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The Efficiency of κ-Carrageenan-Chitosan-PVA-MWCNTs Membranes in Removing Methylene Blue, Rhodamine B, Bromocresol Purple, and Murexid from Water

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Abstract. The electrocoagulation method has been proven to be highly effective in removing metal ions from water, with a removal efficiency of over 97%. However, in terms of removing organic pollutants such as synthetic dyes, the efficiency of electrocoagulation is still relatively low. A hybrid approach combining electrocoagulation with membrane filtration has been proposed to enhance the removal of organic contaminants. Eco-friendly membranes made from renewable natural polymers like carrageenan and chitosan, reinforced with synthetic polymers such as polyvinyl alcohol and carbon nanotubes, have shown to be promising for this application. In this study, membranes with varying chitosan/carrageenan ratios of 0.2, 0.33, 0.5, and 0.71 (g/g) were used to remove synthetic dyes, including methylene blue, rhodamine B, bromocresol purple, and murexid, at a concentration of 200 ppm from 8.5 ml of water. From the SEM images, the four membranes have almost the same surface and cross-section morphology. The results showed that the membrane with a chitosan/carrageenan ratio of 0.71 exhibited the highest removal efficiency for all synthetic dyes. The parameter affecting the membrane's removal efficiency is the interaction between the membrane and synthetic dyes. Murexid, an anionic dye, achieved a 100% removal efficiency, surpassing cationic dyes such as rhodamine B and methylene blue. Besides interactions, the dye's molecular size determines the removal's efficiency. The molecular size of rhodamine B is larger than that of methylene blue, and the removal efficiency of rhodamine B (98.4%) is greater than methylene blue (91%). Bromocresol purple is almost the same size as rhodamine B but not ionic because it has the lowest removal efficiency of 34.55%.

Keywords: Bromocresol Purple, Chitosan, Methylene Blue, Murexid Purple, Rhodamin B, κ-Carrageenan

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INTRODUCTION

The selection of methods for removing contaminants or pollutants depends on the size of the pollutant, with different methods being suitable for different size ranges. Electrocoagulation, ion exchange, and reverse osmosis can be effective for atomic range-sized pollutants like metal ions and salts. Molecular size ranges can be addressed with electrocoagulation, ultrafiltration, and nanofiltration methods, while micro and macro particle ranges require media, microfiltration, or particle filtration methods (Shahedi et al., 2020). Although electrocoagulation is highly effective in removing metals (>97%), it has lower removal efficiency for total suspended solids and total organic pollutants (40% and 84%, respectively) (Widarti and Raharjo, 2021). Therefore, hybrid methods that combine electrocoagulation with filtration have been developed to simultaneously remove pollutants of different size ranges (Tahreen et al., 2020). Infiltration, adsorption, and absorption methods, membranes can be made from synthetic materials derived from petroleum or biopolymers from natural sources (Bandehali et al., 2021). Membranes made from natural polymers such as cellulose/polysaccharides (chitosan, alginate, carrageenan), polyhydroxy alkanoates, and plastic proteins are also widely used in filtration and adsorption (Phan et al., 2021). Synthetic membranes used in water treatment include polyamide, polycarbonate, and polyvinyl alcohol (PVA) (Ngoma et al., 2021).

Carrageenan and chitosan-based membranes have been extensively developed and studied due to their renewable characteristics, excellent water vapor permeability, and abundant availability. K-carrageenan membranes are used to remove organic compounds such as methylene blue and metal ions from water (Udayakumar et al., 2021). Chitosan and its derivatives have been widely used as a pollutant remover from water (Alshahrani et al., 2020). Unfortunately, this natural biopolymer-based membrane has drawbacks such as poor mechanical properties. To overcome this deficiency, natural polymer-based filter membranes are crosslinked with synthetic polymers such as PVA and reinforced with carbon nanotubes (CNTs) (A. A. Alshahrani et al., 2017).

