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Article

Biosorption of Methylene Orange Dye using Langsat Shell by Batch Method

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Abstract. Liquid waste is a major problem in the textile industry environment that has the most widespread influence because physical and aquatic characteristics can have a negative impact on waters. Most of the liquid waste produced by batik comes from the dyeing process and environmental pollution. If it is disposed of directly into the environment without prior processing, the environment has a limited ability to degrade dyestuffs. One alternative method to remove the dye in water contaminated with methyl orange is biosorption using a cheap and easily available biosorbent, such as a langsat shell. This study used a batch method with variations in pH, solution concentration, particle size, stirring speed, and contact time. The results of each variation carried out obtained the optimum conditions for the absorption of Methyl Orange, namely at: pH 4, concentration 150 mg/L, and particle size 150 µm. The adsorption isotherm study was carried out, the Langmuir equation yielded a regression coefficient value that was close to one (R^2 = 0.9964) so that it could be said to be better with a maximum absorption capacity of 3.1164 mg/g

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1. Introduction

Liquid waste is a major problem in the textile industry environment that has the most widespread influence because the physical and chemical characteristics of water can have a negative impact on water [1-2]. Most of the wastewater produced by batik comes from the dyeing process and causes environmental pollution if it is discharged into the aquatic environment directly without prior processing, while the environment has a limited ability to degrade these dyes [3-4]. The aquatic environment becomes colored and changes the quality of the water so that it is not suitable for consumption by living things [5-6]. The liquid waste of this process is one of the sources of water pollution which is quite high if the waste treatment is not carried out [7].

One of the azo dyes that are widely used in the dyeing process is Methyl Orange. Methyl Orange (MO) or Methyl Orange is an organic compound with the formula $C_{14}H_{14}N_3NaO_3S$ [8]. Methyl Orange is prepared from sulfanilic acid and N,N- dimethylaniline [9-10]. Methyl Orange is a dye used to give color to substances, especially fabrics. Methyl Orange is dangerous for health because it is toxic and mutagenic [11]. The structure of Methyl Orange can be seen in Figure 1.

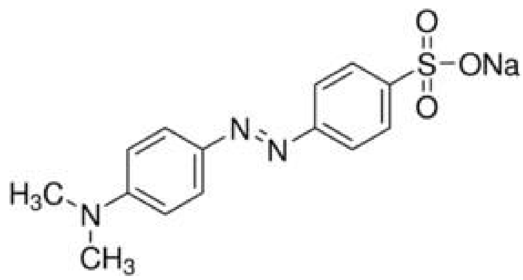

Figure 1. Structure of Methyl Orange [11]

One alternative method to remove the dye in water contaminated with methyl orange is biosorption using a cheap and easily available biosorbent, such as a langsat shell. Several classifications of compounds known to have secondary metabolites such as terpenoids, alkaloids, flavonoids, and saponins were found to be contained in langsat plants. Research on biosorption has been widely developed in the use of biomaterials lately. In the last few years, for example, green shells [12], pine leaves [13], and waste of orange and lemon peel [14]. This research used the parameters to be tested are pH, concentration, and particle size [15-16].

2. Experimental Section

2.1. Materials

The tools used in this study consisted of glassware, a shaker (model: VRN-480), a pH meter (HI2211), analytical balance (ABS 220-4), filter paper, a magnetic stirrer (MR Hei Standard), mortar and pestle. pestle, oven, spray bottle, and sieve (BS410). The instrument used is FTIR (Fourier Transform InfraRed) type Perkin Elmer universal ATL Sampling Accessor 735 B and Spectronic 21. The materials used in this study were langsat shell, aquades, Methyl Orange solution 1000 mg/L, NaOH 0.1 M, HNO_3 0.01 M, HNO_3 0.1 M, HNO_3 1 M, HNO_3 0.5 M, HNO_3 5 M.

