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Adsorption of Methylene Blue Using Composite Fe_3O_4-Ihau Fruit Peel Powder (*Dimocarpus longan* var. malesianus Leenh.)

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Abstract

A study has been conducted on the adsorption of methylene blue dye using Fe_3O_4-ihau fruit peel powder composite as the adsorbent. The Fe_3O_4-ihau fruit peel powder composite adsorbent was synthesized using the co-precipitation method from $FeSO_4.7H_2O$ and $FeCl_3.6H_2O$ in a 3:2 ratio, then composited with ihau fruit peel powder. The resulting Fe_3O_4-ihau fruit peel powder composite was characterized using Fourier Transform Infra-Red (FTIR), Scanning Electron Microscopy (SEM), and X-Ray Diffractometer (XRD). FTIR characterization results of the Fe_3O_4-ihau fruit peel powder composite showed an absorption peak at a wave number of 586.36 cm^{-1}, corresponding to the Fe-O group. SEM revealed that the Fe_3O_4-ihau fruit peel powder composite has an uneven surface and smaller pores compared to the ihau fruit peel powder, and XRD showed a diffractogram of the Fe_3O_4-ihau fruit peel powder composite that closely resembled that of Fe_3O_4. Methylene blue adsorption by the Fe_3O_4-ihau fruit peel powder composite adsorbent was optimal at pH 4 with an optimum contact time of 75 minutes, and it had a maximum adsorption capacity of 43.7267 mg/g. The adsorption isotherm followed the Langmuir isotherm, and the adsorption of methylene blue dye using Fe_3O_4-ihau fruit peel powder composite adsorbent occurs spontaneously, endothermically, and by physisorption.

Keywords: Adsorption, Composite, Fe_3O_4, Ihau, Methylene Blue

INTRODUCTION

The chemical industry is currently growing very fast along with the increasing population in the world. Industries such as textiles, paper, food, medicine, leather, cosmetics, printing, and rubber also use synthetic dyes in their product loading process (Asiah et al., 2022). Synthetic dyes derived from industrial waste will harm the environment. Methylene blue is one compound widely used in the fabric, leather and printing coloring industry (Riwayati et al., 2019). Methylene blue is a widely used dye from the thiazine or cationic group, which stands out among other dyes in its category. It represents dyes that are usually large in molecular size and difficult to decompose in the natural environment. These dyes are commonly applied to cotton, wool, silk, textiles, and leather, as well as used in calico printing and biological dyeing. The release of methylene blue dye into rivers, groundwater and other water sources poses a significant pollution problem (Susanti et al., 2022). Methylene blue, with the chemical formula $C_{16}H_{18}ClN_3S$, is a toxic aromatic hydrocarbon compound and a cationic dye known for its strong absorption capacity. This substance appears as dark green crystals that form a blue solution when dissolved in water or alcohol. It has a molecular weight of 319.86 g/mol, a melting point of 180 °C, and a water solubility of 35.5 g/L. The use of methylene blue can lead to side effects such as digestive issues and skin irritation if inhaled. In addition to degrading water quality, methylene blue pollutants pose significant health risks, including toxicity, carcinogenicity, mutagenicity, and teratogenicity (Tehubijuluw et al., 2023).

To treat effluents containing synthetic dyes, various methods have been used, including biological, physical, and chemical processes such as adsorption, membrane filtration, biosorption, ozonation, coagulation or flocculation, advanced oxidation, and liquid-liquid extraction (Riwayati et al., 2019). One of the most commonly used physical methods for treating effluents containing synthetic dyes is adsorption, as it is cost-effective, easy to implement, and effective against various types of pollutants. This method typically uses inexpensive and safe natural materials (Baunsele et al., 2022). Currently, many studies have been developed to obtain adsorbent materials that are relatively easier than activated carbon, such as kiambang powder (Wiranata et al., 2020), teak wood sawdust (Firmanto et al., 2021) and lai fruit peel powder (Oliviani et al., 2023).

