Adsorption of basic dye methylene blue by brown algae
Sargassum duplicatum

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Abstract. The ability of raw and dried Sargassum duplicatum to remove methylene blue (MB) from aqueous solution was evaluated. Brown algae. S. duplicatum before and after MB adsorption was characterised by Fourier transform infrared spectroscopy (FT-IR). Batch experiments were conducted to examine the effects of parameters such as initial pH, biomass dosage, contact time, and initial dye concentration on MB Adsorption. The optimum adsorption was found at around pH 5, adsorbent dosage 1 g/L, and initial concentration of MB at 20 mg/L. Adsorption occurs very fast in first 5 min and reaches the equilibrium at 70 min. The maximum percentage of dye removal was 88.9%. This study suggests that S. duplicatum has good potential capacity to remove MB dye and could offer promising opportunity as a low-cost biosorbent.

1. Introduction
Dyes were used in many industries, such as food, pharmaceutical, cosmetic, dyestuffs textile, paper, leather, rubber, and plastic. Industrial waste containing synthetic colouring agents which are discharged into the environment has potential to cause pollution. The presence of dyes in wastewater causes problems in several ways: dyes in water are very visible and reduce clarity, the colour interferes with penetration of sunlight into the waters, inhibits photosynthesis and growth of aquatic biota, or even leading to direct poisoning of living organisms [1–5]. These synthetic dyes cannot be decomposed easily. Various conventional methods such as coagulation and flocculation [6], chemical oxidation [7], electrochemical treatment [8] and adsorption [3] have been tried to removed dyes from wastewater. Adsorption is known to be simplest and most economical way to remove dyes from waste [9].

Marine algae are commonly known as seaweeds had great potential as a promising biosorbents material. Seaweeds are classified into the three main groups, namely: green (Chlorophyta), red (Rhodophyta), and brown (Phaeophyta) algae. Among them, the brown algae provided the best adsorption capacities due to their cell wall structure and components. Brown algae have cell walls that contain many chemically active functional groups such as carboxylic acids, hydroxyl, imidazole, amine, phosphate, phenolic, thioether, and sulfhydryl which allow selective binding and interaction with metals and pollutants in the biosorption process [10]. The largest part of brown algae is cellulose,
alginate, which is a type of polysaccharide (anionic copolymer) and a group of sodium, potassium, and calcium salts.

In this study, we investigated the abilities of S. duplicatum, which is one of the brown algae as biosorbent for synthetic dyes in aquatic environment. Methylene Blue [(7-Dimethylamino) phenothiazin-3-ylidene] dimethylazanium chloride, molecular formula: C₁₆H₁₈N₃SCl) is used to test the adsorption mechanism and quantification between the adsorption capacities of various sorbents [11].

2. Materials and methods

2.1. Material

2.1.1. Preparation of reagents

Methylene blue C.I.52015 (Merck) is used as a dye source. The dye solution was prepared by dissolving accurately weighed dye in the distilled water to the different initial concentration. Dye concentration determined was performed colorimetrically using a Halo UV-VIS Spectrophotometer RB-10. The absorbance of colour was read at 665 nm. The initial pH was adjusted with concentrated Hydrochloric Acid (Merck) or Sodium Hydroxide (Merck).

2.1.2. Preparation of adsorbent

S. duplicatum (brown algae) was collected from Sepanjang Beach, Kemadang, Tanjungsari, Gunungkidul Regency, Special Region of Yogyakarta during September 2017. The collected algae were washed with seawater, tap water, and then distilled water several times. The washed algae were sun-dried for several days. The dried algae were ground as a powder using an electric mill and sieved to uniform particle size 310 μm.

