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Isolation of Na-alginate from Brown Seaweed (*Padina* sp.) and Synthesis of Na-alginate-chitosan Polyelectrolytecomplex (PEC) Film as Methylene Blue Adsorbent

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Abstract

Na-alginate has been isolated from brown seaweed (*Padina* sp.) and then used to make na-alginate-chitosan complex polyelectrolyte films as methylene blue adsorbent. Characteristics of na-alginate, chitosan, and PEC films before and after adsorption were carried out using an FT-IR spectrophotometer. Na-alginate-chitosan PEC film was made by mixing a 0.3% (w/v) Na-alginate solution with a 1% (w/v) chitosan solution with a chitosan-alginate volume ratio (1:3). The film formed was tested for its resistance in pH 3-11 for 7 days and showed that the film could survive in acidic or alkaline media. The adsorption study carried out resulted in maximum concentration data occurring at 75 mg/L with a capacity of 30.2768 mg/g.

Keywords: Alginate, adsorption, chitosan, complexpolyelectrolite, films, methylene blue

INTRODUCTION

Brown seaweed (*Padina* sp.) is seaweed that belongs to the Phaeophyta class and is abundant depending on the season. *Padina* sp. lives among water pools on rocks along the coast (Rhein-Knudsen, et al., 2017). The color is yellowish brown or sometimes white because there is calcification. Brown seaweed (*Padina* sp.) is a marine natural resource that grows naturally in Indonesian coastal waters, particularly in the areas around Maluku. It is also quite abundant. The main content of brown seaweed is alginate. Alginate is a linear organic polysaccharide polymer consisting of the monomers α-L guluronic acid (G) and β-D mannuronic acid (M), or can be a combination of these two monomers (Rashedy et al., 2021). Alginate can be obtained from brown algae from the genera Ascophyllum, Ecklonia, Durvillaea, Laminaria, Lessonia, Macrocystis, Sargassum, Padina and Turbinaria (Kulig et al., 2016; Segale et al., 2016).

Na-alginate is a biopolymer that has a carboxyl group which can function as an active site in adsorption. Apart from that, Na-alginate has high hydrophilicity which is characterized by its high solubility in water, so it is very good when used in solving environmental problems (Fajarwati et al., 2018). Chitosan, also known as 2-samino-deoxy-β-D-glucose, is a cationic polymer that is derived from chitin. It is composed of one amino group and two hydroxy groups on each glucose ring, with the acetyl group removed either chemically or enzymatically (ALSamman & Sánchez, 2022). In dilute solutions at low ionic strength, chitosan molecules are more compact compared to other polysaccharide solutions. This may be due to the high charge density. The flexibility of this charge makes it sensitive to changes in pressure, so that the chitosan chain becomes more flexible (Rahayu et al., 2020). Chitosan is a biosorbent that can be used as an adsorbent because it has amino and hydroxyl groups, which can function as active sites. However, chitosan is less effective if used directly as an adsorbent because of its low hydrophilicity, so a modification is needed to correct this deficiency of chitosan (Vakili et al., 2014; Rahayu et al., 2022). A method using a combination of na-alginate and chitosan, which are two types of polymers with different contents, is often called the use of polyelectrolyte complex (PEC), which comes in film or bead form, can help solve the issue of environmental contamination. Adsorbents like PEC can be used to remove heavy metals and dyes from the environment. The most popular technique for resolving issues with environmental pollution is adsorption, particularly when it comes to heavy metal or dye contamination (Baunsele et al., 2022; Rahayu et al., 2023). One of the dyes that is dangerous in the environment is methylene blue dye (Baunsele et al., 2024). Synthetic dyes like methylene blue are frequently utilized in the textile sector. If this dye is in the environment in amounts above the permitted threshold, it will pollute the surrounding environment, so it is carcinogenic to living creatures contaminated with this methylene blue dye (Kumar et al., 2019; Gürses et al., 2014; Rahayu et al., 2022; Purnaningtyas et al., 2020).