2.2. Procedure

The langsat shell is cleaned of dirt, cut, washed with water, and air-dried for ± 2 months without being exposed to sunlight. Samples were mashed using a mortar and pestle and sieved using sieves of 150, 180, 250, and 355 µm. A total of 20 grams of langsat shell was activated with 0.1 M HNO_3 for 2 hours, then washed with distilled water until neutral, and air-dried [17].

2.2.1 Effect of Solution pH

Prepared 25 mL of Methyl Orange dye solution with a concentration of 100 ppm with variations in pH 2, 3, 4, 5, 6, and 7 then each solution was contacted with 0.2 grams of langsat shell using a batch system, the solution was then shaken at a speed of 200 rpm for 30 minutes. Then the solution was filtered and the filtrate was accommodated and measured spectronic 21.

2.2.2 Effect of Solution Concentration

Prepare 25 mL of Methyl Orange solution with concentrations of 50, 100, 150, 200, and 250 mg/L at optimum pH, then each solution is contacted with 0.2 grams of 150 µm langsat shell using a batch system, the solution is shaken at 200 rpm for 30 minutes. Then the solution was filtered and the filtrate was accommodated and measured spectronic 21.

2.2.3 Particle Size Effect

A total of 0.2 grams of langsat shell with variations in particle size of 150 µm, 180 µm, 250 µm, 355 µm, and 425 µm were contacted with 25 ml of Methyl Orange solution with optimum pH and concentration, then each solution was contacted using a batch system, the solution shaken at 200 rpm for 30 minutes. Then the solution was filtered and the filtrate was accommodated and measured spectronic 21.

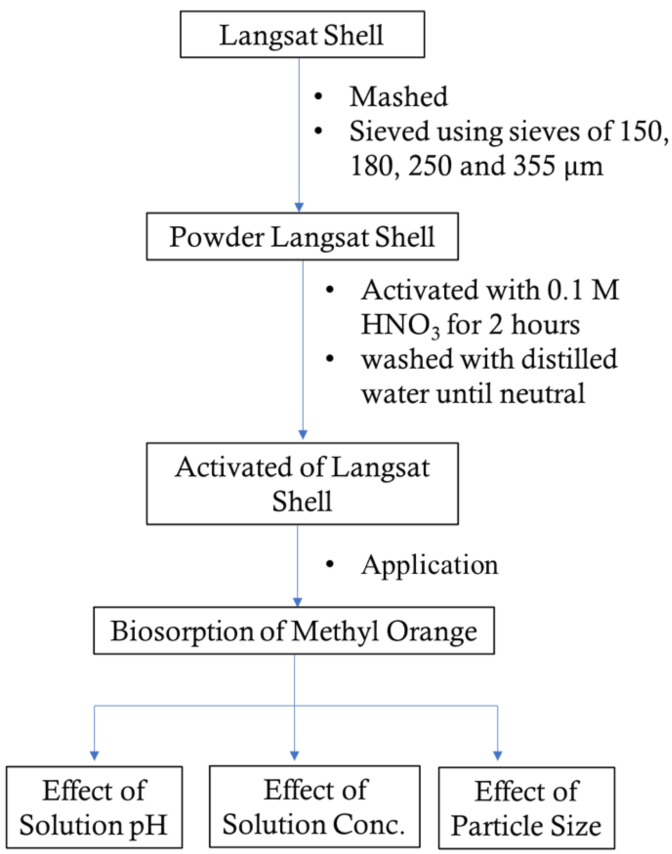

Figure 2. Procedure Biosorption of Methylene Orange Dye

3. Results and Discussion

3.1 FTIR Characterization

FTIR characterization was carried out to determine the functional groups present in the langsat shell. Functional groups play a very important role during the dye absorption process which is influenced by the number of functional groups, types of functional groups, interaction processes, chemical structure, and bio-sorbent affinity for dyes [18]. In this study, the wave number of 4000-500 cm^{-1} was used [19].