The adsorbent of ihau fruit peel (*Dimocarpus longan* var. malesianus Leenh.) was obtained from a local fruit shop, where ihau fruit peel is an unused waste that can be obtained from local fruit shops. However, the adsorbent from the ihau fruit peel has the disadvantage that it is difficult to separate from the sample solution after the adsorption process.

One of the disadvantages of using powder adsorbents is that screening techniques are required in their separation. To overcome this, magnetic adsorbents can be used to make composites by combining adsorbent materials and magnetic materials to create new composites that have two properties: adsorption properties and magnetic properties. The magnetic properties allow the use of magnets to separate composite particles in water. The advantage of magnetic separation is that the retrieval of adsorbents from wastewater becomes easier, simpler and more efficient (Reknosari et al., 2021).

Based on the description above, this research was conducted by utilizing the Ihu fruit peel waste (*Dimocarpus longan* var. malesianus Leenh.), which will be composited with magnetite (Fe_3O_4) into a magnetic adsorbent (Reknosari et al., 2021). The Fe_3O_4-ihau fruit peel powder composite will be used to adsorb methylene blue dye, so it is hoped that the results of this study can be one method of utilizing ihau fruit leather waste and can help in the problem of methylene blue dye waste pollution.

METHODOLOGY

Materials and Instrumentals

The materials used were hau fruit peel powder, methylene blue (pa Merck), HCl 37% (pa Merck), NaOH Pellet Merck, $H_2SO_{4(p)}$ (pa Merck), $FeCl_3.6H_2O$ (pa Merck), $FeSO_4.7H_2O$ (pa Merck), NH4OH 25% (pa Merck), n-hexane (pa Merck), distilled water, aluminum foil and plastic wrap. The instrumentations that have been used in research are glassware, blender, Heratherm oven, Ohaus PR series analytical balance, vacuum pump, Buchner funnel, 60 mesh sieve, spatula, stirring rod, mortar, pestle, hot plate magnetic stirrer, pH meter Orion Star A211, thermometer, sonicator, JISICO waterbath shaker, UV-Vis spectrophotometer Orion AquaMate 8100, Fourier Transform Infra Red (FTIR) Shimadzu 8400S, Scanning Electron Microscope (SEM) JEOL SSM-6510 and X-Ray Diffractometer (XRD) Brucher Eco D8 Advance.

Methods

Sample Preparation

The ihau fruit peels are dried in the sun until dry. The ihau fruit bark is cut into small pieces. The ihau fruit peel is pulverized to a fine powder. The powder was sieved using a 60 mesh sieve. The powder was sonicated for 15 minutes in n-hexane and repeated 3 times until oil was released and dried in an oven at 105 °C until dry. The ihau fruit peel powder was washed and vacuumed repeatedly with boiling distilled water to produce a colorless filtrate. The ihau fruit peel powder was dried in an oven at 105 °C until dry. The ihau fruit peel powder was crushed and sieved using a 60 mesh sieve.

Chemical Activation

The ihau fruit peel powder was immersed in a 2 M HCl solution and stirred with a magnetic stirrer for 2 hours, then left to stand for 24 hours. After 24 hours, it was stirred again for 2 hours using a magnetic stirrer and then filtered. The powder was then rinsed with distilled water until its pH matched that of distilled water. Then the powder was dried in an oven at 105 °C for 2 hours. Then the dried ihau fruit peel powder was ground and sifted through a 60 mesh sieve.

Preparation of Fe_3O_4-Ihau Fruit Peel Powder Composite

$FeCl_3.6H_2O$ solids of 6 grams were dissolved in 100 mL of distilled water. A total of 3.9 grams of $FeSO_4.7H_2O$ was dissolved with 50 mL of hot distilled water, then a few drops of $H_2SO_{4(p)}$ solution were added until the solution was lighter in color. $FeCl_3$ solution and $FeSO_4$ solution were mixed while stirring using a magnetic stirrer. In another container, 10 grams of ihau fruit peel powder was put in 100 mL of distilled water and stirred using a magnetic stirrer while being heated at 70 ºC. The mixture was added a mixture of $FeCl_3$ and $FeSO_4$ solutions, and then added with a 25% NH_4OH solution of 100 mL drop by drop (kept the temperature at 70 ºC for 3 hours). The mixture was filtered using a Buchner funnel and vacuum pump; the precipitate was washed until the pH of the filtrate was equal to the pH of distilled water. The precipitate was dried in an oven at 100 ºC for 3 hours and put into a desiccator. The Fe_3O_4-powder composite of ihau fruit peel was crushed and sieved using a 60 mesh sieve.