METHODOLOGY

Materials and Instrumentals

The tools used in this research include a set of glassware (pyrex), porcelain cup, knife, blender, petri dish, hot plate, strainer, magnetic stirrer, shaker, pH meter, oven, filter, UV–Vis Spectrophotometer (Thermo Scientific Genesys 10), FT-IR Spectrophotometer (Prestige 21 Shimadzu). The materials used in this research were brown seaweed from Osi Island, distilled water, sodium carbonate (p.a. Merck), HClO, commercial chitosan (Ocean Fresh CV), methylene blue ($C_{16}H_{18}NSCl$) (p.a. Merck), HCl (p.a. Mecrk), NaOH (p.a. Merck), universal pH (Merck).

Methods

Sample preparation

The collected brown seaweed is then washed to remove impurities and to reduce the salt content, the seaweed is then dried in the sun until dry. Next, the seaweed is cut into smaller pieces.

Na-alginate extraction

Add 50 grams of seaweed and distilled water and wash, then blend until it has a smooth texture. Transfer the blender results into a beaker and add sodium carbonate and heat at 70–80 ºC for 24 hours. Remove the heating product and filter it with a filter cloth. Next, concentrated HCl is added to the filtered results until it becomes acidic. Then HClO is added to remove the dye. Next, filter and rinse with distilled water until neutral. then soaked with 5% sodium carbonate and dried at a temperature of 70–80 ºC for up to 24 hours. Separate the na-alginate precipitate and then dry it in an oven at 60 ºC. After it dries, place it in a blender and process until Na-alginate powder is produced, which is then identified by FT-IR.

Making Na-alginate-chitosan polyelectrolyte complex (PEC) films

Chitosan-alginate PEC films were made with a chitosan:alginate ratio (1:3). The alginate solution was made by mixing the 0.3% alginate solution into the 1% chitosan solution in CH_3COOH, then homogenizing using a stirrer for 30 minutes. A total of 10 ml of the mixed solution was printed using a petridish and then evaporated at a temperature of 60–70 °C for 4 hours. The dried film was then soaked in 0.2 M NaOH for ± 12 hours, followed by washing using distilled water until the pH was neutral. The PEC film formed can then be characterized with FT-IR as a film before adsorption.

Stability test of Na-alginate-chitosan PEC film in acidic and alkaline media

After forming, the Na-alginate-chitosan PEC film was ready and weighed. After that, the film was immersed for seven days in 10 milliliters of distilled water, the pH of which had been raised to 11 by mixing 1 milliliter of HCl and 0.2 milliliter of NaOH. The physical alterations in the film were seen following the soaking procedure.

Creation of a standard curve

Methylene blue was dissolved to create a standard curve at concentrations of 1, 2, 3, 4, and 5 mg L^{-1}. A UV-Vis spectrophotometer was then used to measure each solution's absorbance at the maximum wavelength that was attained. The relationship between absorbance and methylene blue concentration was then plotted on a relationship curve. The resulting curve serves as a standard curve.

Determination of adsorption capacity at varying concentrations

A 0.05 g Na-alginate-chitosan PEC film was shaken for the ideal amount of time after being placed in 30 mL of methylene blue at a concentration of 25, 50, 75, 100, 125, and 150 mg L^{-1} at an optimal pH. The PEC film detached from the solution after shaking. The amount of residual methylene blue was determined with a UV-Vis spectrophotometer.

RESULTS AND DISCUSSION

Isolation of Na-alginate from brown seaweed

The isolation process begins by washing the seaweed clean of impurities and then drying it in the sun for 3 days. In order to facilitate the following step, the dried seaweed is then chopped into tiny pieces. After cutting 50 grams of seaweed into small pieces, sodium carbonate is added and heated to a temperature of 70 to 80 degrees Celsius in order to dissolve it and create a seaweed gel solution. Next, the gel is filtered and seaweed extract is obtained. This extract is then added with concentrated HCl and soaked for 1 day to reduce the mineral salts that are still attached to the seaweed. After that, the HClO solution is added which functions to remove the dye. The results of this washing are then added with sodium carbonate to obtain sodium alginate. The resulting na-alginate is still in the form of a gel so it needs to be dried in an oven at a temperature of 60–70 ºC and then blended to get na-alginate powder. The Na-alginate powder produced was 12.8065 grams or 25.16%. FT-IR was then used to describe the Na-alginate powder.