Testing on samples of langsat shell before activation to determine the functional groups contained in langsat shell, testing of activated langsat shell to determine functional groups and structural changes that occur in langsat shell, then testing of langsat shell that has been in contact with Methyl Orange is carried out to determine the functional groups that can bind the Methyl Orange compound [20]. The results of the analysis were carried out on the langsat shell before and after activation and after contact with the langsat shell. The results of the testing of each of these biosorbents can be seen in Figure 5.

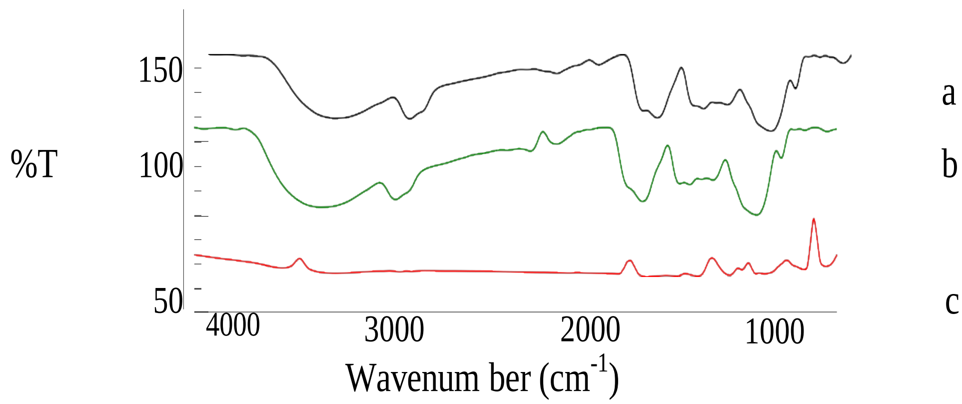

Figure 3. FTIR spectrum (a) Biomass of langsat shell before activation (b) Biomass of langsat shell has been activated with 0.01 M HNO_3 for 2 hours (c) Biomass of langsat shell which has been in contact with Methyl Orange solution.

In Figure 3. it can be seen that for the langsat shell which is not activated, the hydroxyl peak (–OH) appears at a wave number of 3330 cm^{-1} with a transmittance value of 18.96% T. This wave number indicates that the presence of a free hydroxyl group from polymeric compounds, this corresponds to the frequency range for the hydroxyl group between 3600-2800 cm^{-1} which indicates the presence of polymeric compounds [21]. At wave number 2934 cm^{-1}, there is a –CH functional group with a transmittance value of 18.23% T in the frequency range 2800-3000 cm^{-1}, and at a wave number of 1625 cm^{-1}, there is a C=O (carbonyl) functional group with a value of transmittance of 19.51% T frequency range 1640–1820 cm^{-1}[22].

Inactivated langsat shell biomass, the hydroxyl peak (–OH) appears at a wave number of 3329 cm^{-1} and a transmittance value of 11.99 %T. For the –CH group there was no change in the absorption band with a shift in wave number from 2934 cm^{-1} and the transmittance value obtained was 20.19% T. And in the –C=O functional group it appeared at a wave number of 1627 cm^{-1} and the transmittance value was obtained that is equal to 18.07% T [14].

In the langsat shell biomass which has been contacted with Methyl Orange solution, it can be seen that there is a change in the absorption of each functional group where the OH functional group appears at a wave number of 3532 cm^{-1} and a transmittance value of 6.03% T. The –CH functional group appears at a wave number of 2849 cm^{-1} with a transmittance value of 4.66% T. And the C=O functional group appears at a wave number of 1609 cm^{-1} and the transmittance value obtained is 1.91% T.

3.2 Standard Curve Preparation of Langsat Shell

Preparation of the s-curve In this study, before carrying out the optimum conditions of the Methyl Orange solution, a standard curve was needed for the Methyl Orange to be analyzed properly[23]. According to Lambert-Beer's law, if the concentration increases, the number of molecules through which a beam of light passes will increase, so that the absorption will increase [24][25]. This is the same as the results of the calibration curve below which shows that the greater the concentration, the absorbance of the Methyl Orange solution will increase. The linear equation Y = 0.0732 x – 0.0006 with a value of R^2 = 0.9996 can be used to determine the optimum conditions for Methyl Orange in this study [26-27]. The Calibration Curve Standard solution of Methyl Orange can be seen in Figure 4 langsat shell standard.