Characterization Test

Fourier Transform Infra Red (FTIR)

The ihau fruit peel powder, magnetite (Fe_3O_4) and Fe_3O_4-ihau fruit peel powder composite were analyzed using FTIR to determine the functional groups of the ihau fruit peel powder, magnetite (Fe_3O_4) and Fe_3O_4-ihau fruit peel powder composite.

Scanning Electron Microscope (SEM)

The ihau fruit peel powder, magnetite (Fe_3O_4) and Fe_3O_4-ihau fruit peel powder composite were analyzed using SEM to determine the surface morphology of the ihau fruit peel powder, magnetite (Fe_3O_4) and Fe_3O_4-ihau fruit peel powder composite.

X-Ray Diffractometer (XRD)

The ihau fruit peel powder, magnetite (Fe_3O_4) and Fe_3O_4-ihau fruit peel powder composite were analyzed using XRD to determine the structure and crystal arrangement of the ihau fruit peel powder, magnetite (Fe_3O_4) and Fe_3O_4-ihau fruit peel powder composite.

Adsorption of Methylene Blue Dye

Determination of Optimum pH

The Fe_3O_4-ihau fruit peel powder composite, as much as 0.01 gram, was put into 25 mL of 5 mg/L methylene blue dye solution whose solution pH has been adjusted to 3, 4, 5, 6, 7, 8, 9 and 10 by adding NaOH solution or HCl solution. The mixture was stirred using a magnetic stirrer for 30 minutes. The mixture was separated using an external magnet, and the filtrate was determined for dye concentration using a UV-Vis spectrophotometer at a wavelength of 664 nm. The optimum pH value is the pH that has the greatest % adsorption efficiency and adsorption capacity value. According to Masrullita *et al.* (2021), the % adsorption efficiency can be calculated with the following equation:

$$\% \text{ adsorption} = \frac{C_i - C_e}{C_i} \times 100\ \% \tag{1}$$

Description:
C_i = initial concentration (mg/L)
C_e = final concentration (mg/L)

The value of adsorption capacity according to Masrullita *et al.* (2021) can be calculated with the following equation:

$$q_e = \frac{(C_i - C_e)V}{m} \tag{2}$$

Description:
V = volume of solution (L)
m = adsorbent mass (g)
C_i = initial concentration (mg/L)
C_e= final concentration (mg/L)
q_e= adsorption capacity (mg/g)

Determination of Optimum Time

The Fe_3O_4-ihau fruit peel powder composite as much as 0.01 gram was put into 25 mL of 5 mg/L methylene blue dye solution, the mixture was stirred using a magnetic stirrer for 5, 10, 15, 30, 45, 60, 75, 90 and 120 minutes respectively, where the pH of the solution was set at the optimum pH. The mixture was separated using an external magnet, and the filtrate was determined for dye concentration using a UV-Vis spectrophotometer at a wavelength of 664 nm.

Determination of the Adsorption Capacity of Concentration Variation

The Fe_3O_4-ihau fruit peel powder composite, as much as 0.01 gram, was put into 25 mL of methylene blue dye solution with concentrations of 10, 20, 30, 100, 150, and 200 mg/L, where the pH of the solution was set at the optimum pH and stirred using a magnetic stirrer at the optimum time. The mixture was separated using an external magnet, and the filtrate was determined by using a UV-Vis spectrophotometer at a wavelength of 664 nm. According to Ismadji et al. (2021), Langmuir adsorption isotherm determination can be determined using the following equation:

$$\frac{1}{q_e} = \frac{1}{K_L q_{max}}\left(\frac{1}{C_e}\right) + \frac{1}{q_{max}} \tag{3}$$

