Methylene blue adsorption by langsat peel waste …… (Desy Kurniawati et al.)

Methylene blue adsorption by langsat peel (Lansium domesticum) waste

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ABSTRACT
The potential of langsat peel (LP) as an absorbent to remove methylene blue (MB) dye from the textile industry was investigated in this study. A batch method was employed to determine the optimum conditions and adsorption capacity of langsat peel with variations in pH, initial dye concentration, and particle size of the adsorbent. The analysis principle relied on measuring the absorbance of the MB dye before and after adsorption using a Spectronic 20D+ spectrophotometer at a maximum wavelength of 665 nm. The results indicated that the optimum conditions were pH 6, a concentration of 300 ppm, and a particle size of 150 µm. The adsorption process followed the Freundlich isotherm with an R² value of 0.918 and Kf values of 4.655 mg/g. According to the Langmuir isotherm, the maximum adsorption capacity obtained was 44.843 mg/g.

1. Introduction
Synthetic dyes are widely used in various industries such as textiles, paper, office supplies and cosmetics. The use of synthetic dyes causes the production of liquid waste which can pollute the environment (Syafila et al., 2022). Among 15-20% of the dyes used will remain in the wastewater which will eventually enter the surrounding environment (Chatterjee et al., 2008). The presence of dyes in waste is very dangerous for the environment because most of them are toxic, mutagenic and carcinogenic (Soni et al., 2012). The dye also prevents light penetration, which can reduce photosynthetic activity in waters and upset the aquatic balance (Shakoor and Nasar, 2016).

Methylene blue (MB) is a cationic thiazine dye, which is widely used to dye cotton, wood and silk because it is easy to apply, and has good resistance to materials (Auta and Hameed, 2014). However, Methylene blue can cause several harmful effects to humans such as irritation of the mouth, throat, esophagus and stomach, increased heart rate, vomiting, shock, cyanosis, jaundice, and necrosis (Shakoor and Nasar, 2016)(Kumar et al., 2011). Therefore, it is necessary to...
make an effort to remove MB dye from wastewater (Dinh et al., 2019). Various physical and chemical methods have been used for the removal of dyes from wastewater, but the adsorption method is considered to be superior to other methods (Subramaniam and Kumar Ponnumusty, 2015). This is associated with low cost, high efficiency, minimal use of chemicals, and easy application (Yang et al., 2014).

The efficiency of the adsorption process mainly depends on the cost and the removal capacity of the adsorbent used. Currently, agricultural waste is getting more attention as an adsorbent for removing dye from wastewater due to its economical nature and good availability (Gupta et al., 2016). Several studies have been conducted using agricultural waste such as yellow passion fruit peel (Lin et al., 2022), jackfruit peel (Dani Nandiyanto et al., 2023), banana peel (Akter et al., 2021), banana stem (Nandiyanto et al., 2021), and longan peel (Wang et al., 2016) to adsorb methylene blue. Apart from these wastes, langsat peel can also be used as an adsorbent. Langsat peel has the potential to become an adsorbent because it contains several groups of compounds such as terpenoids, flavonoids and saponins which can bind dyes but that research are just studied about the effect of dye concentration; string; and mass of biosorbent (Prestica and Kurniawati, 2020). From some of these explanations, a study was conducted using activated langsat peel adsorbent to adsorb methylene blue by studying the effect of process variables such as pH, solution concentration, and adsorbent particle size, with the hope that it can produce better adsorption.

2. Method

2.1. Material

Langsat peel (LP) from leg trader, Methylene blue (MB) Sigma Aldrich, Aquades, HNO₃ 0.1 M Sigma Aldrich and NaOH 0.1 M Sigma Aldrich. The apparatus used in this study were glassware, shakers (model: VRN-480), pH meter (HI2211), analytical balance (ABS 220-4), filter paper, magnetic stirrers (MR Hei Standard), mechanical grinder, spray bottle, sifter (BS410). The instrument used was FTIR (Fourier Transform Infra Red) type perkin elmer universal ATL Sampling Accessor 735 B and Spectronic 20D⁺ (spectrophotometer visible).