FT-IR Characterization

After being separated from brown seaweed, the fungal groups included in the Na-alginate powder were identified by FT-IR. Additionally, FT-IR analysis of PEC and chitosan films was done both before and after adsorption. Figure 1 shows the results of FT-IR characterization of the four samples.

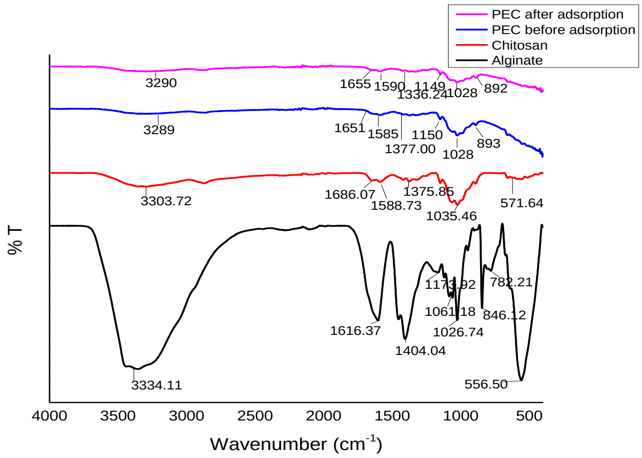

Figure 1. FT-IR characterization of Na-alginate, chitosan, PEC films before and after adsorption

From the FT-IR spectrum intensity it can be seen that there is wide absorption as a characteristic of the OH group at wave numbers 3000-3500 cm^{-1} in chitosan and in na-alginate. In chitosan and insulating na-alginate, the C=O group is shown by a strong absorption at wave numbers 1686.07 cm^{-1} and 1616.37 cm^{-1}, respectively. The absorption at the wave number is 1375.85 cm^{-1} in chitosan and 1404.04 cm-1 in na-alginate which shows that there is absorption in the C-O group from the C-O-H bond. The absorption of the C-H group from the C-C-H bond was shown at a wave number of 1035.46 cm^{-1} in chitosan and at a wave number of 1173.92 cm^{-1} to 1026.74 cm^{-1} in insulating Na-alginate. In the film spectrum before adsorption there is a shift in the absorption of the O-H group to 3289.28 cm^{-1} and in the film after adsorption it shifts to 3290 cm^{-1} due to hydrogen bonding between chitosan and alginate. Next, there is a shift in the wave number of the C=O group, namely absorption at 1655 cm^{-1} before adsorption and 1651 cm^{-1} after adsorption. The presence of a spectrum at a wave number of 1377.00 cm^{-1} and 1336.24 cm^{-1} of the film before and after adsorption strengthens the bond between N-H and C-O from the alginate when adsorption occurs. The absorption of N-H on NH_2 exhibits an absorption shift of 1585.32 cm^{-1} and 1590.26 cm^{-1}. This shift in absorption shows that there has been an interaction that forms the na-alginate-chitosan film and the interaction between the film and methylene blue (Rahayu et al., 2023).

Making Na-alginate-chitosan polyelectrolyte complex (PEC) films

The process of creating films involved creating a solution combination containing 1% (w/v) chitosan and 0.3% (w/v) na-alginate in a volume ratio of 3:1. After the two solutions were mixed completely, the solution was molded into a petridish of 10 mL and dried at a temperature of 60–70 ºC. The dried film is soaked with NaOH to make it easy to remove, then washed until the pH is neutral. The film that has been formed can then be used for adsorption. The shape of the printed film is shown in Figure 1.