Membranes made of chitosan and carrageenan that have been reinforced with PVA and carbon nanotubes need to be tested for their ability to remove organic pollutants. Carrageenan is known for its ability to increase membrane porosity, which impacts filtration efficiency. While chitosan can influence the hydrophobic properties of the membrane and its interaction with organic pollutants, thereby influencing removal efficiency. The differences in function between carrageenan and chitosan membranes were made by varying the ratio to obtain the best ratio of chitosan/carrageenan membrane in removing organic compounds. The selected organic compounds are synthetic dyes such as methylene blue and rhodamine B widely used in the paper, textile, and leather industries. In contrast, bromocresol purple and murexid are used in chemical analysis laboratories. These organic synthetic dyes cause water pollutants. This study was carried out to determine the efficiency of membrane κ-Carrageenan-Chitosan-PVA-MWCNTs with chitosan/carrageenan ratios of 0.2, 0.33, 0.5, and 0.71 in removing methylene blue, rhodamine B, bromocresol purple, and murexid from water.

MATERIALS AND METHOD

Materials

The κ-carrageenan used in this study was of food grade, with a particle size of 60 mesh, and was purchased from Indofood Chem. Meanwhile, the chitosan was sourced from shrimp with a high deacetylation degree of 98.28%, and pharmaceutical-grade purity of 98%. It was obtained from a local Indonesian home industry production. PVA with the hydrolyzed degree of 98% and MWCNTs with purity >97%, length of 8-10 μm, and diameter of 10 nm were purchased from China. Glutaraldialdehyde with a concentration of 25%, anhydrous methanol, rhodamine B, methylene blue, murexid, and bromocresol purple were all purchased from Merck Indonesia.

Membrane Fabrication

To activate, approximately 1 gram of MWCNTs was added to a 100 ml solution of 3 M HNO_3:H_2SO_4 in a 1:3 (v/v) ratio. The mixture was sonicated in an ultrasonic water bath for 3 hours at 70°C and refluxed at 127°C for 12 hours. The activated MWCNTs were washed with deionized (DI) water and dried in an oven at 80°C for 5 hours (Sianipar et al., 2017). Activated MWCNTs were characterized using FTIR and the number of acid groups was determined by the Boehm Titration method (Larasati et al., 2022)

Four membranes were fabricated using chitosan and carrageenan in different ratios of 0.2, 0.33, 0.5, and 0.71. The following steps were followed to prepare the membrane with a chitosan/carrageenan ratio of 0.71. Approximately 1.5 g of chitosan was dissolved in 37.5 ml of water. In addition, about 4.4 ml of 50% (g/g) acetic acid was dropped into the mixture and refluxed at 85°C until the chitosan dissolved. 5 g of PVA was dissolved in 35 ml of water and refluxed for 1 hour at 75°C. About 1.5% (g/g) of activated MWCNTs were poured into a PVA solution and sonicated in a water bath sonicator for 30 minutes at 70°C. This process was followed by refluxing about 2.1 g of carrageenan in water at 85°C until dissolved. Chitosan, PVA added by activated MWCNTS, and carrageenan solution were mixed and stirred at 85°C for 30 minutes. Furthermore, about 15 ml of glutardialdehyde 25% was added to the mixture and stirred for 5 minutes at 85°C. The mixed solution was transferred into a 20 x 20 cm^2 glass mold and treated for 48 hours at 40°C. The molded membrane was removed, rinsed with alcohol and DI water, and dried at room temperature for 24 hours. Membranes with other chitosan/carrageenan ratios were prepared similarly.

The surface and cross-section morphology of the membrane was examined using a Zeiss EVO 10 scanning electron microscope. Small membrane samples were immersed in liquid nitrogen for 60-90 seconds, dried in a chamber, and sprayed with gold. The gold-coated samples were then viewed under the scanning electron microscope at 10 kV to obtain visual information on the surface and cross-section of the membrane.

The Performance of The Membrane as a Synthetic Dye Remover

The 2 mm thick membrane was immersed in DI water, cut into rounds, and inserted into a 4 cm diameter Buchner funnel. The four synthetic dyes were dissolved in DI water at a concentration of 200 ppm. The 8.5 ml synthetic dye solution was filtered by membrane using gravity for 48 hours. The filtrate concentration was determined using a UV-VIS spectrometer (BEL Photonics). The

filter efficiency was calculated using Eq. (1).

$$\text{Removing efficiency} = \frac{C_{initial} - C_{filtrate}}{C_{initial}} \quad (1)$$

$C_{initial}$ is the synthetic dye concentration before removing, and $C_{filtrate}$ is the filtrate concentration.