2.2. Methods

Adsorption experiment was carried out in the batch condition. A series of 250 mL Erlenmeyer flask containing 200 mL dye solution of known initial concentration 20 mg/L were prepared at room temperature (25 ± 2°C). Weighted amounts (1 g/L) of dried algae biomass were added to each flask and agitated continuously using an orbital shaker. The pH of the mixture was kept without measurement. Equilibrium process is directly correlated with time. The sample was drawn at suitable time intervals 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, and 120 min, and then centrifuged for 10 min at 2000 rpm. The left out the concentration of dye in supernatants were analyzed using the spectrophotometer by monitoring the absorbance changes at a wavelength of 665 nm.

Effect of pH was tested at pH 3,4,5,6,7,8 and 9. To verify the effect of adsorbent amount, different weight of algae biomass amounts was variated to 0,5; 1; 1,5; and 2 g/L. The dye removal from aqueous solution depends on the initial MB concentration that carried at different concentration (10, 15, 20, and 25 mg/L).

Biosorption capacity (qe), the amount of dye adsorbed per gram of biosorbent (mg/g) can be calculated as follows:

\[ q_e = (C_o - C_e) \frac{V}{m} \]

Where \( C_o \) is initial dye concentration (mg/L), \( C_e \) is the equilibrium concentration of dye (mg/L), \( V \) is the volume of solution (L), and \( m \) is the mass of biosorbent (g). Percentage of dye removal can also be displayed by the percentage of dye removal as follow:

\[ \text{Dye removal} \% = 100 \left( \frac{C_o - C_e}{C_o} \right) \]
3. Results and discussions

3.1. FTIR Analysis

FTIR analysis was applied to identify the various functional group in *S. duplicatum*, which were liable for the sorption process. The peaks showing in the FTIR spectrum were appointed to various functional groups in line with their several wavenumbers as according in the literature. Dried *S. duplicatum* before and after MB dye sorption, were analysed using FTIR spectroscopy analysis within the range of 400-4,000 cm\(^{-1}\) (figure 1). As seen in figure 1, each spectrum of unloaded and MB loaded biomasses generally show similar pattern excepting some little changes. The bands at 3,400 cm\(^{-1}\) similar to stretching vibration of O-H [12], a shifting wavelength is additionally indicated by a decrease in intensity. The peak at 2,931 cm\(^{-1}\) disappears within the spectrum after sorption of MB dye, this peak associated with C-H [13]. The peaks intensity at 2,337 cm\(^{-1}\) wavelength decrease when MB dye loaded by biomass; these peaks may has associated with C-N. The strong peak placed around 1,600 cm\(^{-1}\) indicated a stretching vibration of C=O from carbonyl. The bands at 1,033 cm\(^{-1}\) indicates functional group of C-O from carboxyl [14].

![FTIR analyses for S. duplicatum biomass before and after MB dye adsorption.](image_url)

3.2. Effect of initial pH

The removal efficiency of dyes is substantially affected by an initial pH of solution since its impact on each surface binding sites of the biosorbent and the ionisation/ aggregation process of the dye molecules[15]. The effect of initial pH on adsorption of MB was investigated over a range of pH from 3 to 9 under constant parameters, MB concentration 20 mg/L, adsorbent dose 1 gr/L, contact time 120 min, and temperature 25°C ± 2°C. The pH scale was adjusted using 0,1 M HCl and 0,1 M NaOH. The solution was agitated continuously using an orbital shaker. The effect of pH variation on dye removal percentages are represented in figure 2. The result showed lower removal efficiency at low pH value. MB adsorption raised as increasing the pH value and decreased after maximum adsorption capacity is reached at pH 5. This condition is achieved due to the cationic properties of MB are more apparent on the addition of acid pH, and more H\(^+\) ions are added, the more MB is bounded to the biosorbent. At a more alkaline pH, the presence of the added OH ion decreases the cationic properties of the MB, this causes a decrease in the ability of adsorption after the pH raised [16]. At a lower pH, the algae surface charge could become charged, lead to hydrogen ions to vie with dye cations, leading to a decrease in dye adsorption. At a higher pH, the algae polymeric composition could get negatively charged, which increased the biosorption capacity through electrostatic attractions [15].
Active sorption sites were restricted, so the adsorption capacity did not ongoingly elevate as the pH became higher [17]. MB as cationic dye may be easily adsorbed on the algae surface through the electrostatic attraction. Indeed, the surface of the algae becomes negatively charged because of the deprotonation functional groups such as amino, hydroxyl, carboxyl, sulfate, and amine [18,19].