2.2. Preparation and characterization of langsat peel

LP waste was washed to remove impurities and dried in the sunlight until LP become crisp. The dried LP was mashed into powder by the mechanical grinder and then sieved to sizes 150 μm; 180 μm; 250 μm; 355 μm and 425 μm. 20 grams of each sample size was soaked in 100 ml HNO₃ 0.1 M. It was then rinsed with aquades and dried again.

The functional groups of LP before-after activation and their effect on dye adsorption were analyzed by Fourier Transform Infrared (FTIR) spectrophotometer within the wavenumber range 4000-600 cm⁻¹.

2.3. Batch adsorption experiments

Batch adsorption experiments were conducted in an Erlenmeyer containing 25 ml of the MB dye solution with known concentration. The fixed mass of adsorbent (0.2 g) was added to each Erlenmeyer and stirred on a shaker operating at a constant speed of 200 rpm for 30 minutes. The effect of pH (2; 3; 4; 5; 6; and 7), initial Concentration of MB (100; 150; 200; 250; and 300 mg/L), and particle size (150; 180; 250; 355; and 425 μm) were evaluated. The Langsmyer containing the samples was taken from the shaker, and filtered after that the final concentration of the MB dye was measured by spectronic 20D⁺ at λmax of 665 nm. The pH of the solution was adjusted using 0.01 M HNO₃ or 0.1 M NaOH. The amount of MB dye adsorbed at equilibrium was determined using the equation:

\[ q_e = \frac{(C_0-C_f)}{m} \times V \]  

Where, \( q_e \) is the adsorption capacity at equilibrium (mg/g), \( C_0 \) and \( C_f \) are the initial and equilibrium concentration of dye (mg/L), \( m \) is the adsorbent mass and \( V \) is Volume of dye solution. The percentage removal of dye was calculated using the equation:

\[ \% \text{ removal} = \frac{(C_0-C_f)}{C_0} \times 100\% \]  

3. Results and discussion

3.1. Characterization of langsat peel

FTIR characterization was used to determine the functional groups on the surface of LP and the changes that occur in it. Functional groups were played a role in the adsorption process of dyes that influenced by the number and type of functional groups, interaction process, and chemical structure (Bhernama, 2017). The FTIR spectrum of LP before-after activation and after the adsorption of MB were shown in Fig.1.

The peaks of the functional groups were detected in LP before activation such as hydroxyl groups (-OH) 3600-3200 cm⁻¹, (-CH) 3000-2900 cm⁻¹, carbonyl groups (C=O) 2000-1700 cm⁻¹ and (C=C) 1650-1500 cm⁻¹. These functional groups were also detected in LP after activation and after the adsorption of MB (Zein et al., 2023). But, there was a shift of peak functional groups as shown in Table 1. These shifts were caused by the effect of activation and interaction between the functional
Table 1. Changes in functional group wavelength before activation, after activation and after adsorption

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>Before Activation (cm(^{-1}))</th>
<th>After Activation (cm(^{-1}))</th>
<th>After Adsorption of MB (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>O – H</td>
<td>3330</td>
<td>3329</td>
<td>3292</td>
</tr>
<tr>
<td>C - H</td>
<td>2934</td>
<td>2934</td>
<td>2865</td>
</tr>
<tr>
<td>C = O</td>
<td>1934</td>
<td>2080</td>
<td>1765</td>
</tr>
<tr>
<td>C = C</td>
<td>1625</td>
<td>1627</td>
<td>1646</td>
</tr>
</tbody>
</table>

3.2. Effect of pH

pH is one of the factors that highly affects the adsorption process because it can determined the adsorbent surface charge and the degree of dye ionization (Asfaram et al., 2014). Variation of pH was done to determine the optimum pH that can produce optimal adsorption of MB. The effect of pH on the adsorption of MB by Langsat peel was shown in Fig. 2.

Adsorption capacity has increased from pH 2 up to optimum at pH 6 with an adsorption capacity value of 12.960 mg/g. At low pH, protonation has occurred on the adsorbent surface which can block the MB dye ion from binding to the active site of the adsorbent. This was caused by the solution containing a lot of H\(^+\) ions so there was a competition between protons and MB which are cationic dyes (Yang et al., 2015). In addition, the adsorbent surface was covered by H\(^+\) which produces electrostatic repulsion with MB cations. As the pH increased, the amount of H\(^+\) ions decreased and there was a decrease in the repulsive force which made the adsorption capacity increase (Shakoor and Nasar, 2016). At pH 6 it shows the optimum pH because the active site wasn’t protonated so it was negatively charged and can bind more positively charged MB ions (Tammi et al., 2013). It was found that the adsorption capacity MB was less at low pH and optimum at pH 6. Therefore, all the experiments were carried out at pH 6.