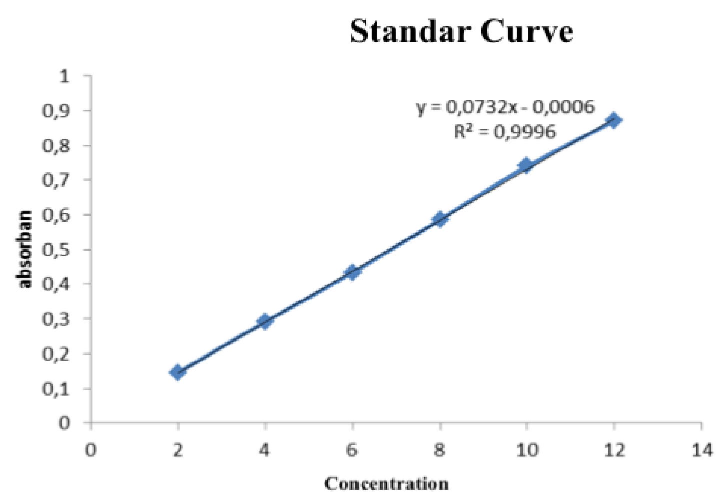

Figure 4. Standard Solution Calibration Curve of Methyl Orange

3.3 Effect of Solution pH

pH has an important role in the biosorption process because it can determine surface changes at the active site of the biosorbent [28]. The effect of pH on the absorption capacity of methyl orange dye by langsat shell biosorbent is shown in Figure 5.

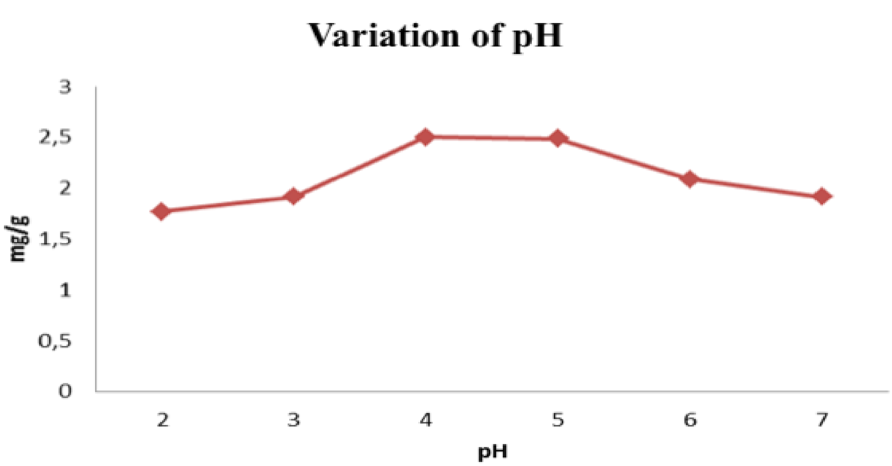

Figure 5. Effect of solution pH on the absorption capacity of Methyl Orange using activated langsat shell (0.2 gram biosorbent, 25 mL Methyl Orange solution 50 mg/L, 150 µm biosorbent particle size, 200 rpm for 30 minutes)

Figure 5. shows that adsorption of Methyl Orange using langsat shell bio sorbent occurs maximally at pH 4 with an absorption capacity of 2.5017 mg/g. Equilibrium is reached when all the exchange of Methyl Orange and anions on the outer and inner surfaces of the biosorbent has been reached [29-30]. This is related to protonation or deprotonation of the surface active site of the biosorbent [31-32].