(a)


(b)

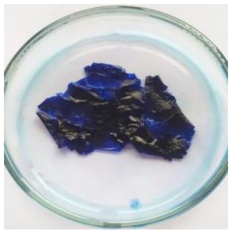
(c)

Figure 2. (a). PEC film when printed, (b). PEC film after drying, (c). PEC film after adsorption

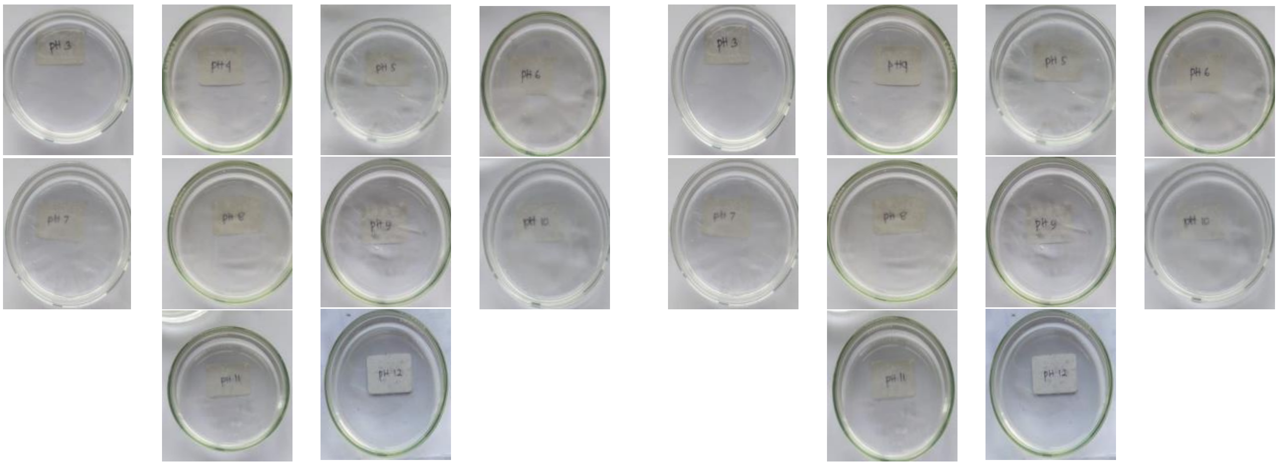
(a) (b)

Figure 3. (a). Film condition on day 1, (b). Film condition on day 7

Test of film resistance in acidic and alkaline pH media

This test aims to determine the durability of the film when in a medium with various pH variations or in acidic or alkaline conditions. This durability test was carried out by immersing the film into pH 3-11 for 7 days. The test results showed that the film remained stable from day 1 to day 7 of immersion. This means that the PEC film Na-alginate-chitosan can survive or its texture is not destroyed in all pH mediums. Figure 3. shows the results of soaking the PEC film in acidic and alkaline medium for 7 days. These results are different from those obtained by Fajarwaty et al (2018) which uses commercial alginate and chitosan where the film results did not survive or form a gel at pH 3 and 4, while at a greater pH it remained stable until day 7. This may indicate that the results of Na-alginate isolation from brown seaweed can better maintain the texture of the film when combined with chitosan or the constituent groups of the two polymers.

Preparation of standard curve

The absorbance of methylene blue solution at concentrations of 5, 10, 15, 20, and 25 mg/L at a wavelength of 664 nm was measured in order to create the standard curve. Based on the measurement outcomes, the curve in Fig. 4 with the equation y = 0.0401x + 0.02136 with R^2 = 0.9972.