Description:
q_e = adsorption capacity (mg/g)
K_L = Langmuir constant (L/mg)
C_e = final concentration (mg/L)
q_{max} = adsorption capacity (mg/g)

By making a graph between 1/Ce (x axis) and $1/q_e$ (y axis) with a slope of $1/K_L q_{max}$. While the Freundlich adsorption isotherm can be determined using the following equation:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{4}$$

Description:
q_e = adsorption capacity (mg/g)
C_e = final concentration (mg/L)
K_F = adsorption capacity (mg/g)
n = Freundlich constant (mg/g)

By making a graph between Log Ce (x axis) and Log qe (y axis) with a slope of 1/n. The appropriate isotherm can be seen from the larger R^2 value.

Determination of Adsorption Thermodynamics of Temperature Variation

The Fe_3O_4-ihau fruit peel powder composite, as much as 0.01 gram, was put into 25 mL of 5 mg/L methylene blue dye solution with temperatures of 30, 40 and 50 °C, where the pH of the solution was set at the optimum pH and stirred using a shaker at the optimum time. The mixture was separated using an external magnet, and the filtrate was determined by using a UV-Vis spectrophotometer at a wavelength of 664 nm. According to Ismadji et al. (2021), the thermodynamic determination of adsorption of an adsorbent can be calculated by the following equation:

$$\ln(K_d) = \frac{-\Delta H°}{RT} + \frac{\Delta S°}{R} \quad (5)$$

Description:
T = solution temperature (K)
K_d = thermodynamic equilibrium constant
R = gas ideal constant (8.314 J/mol K)
ΔH°= enthalpy change
ΔS° = entropy change

Adsorption thermodynamic parameters can be determined by calculating the adsorption thermodynamic equilibrium constant (Kd) at different temperatures. The In (Kd) value is then plotted against 1/T, following the linear form of the van't Hoff equation, as shown below:

$$\Delta G° = -RT\ln(K_d) \quad (6)$$
$$\Delta G° = \Delta H° - T.\Delta S° \quad (7)$$

Description:
T = solution temperature (K)
K_d = thermodynamic equilibrium constant
R = gas ideal constant (8.314 J/mol K)
ΔH° = enthalpy change
ΔS° = entropy change
ΔG° = Gibbs free energy change

RESULTS AND DISCUSSION

Characterization Test

Fourier Transform Infra Red (FTIR)

Characterization of ihau fruit peel powder, magnetite (Fe_3O_4) and composite Fe_3O_4-ihau fruit peel powder based on the results of analysis using FTIR aims to determine the functional groups present in ihau fruit peel powder, magnetite (Fe_3O_4) and composite Fe_3O_4-ihau fruit peel powder. The characterization results can be seen in Figure 1.

Based on the results of the spectrum on the Fe_3O_4-ihau fruit peel powder composite, there is a wide absorption at a wave number of 3425.58 cm^{-1}, which shows there is an O-H stretching vibration group, indicating the presence of hydrogen bonds.

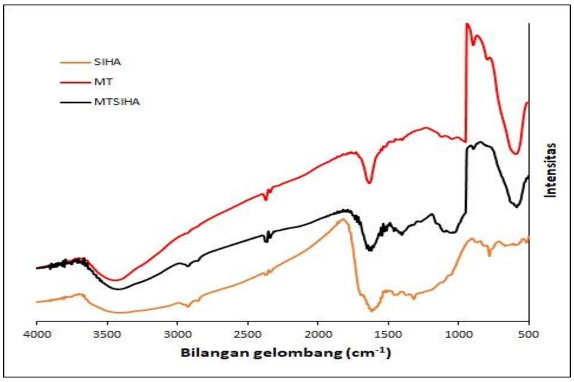

Figure 1: FTIR Spectrum Results of Ihau Fruit Peel Powder (SIHA), Fe_3O_4 (MT) and Fe_3O_4-Ihau Fruit Peel Powder Composite (MTSIHA).