At a low and acidic pH, the surface of the biomass wall is protonated so that the absorption of Methyl Orange becomes larger, while at a high pH, the absorption of Methyl Orange becomes smaller [33]. This is because in water, at a high pH, the surface of the biomass wall of langsat shell powder is negatively charged and the soluble dye component is an anion so that the absorption of the dye will be blocked and repel each other [34-35].

3.4 Effect of Solution Concentration

The effect of concentration on the absorption capacity of Methyl Orange dye by langsat shell biosorbent is shown in Figure 6.

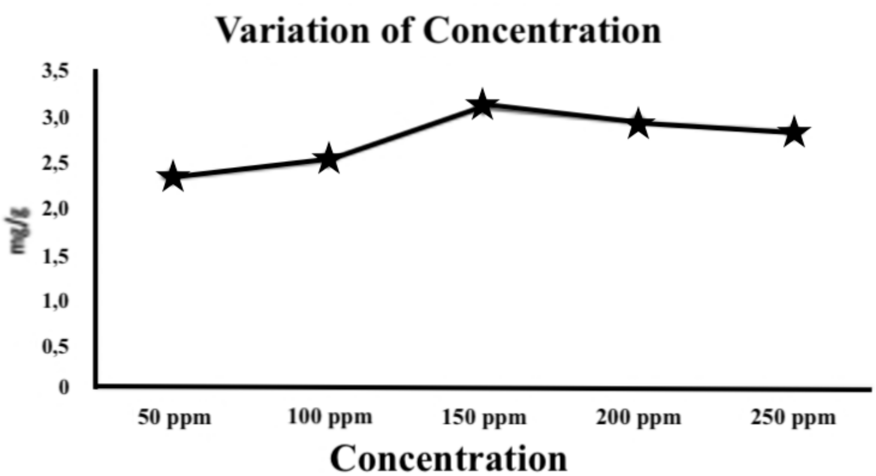

Figure 6. Effect of solution concentration on the adsorption capacity of Methyl Orange using activated langsat shell (0.2 grams of biosorbent, 25 mL of optimum pH 4, 150 µm particle size of biosorbent, 200 rpm for 30 minutes)

The concentration of the solution in general will increase the biosorption of Methyl Orange dye. The concentration of a substance will continue to increase at a point when the concentration no longer affects absorption[36-37]. This can happen because the concentration of the dye is proportional to the number of active sites on the surface of the biosorbent, causing the active sites to have reached an equilibrium state [38-39].In Figure 8 it can be seen that increasing the concentration can increase the absorption capacity of Methyl Orange dye. However, when the active site is saturated, the absorption capacity will decrease. The increase occurred from a concentration of 50 mg/L to the optimum at a concentration of 150 mg/L. Optimum absorption occurred at a concentration of 150 mg/L with an absorption capacity of 3.1164 mg/g. Based on the Langmuir adsorption theory, it is stated that on the surface of the biosorbent, some active sites are proportional to the surface area of the biosorbent [9][13].

The Langmuir isotherm model shown in Figure 7 has a value of $R^2 = 0.99964$. If the value of R^2 is close to one, then the result is good or linear. Based on the value of $y = 0.2966x - 0.1701$, the maximum absorption capacity (Qmax) of the Methyl Orange solution that can be absorbed is 3.3715 mg/g. The value of the isotherm equilibrium constant (KI) was obtained at 1.7439 L/mg. The greater the KI value, the greater the adsorbent affinity for the dye [40-41].

