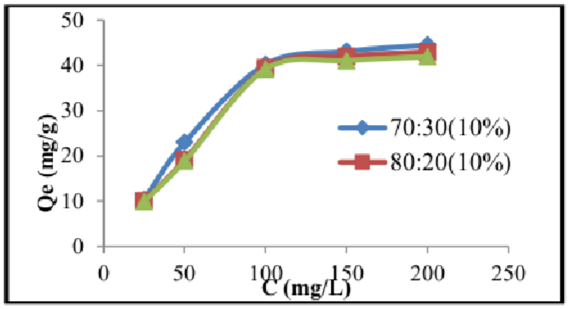

Fig.-4: Graph of the Relationship between the Absorptive Capacity of Cross-linked Using Glutaraldehyde Chitosan/Pectin Membrane and the Concentration of Methylene Blue

The adsorption of methylene blue tends to increase at concentrations of 25-100 mg/L, but at concentrations of 150 and 200 mg/L, there is a decrease in absorption. The maximum adsorption of methylene blue occurred at an adsorbate concentration of 100 mg/L with an adsorption capacity of 40.244 mg/g for 70:30 membranes, 39.462 mg/g for 80:20 membranes, and 39,229 mg/g for 90:10 membranes. Initially, it was able to absorb a low concentration of methylene blue, while at an equilibrium of 100 mg/L the adsorption decreased because the active site of the membrane was already saturated.

Cross-linked using Glutaraldehyde Chitosan/Pectin Adsorption Isotherm

The adsorption isotherm was determined using various concentrations of methylene blue 25 mg/L, 50 mg/L, 100 mg/L, 150 mg/L, and 200 mg/L with a volume of 50 mL. Measurements were made at the optimum contact time and optimum pH. The isotherm pattern of methylene blue adsorption by chitosan/pectin cross-linked with glutaraldehyde was analyzed using the Langmuir and Freundlich isotherm pattern. The maximum adsorption capacity, equilibrium constant, and adsorption energy were determined from the adsorption isotherm. The Langmuir and Freundlich isotherm curves are shown in Fig.-6. The crosslinked using glutaraldehyde chitosan/pectin membrane adsorption isotherm follows the Langmuir isotherm, which is the adsorption of one layer of methylene blue adsorbed on each membrane surface. The Langmuir isotherm correlation value (R^2) is close to 1 compared to the Freundlich correlation isotherm shown in Table-2.

Table-2: Langmuir and Freundlich Adsorption Isotherm Constants

Adsorbent Composition	Langmuir			Freundlich		
	q_{max} (mg g^{-1})	K_L (L mol^{-1})	R^2	1/n	K_F (mg g^{-1})	R^2
70:30 (10%)	108.7	1.42×10^4	0.99	0.70	6.63	0.93
80:20 (10%)	85.5	1.12×10^4	0.97	0.62	4.96	0.87
90:10 (10%)	80.0	1.07×10^4	0.97	0.59	5.03	0.85

CONCLUSION

The formation of the crosslinked using glutaraldehyde chitosan/pectin polyelectrolyte membrane as indicated by the absorption of the hydroxide group (-OH) at wave numbers 3343 cm^{-1} and 1604.77 cm^{-1} indicating an interaction between crosslinked chitosan/pectin and glutaraldehyde. The crosslinked using glutaraldehyde chitosan/pectin polyelectrolyte membrane has a maximum adsorption capacity of 108.7 mg/g at a composition of 70:30 (10%) and is not damaged at pH 2. The adsorption isotherm of the crosslinked using glutaraldehyde chitosan/pectin polyelectrolyte membrane follows the Langmuir isotherm.

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