**Figure 2.** Effect of initial pH on the biosorption of MB onto *S. duplicatum*.

### 3.3. Effect of biosorbent dosage

Biosorption dosage is a crucial parameter because it verifies the percentage of decolorisation and may also generally used to predict the optimum value of biomass per unit of the dye solution to be treated. The effect of varying the biosorbent dosage 0.5 – 2 g/L was investigated using 200 ml dye solution, while the initial pH, dye concentration, temperature, and contact time were remain constant at pH 7, 25 mg/L, 25±2°C, and 120 min. Figure 3 Shows that high adsorbent quantity leads to a low adsorption capacity value. At low adsorbent mass, all form of sites are entirely exposed, and also adsorption on the surface is saturated faster [12]. High biosorbent amounts are investigated to cause cell agglomeration and as a consequence, it reduces the intracellular distance and creates a screen effect between the dense layer of cells, obstructing the binding sites of metal ions [20]. The rapid increase of MB removal was attributed to availability of additionally active adsorption sites. Similar behavior was observed for methylene blue adsorption onto marine alga *Ulva lactuca* [21,22] *Enteromorpha spp.* [15], *Sargassum muticum* [12] and *Sargassum hemiphyllum* [17].

**Figure 3.** Effect of biosorbent dosage on the biosorption of MB onto *S. duplicatum*. 
3.4. Effect of contact time
To determine the equilibrium contact time necessary to achieve the removal of MB dye, dried biomass was stirred in 200 ml of MB dye solution with an initial concentration of 20 mg/L at pH 7 and temperature 25 ± 2°C. The removal efficiency of MB at contact time is given in figure 4. Maximum adsorption efficiency was reached within the first 5 minutes, and then adsorption rate increased gradually until attaining equilibrium at about 70 min at contact time. These changes within rate of removal may be due to that initially all adsorbent sites are vacant and also the matter concentration gradient is high [19]. The fast adsorption at the initial contact time is undoubtedly due to the availability of negatively charged Sargassum duplicatum biomass which leads to the fast electrostatic adsorption of the cationic MB at initial pH of 7 [12].

A similar trend has additionally reported in the literature where rapid sorption of the dye on many biosorbents has been determined during the initial stages of the contact time followed by slower sorption near the equilibrium [12,17,19]. A larger number of available free surface site was certainly responsible for the initial high sorption rate at the beginning, while the subsequent declaration was determined when the availability site become saturated [23].

3.5. Effect of initial dye concentration
The influence of initial MB concentration on biosorption by S. duplicatum biomass presented in figure 5. The percentage of dye removal increased as dye concentration increased. The result is also attributed to extending the driving force and collisions between sorbent and sorbates at lower dye concentration [23], and then no more increase in adsorption capacity implied that the available sites on the biosorbent are restricted in higher initial dye concentration [5].
Figure 5. Effect of initial dye concentration on the biosorption of MB onto S. duplicatum

4. Conclusion
The experiment conducted in this study focused on the adsorption MB dye into S. duplicatum. The ability of the S. duplicatum in removing the dye colour was dependent on contact time, amount of alga biomass, dye concentration, and pH. The optimum adsorption was found to occur at around pH 5; adsorbent dose 1 g/L; and initial concentration 20 mg/L. Adsorption occurs very fast in first 5 min and reaches the equilibrium at 70 min. The maximum percentage of dye removal value was 88.9%. The result shows that brown algae S. duplicatum could be used as biosorbent material for dyes removal from aqueous solution.

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