In addition, there is an absorption at wave number 1604.77 cm^{-1}, which shows there is an O-H bending vibration group indicating the presence of hydroxyl bonds and an absorption at wave number 586.36 cm^{-1}, which shows there is an Fe-O group. This indicates that the Fe_3O_4 material is successfully composited on the surface of the ihau fruit leather powder. The table of functional groups on the ihau fruit peel powder, magnetite (Fe_3O_4) and Fe_3O_4-ihau fruit peel powder composite is as follows:

Table 1. Functional Groups of SIHA, MT and MTSIHA Materials

Functional Groups	Wave Number (cm^{-1})			
	SIHA	MT	MTSIHA	Literature
Fe-O *stretching*	-	583.32	586.36	500-700 (Fisli *et al.*, 2018)
O-H *bending vibration*	1620.21	1628,73	1604.77	±1600 (Jannah & Onggo, 2019)
O-H *stretching vibration*	3448.72	3404.37	3425.58	3300-3600 (Fisli *et al.*, 2018)

Scanning Electron Microscope (SEM)

SEM analysis aims to determine the surface morphology of the ihau fruit peel powder material before activation, ihau fruit peel powder after activation and Fe_3O_4-ihau fruit peel powder composite. The following is a photo of the SEM characterization results can be seen in Figure 2.

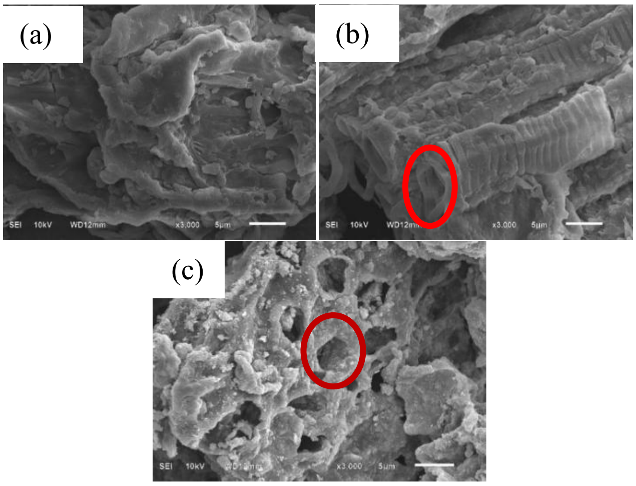

Figure 2. SEM Image Results with 3,000x Magnification (a) SIHA Before Activation, (b) SIHA After Activation and (c) MTSIHA

Based on Figure 2, it can be seen that the ihau fruit peel powder adsorbent before activation forms a non-porous surface and is still tightly bound to each other, but after activation, it has a porous surface shape. This can occur due to the process of chemical activation using a 2 M HCl solution. According to Daulay et al. (2022), this 2 M HCl solution can function to purify a material in order to produce high purity and reduce impurities in an adsorbent so that more pores are formed and the absorption process of the adsorbate is maximized. Meanwhile, the Fe_3O_4- ihau fruit peel powder composite shows that this composite has tighter pores than the ihau fruit peel powder after activation and has a rough texture. This is due to the presence of magnetite material (Fe_3O_4), which is spherical (small rounds), filling the powder pores so that the surface looks textured. The presence of Fe_3O_4 in the pores indicates that the ihau fruit peel powder has been successfully composited with magnetite (Fe_3O_4).

X-Ray Diffractometer (XRD)

XRD analysis aims to determine the phase of iron oxide formed in the adsorbent in the ihau fruit peel powder, magnetite (Fe_3O_4) and Fe_3O_4-ihau fruit peel powder composite. The following XRD characterization results can be seen in Figure 3.

Based on Figure 3, the XRD characterization results of the ihau fruit peel powder, magnetite (Fe_3O_4) and Fe_3O_4-ihau fruit peel powder composite materials, it can be seen that the Fe_3O_4-ihau fruit peel powder composite mineral type has a diffraction pattern similar to the magnetite (Fe_3O_4) mineral type. The synthesized iron oxide has a diffraction pattern similar to the XRD data base from JCPDS No. 11-0614 catalog, namely: 18.277(40), 30.105(70), 35.451(100), 43.123(70), 53.478(60), 57.012(85), 62.585(85), 70.967(20), 74.063(30) which is the mineral type of magnetite (Fe_3O_4).