Water Contact Angle

The membrane water contact angle was determined by measuring the contact angle between the membrane and the water droplets. Water was dripped onto the surface of the membrane using 0.005 ml syringe, and the angle was determined using a computer-aided design (CAD).

RESULTS AND DISCUSSION

Figure 1 shows FTIR spectra of activated MWCNTs. The peaks at 1705 show C=O stretching, 1537 shows C=O vibration, and 1058 cm^{-1} shows C-O vibration. A broad peak at 3396 cm^{-1} indicates the vibration of –OH groups. The number of acidic functional groups obtained is 3 meq/g.

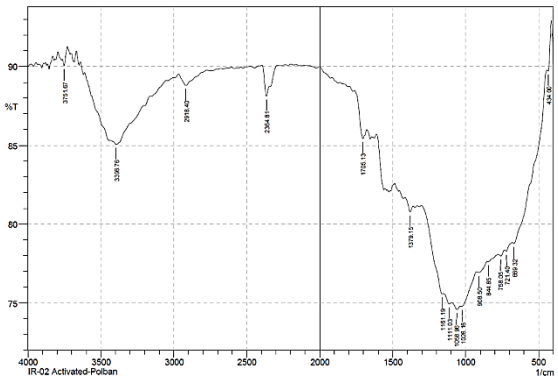

Fig. 1: FTIR spectra of activated MWCNTs

The surface and cross-section of the membrane are shown by Figure 2. The surface image presents scattered MWCNTs particles with varying sizes and distribution, indicating less homogeneity. On the other hand, the cross-section image shows a lower number of MWCNTs compared to the surface, suggesting that MWCNTs are less trapped within the membrane and more dispersed on the surface. This observation differs from previous results, where MWCNTs were more widely distributed in the cross-section due to different manufacturing methods. In this study, the membrane was cast, causing MWCNTs to float on the surface, while the previous study utilized a vacuum method that led to MWCNTs being sucked into the membrane (A. Alshahrani et al., 2021).

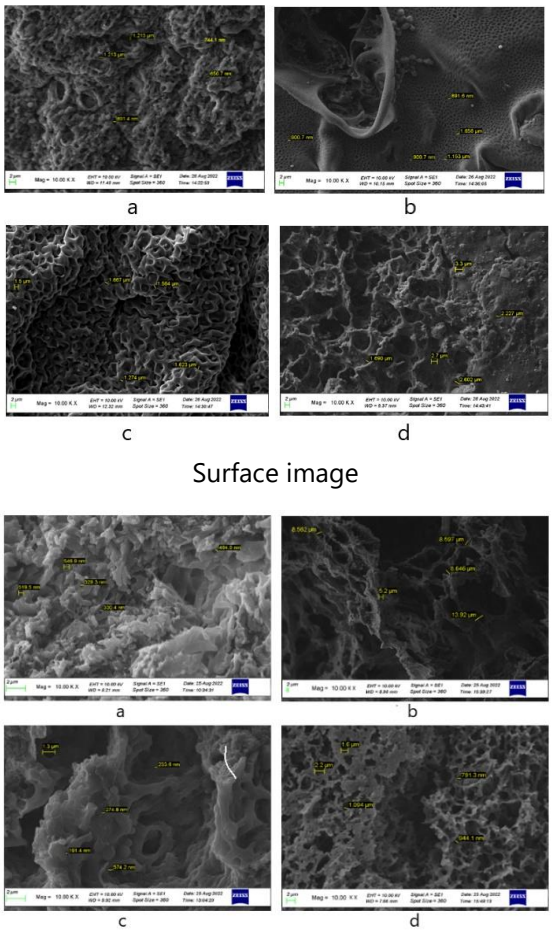

Fig. 2: SEM images of the κ-Carrageenan-Chitosan-PVA-MWCNTs membranes at 10000× magnification and chitosan / carrageenan ratio (g/g) (a) 0.2 (b) 0.33 (c) 0.5 (d) 0.71

The casting method used in this study resulted in a membrane with inhomogeneous

porosity sizes, ranging from 0.4-14 µm in the cross-section and 0.6-4 µm on the surface. Similar surface and cross-section morphology were observed in the four membranes with variations in the chitosan/carrageenan ratio of 0.2, 0.33, 0.5, and 0.71 (g/g).