3.3. Effect of initial dye concentration

The initial MB concentration can affect the adsorption ability of LP. The higher the concentration of MB, the greater the chance of adsorption (Salleh et al., 2012). The amount of MB adsorbed by LP as a function of the initial MB concentration is shown in Fig. 3.

In the concentration range used, the optimum conditions were obtained at a concentration of 300 ppm with an adsorption capacity of 36.857 mg/g. The amount of MB adsorption still was grown, which means that the adsorbent was not yet saturated. Determination of maximum adsorption capacity was done using adsorption isotherms. The adsorption isotherm model that occurs in the adsorption process of Methylene blue by Langsat peel adsorbent is determined by testing the
linear regression equation of the Langmuir adsorption isotherm and the Freundlich isotherm equation which is shown in Fig. 5 and 6 (Muhammad and Abdurrahman, 2020).

![Figure 5. Langmuir isotherm for adsorption MB using LP](image)

![Figure 6. Freundlich isotherm for adsorption MB using LP](image)

Based on the figure, the correlation coefficient (R²) obtained from the Langmuir isotherm curve is 0.5737 and the Freundlich isotherm is 0.9183. This shows the tendency of MB adsorption by LP followed by the Freundlich isotherm because the R² value is close to 1. The Freundlich isotherm describes physical adsorption which is a heterogeneous adsorption process because not all adsorbent surfaces have the same adsorption, the shape of the adsorbate layer on the adsorbent surface is a multilayer (Kurniawati et al., 2016).

From the results of calculations using the Freundlich Isotherm equation, the K\text{f} value of 4.655 mg / g was obtained with an n value of 0.691. The K\text{f} value indicates the Freundlich constant. The greater of K\text{f} value, the greater of adsorption capacity of LP to absorb MB. A comparison of the Freundlich and Langmuir isotherm equation values can be seen in Table 2.

<table>
<thead>
<tr>
<th>Freundlich Isotherm</th>
<th>Langmuir Isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td>K\text{f} = 4.655</td>
<td>K\text{f} = 4.655</td>
</tr>
<tr>
<td>N = 0.691</td>
<td>N = 0.691</td>
</tr>
<tr>
<td>R² = 0.9183</td>
<td>R² = 0.9183</td>
</tr>
</tbody>
</table>

Table 2. Freundlich and Langmuir Isotherm Value

3.4. Effect of particle size

The effect of particle size on the adsorption of MB by Langsat peel is shown in Fig. 7. From Figure 7, it can be seen that the difference in the adsorption capacity of adsorbents from the smallest particle size (150 µm) to the largest particle size (425 µm) has decreased. This is because the smaller particle size increases the outer surface area of the adsorbent (Banerjee et al., 2016). Theoretically, the particle size controls the adsorption rate on a solid surface because the adsorption capacity is directly proportional to the total available surface area of the adsorbent particles (Abbas, 2020). If the size of the adsorbent used is greater, it can cause a decrease in the surface area of the adsorbent and available active groups (Chairgulprasert and Waehayee, 2018). In addition, larger particle size can increase the internal diffusion of adsorbent penetration thereby inhibiting equilibrium and consequently decreasing the adsorption capacity (Amin et al., 2017). 150 µm is the optimum particle size with an adsorption capacity of 36.504 mg/g.

![Figure 7. The effect of particle size on the adsorption capacity of MB using LP](image)

4. Conclusion

The results showed that langsat peel waste had a good adsorption ability as an adsorbent to adsorb methylene blue dye with optimum conditions obtained at pH 6 and a concentration of 300 mg/L, and an adsorbent particle size of 150 µm. Determination of the adsorption capacity of MB using LP following the Freundlich isotherm equation with a value of R² = 0.918 obtained a K\text{f} of 4.655 mg/g and based on the Langmuir isotherm the maximum adsorption capacity value obtained was 44.843 mg/g. FTIR characterization showed that LP has several functional groups that can bind dyes.

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