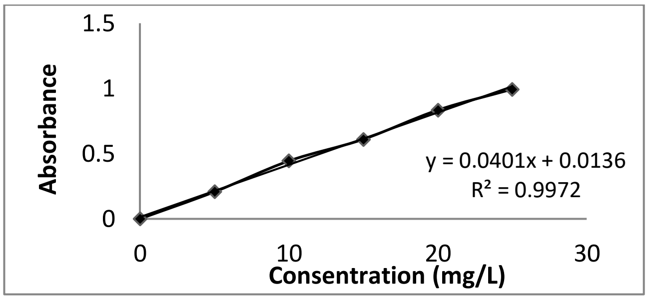

Figure 4. Methylene Blue Standard Curve

Determination of adsorption capacity at varying concentrations

0.05 grams of PEC film were mixed with 25 mL of methylene blue solutions containing 25, 50, 75, 100, 125, and 150 mg/L at pH 9 and shaken for 20 minutes from the maximum condition data obtained by Rahayu, et al (2023) to investigate the adsorption capacity determination at different concentrations. The adsorption results at varying concentrations are presented in Table 1.

Table 1. Adsorption data of Alginate-chitosan PEC film on methylene blue time variation

Initial Concentration (mg/L)	Residual Concentration (mg/L)	Adsorbed Concentration (mg/L)	Capacity Adsorption (mg/g)
25	5.9202	19.0798	11.4479
50	13.2768	36.7232	22.0339
75	2.4539	50.4614	30.2768
100	2.5287	36.7830	22.0698
125	3.5012	37.4688	22.4813
150	3.1521	37.1970	22.3182

Figure 5 shows that from the initial concentration of 25 to 75 mg/L, there is a significant rise in the amount of Na-alginate-chitosan PEC film adsorption on methylene blue. This can happen because the COO^- active sites on the surface of the PEC film's are still unsaturated, allowing more methylene blue molecules to be adsorbed in response to an increase in methylene blue concentration. There was a drop in the quantity of methylene blue molecules adsorbed at concentrations greater than 75 mg/L.

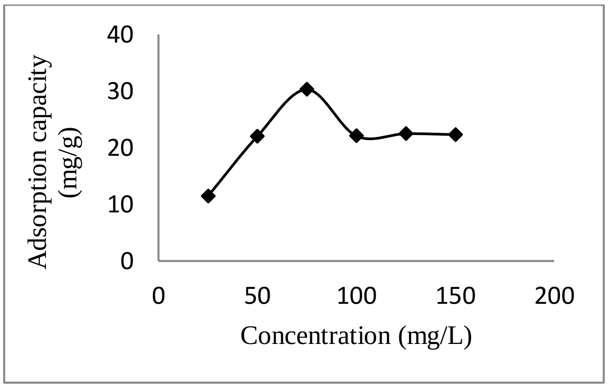

Figure 5. Adsorption capacity at varying concentrations

At concentrations >75 mg/L there is a decrease in the number of methylene blue molecules adsorbed. This indicates that the active sites on the surface of the PEC film have passed the saturation point so that they can no longer bind the remaining methylene blue dye molecules (Sahara, Gayatri, & Suarya, 2018). In Figure 4, it is known that the maximum concentration for the absorption of methylene blue dye occurs at a concentration of 75 mg/L with an adsorption capacity of 30.2768 mg/g. These results are different from those produced by Sulistyawati et al (2020) made potassium crosslinked chitosan microcapsules can adsorb methyl orange dye with a maximum adsorption capacity of 9.06 mg/g at 90 minutes. Apart from that, data on the adsorption capacity of methylene blue on chitosan-alginate beads and films was also found to be different by Fajarwati, et al (2018), namely 0.676 mg/g for beads with a contact time of 45 minutes and 0.0135 mg/g for chitosan-alginate films with a contact time of 30 minutes.The difference in capacity results and optimum conditions during adsorption can be caused by different forms of adsoben.

CONCLUSION

The isolation of 50 grams of brown seaweed (*Padina* sp) can produce 12.8065 grams or 25.16% of Na-alginate. Polyelectrolyte film of na-alginate-chitosan complex can survive and not destroyed in acidic or alkaline medium. Optimum adsorption results occurred at pH 9 with a contact time of 20 minutes and at a concentration of 75 mg/L. The resulting adsorption capacity was 30.2768 mg/g.

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