The presence of chitosan in a chitosan/carrageenan membrane blend is associated with a decrease in the hydrophilic nature of the membrane, making it more hydrophobic (Shaari and Kamarudin, 2015). The membrane-dye interaction can be facilitated through various mechanisms, such as electrostatic interactions, Van der Waals forces, hydrophobic interactions, and hydrogen bonding (Sivakumar and Lee, 2022).

The contact angle describing the wettability properties of the membrane also shows the addition of hydrophobic properties with an increasing chitosan/carrageenan ratio. Increasing the chitosan/carrageenan ratio causes the contact angle of the water droplets to increase in the membrane (Figure 3). At a chitosan/carrageenan ratio of 0.2 (g/g), water droplets spread across the surface of the membrane. This proves that increasing the chitosan in the membrane makes it more hydrophobic.

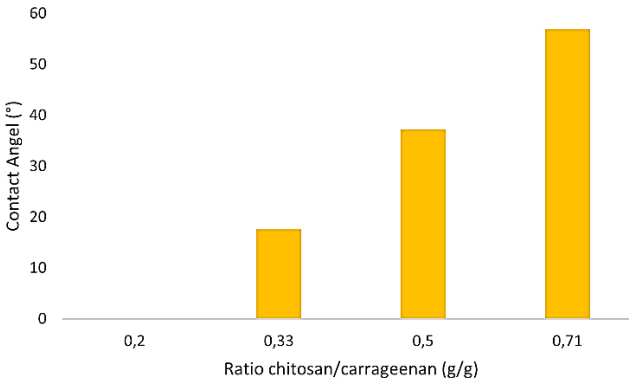

Fig. 3: Membrane contact angle with various chitosan/carrageenan ratio

The membrane with a chitosan/carrageenan ratio 0.71 exhibited the highest removal efficiency among the four synthetic dyes studied. The removal efficiencies for methylene blue, rhodamine B, murexid, and bromocresol purple are 91%, 98.4%, 100%, and 34.55%, respectively, as shown in Figure 4. This can be attributed to the increased hydrophobic nature of the membrane with a higher chitosan/carrageenan ratio, which strengthens the hydrophobic interaction between the membrane and the dye, resulting in higher dye absorption on the membrane and improved removal efficiency. Based on the study results, the optimal chitosan/carrageenan ratio for achieving the highest removal efficiency for these four dyes is 0.71.

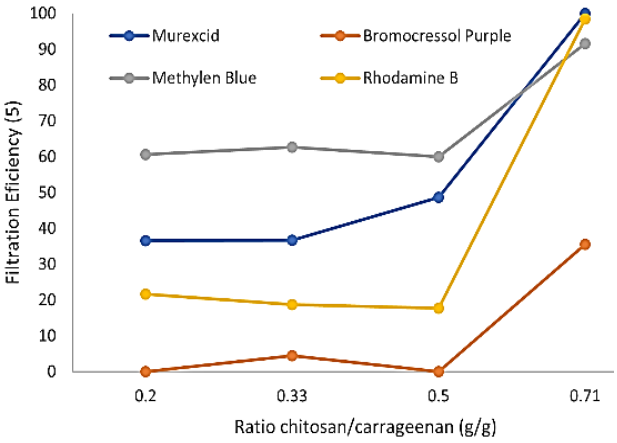

Fig. 4: Membrane removing efficiency of murexid, bromocresol purple, methylene blue, and rhodamine B from water

The variation in removal efficiency among the four synthetic dyes on the membrane with a chitosan/carrageenan ratio of 0.71 is believed to be associated with the molecular structure of these organic compounds, as shown in Figure 5.