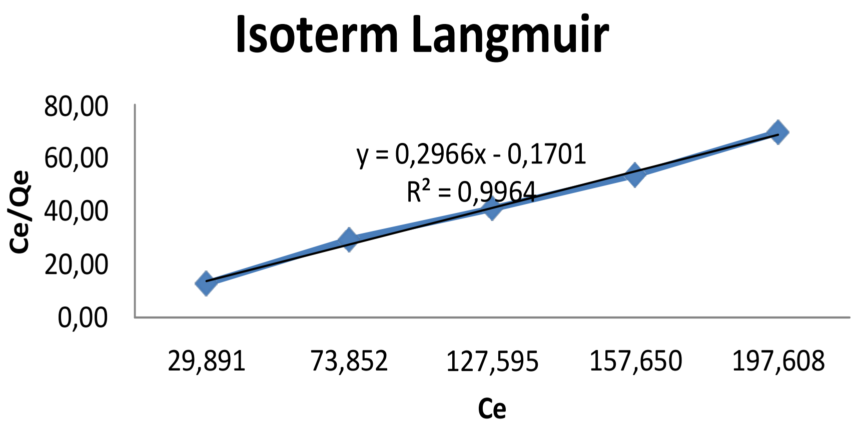

Figure 7. Isoterm Langmuir

Based on the obtained R^2, the Langmuir isotherm equation, the results obtained from R^2 are 0.9964, close to 1 with a maximum capacity of 1.7439 mg/g.

3.5. Effect of Particle Size

Differences in particle size can affect the biosorption ability of dyestuffs. The smaller the size of the biosorbent used, the wider the surface area, so that the active center that can interact with dye cations increases the adsorption power will be better [42-43]. If the size of the biosorbent used is getting bigger, it can cause a decrease in the area of the biosorbent surface and available binding groups[44]. Also, the larger particle size can increase the internal diffusion of the bio-sorbent penetration thereby inhibiting the equilibrium and consequently decreasing the adsorption ability [20][45]. The effect of particle size on the adsorption capacity of Methyl Orange dye by langsat shell biosorbent is shown in Figure 8.

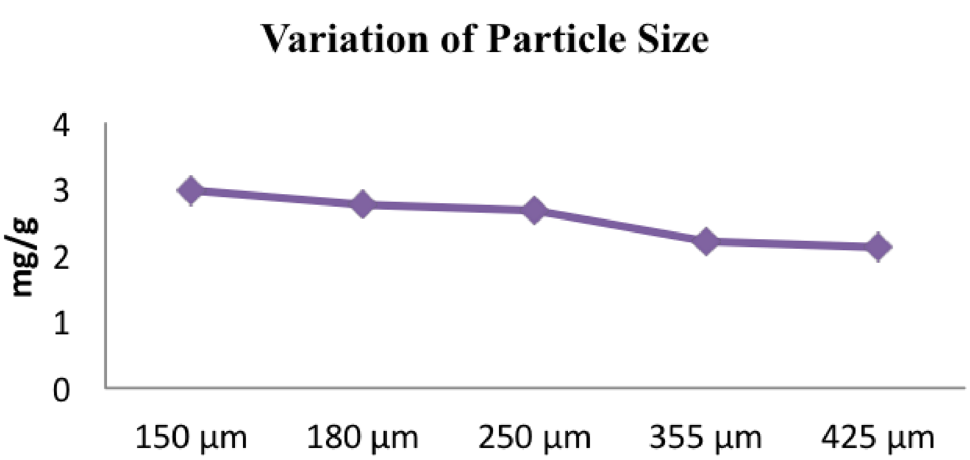

Figure 8. Effect of Particle Size of the solution on the adsorption capacity of Methyl Orange using activated langsat shell (0.2 grams of biosorbent, 25 mL of 150 mg/L solution, optimum pH 4, 200 rpm for 30 minutes)

In Figure 8 it can be seen that there is a decrease in absorption due to the larger particle size. The decrease occurred from the particle size of 180 m to 425 μm. The particle size of 150 μm is the optimum with an adsorption capacity of 2.9883 mg/g.

4. Conclusion

Activated langsat shell can be used as a biosorbent to absorb Methyl Orange with the optimum capacity obtained at a solution pH of 4, solution concentration of 150 mg/L, and particle size of biosorbent 150 μm. The maximum adsorption capacity obtained from the absorption of Methyl Orange at pH 4 2.5017 mg/g, concentration 150 ppm 3.1164 mg/g, particle size 150 μm 2.9883 mg/g

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