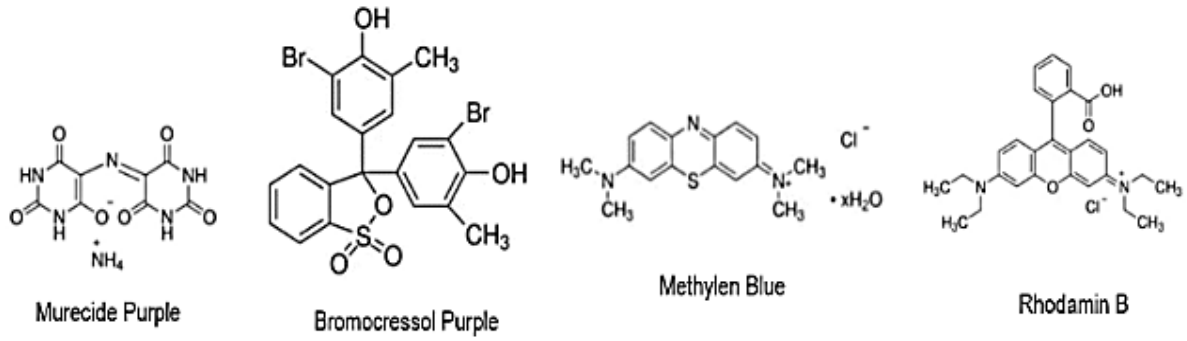

Fig. 5: The molecular structure of synthetic dyes used as a model in membrane performance

These compounds have a different molecular weight related to molecular size and the charge of functional groups in molecules (Table 1).

Table 1. Molecular weight and charge of synthetic dyes

Synthetic dyes	Molecular Weight (g/mol)	Charged of Functional groups
Murexid Purple	284.19	Anion
Bromocresol Purple	540.22	None
Methylen Blue	319.85	Cation
Rhodamine B	479.02	Cation

Bromocresol purple, which has a molecular size comparable to rhodamine B but lacks any ionic functional groups, exhibits weaker interaction with the membrane. Unlike anionic or cationic dyes that can undergo electrostatic interactions, the weak interaction between the membrane and bromocresol purple allows it to easily pass through the membrane, resulting in the lowest removal efficiency among the synthetic dyes studied. This suggests that the absence of ionic functional groups in bromocresol purple may lead to weaker membrane interaction and reduced removal efficiency.

The molecular size of murexid, a synthetic anionic dye, and methylene blue, a cationic dye, is almost the same. When using a chitosan/carrageenan ratio of 0.71 in membrane filtration, the removal efficiency for murexid is slightly higher than that of methylene blue. However, in other chitosan/carrageenan ratios, the removal efficiency of methylene blue is higher than that of murexide. Research on the adsorption of anionic dyes (methyl orange) and cationic dyes (methylene blue) using graphene oxide (GO), crosslinked nanocomposites hydrogels (NCH) of chitosan (CS), and carboxymethyl cellulose (CMC) showed the opposite result. According to Mittal et al. (2021), methyl orange absorption is lower than methylene blue. Other studies have shown that agar/carrageenan is an effective adsorbent in removing cationic dyes such as methylene blue from water (Duman et al., 2020).

The removal efficiency of cationic rhodamine B (98.4%) surpasses that of methylene blue (91%) due to its larger molecular size. The larger size makes it more challenging for rhodamine B to pass through the membrane's pores, resulting in higher removal efficiency than methylene blue.

CONCLUSIONS

In conclusion, the surface morphology and cross-section of the four membranes with variations in the chitosan/carrageenan ratio of 0.2, 0.33, 0.5, and 0.71, showed no significant differences. However, the membrane with a ratio of 0.71 exhibited the highest removal efficiency for the four synthetic dyes used as a model. The results showed that the interaction between the dye and the membrane, as well as the size of the dye molecule, are important factors affecting the removal efficiency, with the interaction effect being more dominant than the molecular size. This is supported by the lower removal efficiency (34.55%) of bromocresol purple, which has a molecular size similar to ionic rhodamine B (98.4% removal efficiency). Furthermore, the interaction between anionic dyestuffs (murexid, 100% removal efficiency) and the membrane appears stronger than between cationic methylene blue (91% removal efficiency) and rhodamine B. The removal efficiency of cationic dyes rhodamine B with a larger molecular size achieves better results than methylene blue.

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