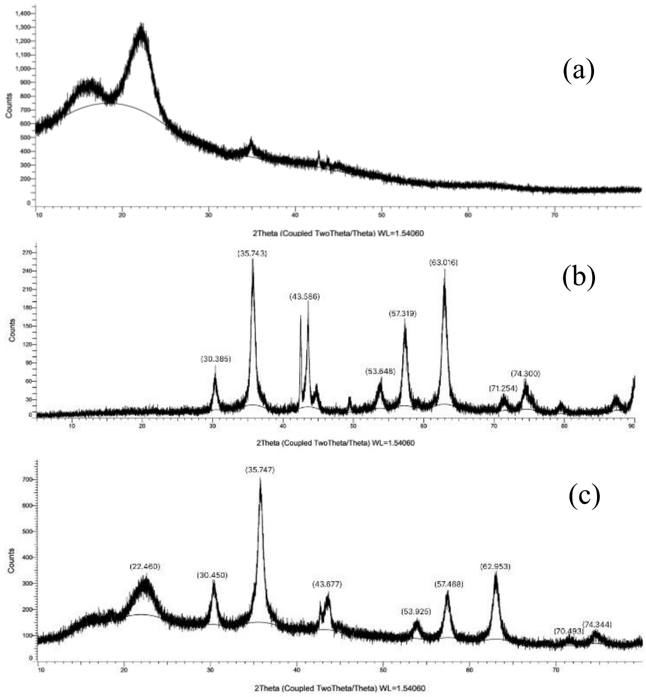

Figure 3. X-ray Difractogram Curve Results of (a) SIHA, (b) MT and (c) MTSIHA

The synthesis of Fe_3O_4-ihau fruit peel powder composite is confirmed to mostly form the Fe-O magnetic phase of iron oxide. The diffraction peaks of ihau fruit peel powder are wide, indicating the amorphous phase of the dominant ihau fruit peel powder structure. After the ihau fruit peel powder was composited with iron oxide, the diffraction peaks originating from the ihau fruit peel powder disappeared, and new diffraction peaks appeared following the diffraction pattern of the magnetite (Fe_3O_4) phase. This shows that on the surface of the ihau fruit peel powder structure, magnetic particles of the Fe_3O_4 phase have been attached. The more iron oxide fraction FeO in the composite, the higher the peak derived from iron oxide.

Adsorption of Methylene Blue Dye

Determination of Optimum pH

In this study, the determination of the optimum pH in the adsorption test was carried out with the aim of knowing the optimum pH of the Fe_3O_4-ihau fruit peel powder composite in adsorbing methylene blue dye.

The following graph of the optimum pH determination is presented in Figure 4.

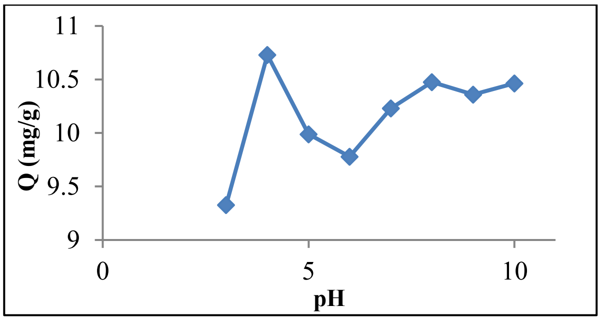

Figure 4. Effect of pH Variation on the Amount of Methylene Blue Adsorbed by Fe_3O_4-Ihau Fruit Peel Powder Composite

Based on the results obtained in Figure 4, it can be seen that the optimum pH occurs at pH 4 with the best adsorption capacity of 10.7297 mg/g. This indicates that the Fe_3O_4-Ihau fruit peel powder composite as an adsorbent can work well at pH 4. The optimum pH of the methylene blue dye is obtained in acidic conditions. Based on (Riwayati et al., 2019), adsorption decreases at high pH because the majority of the adsorbent surface becomes protonated. This leads to competition between H^+ ions, free methylene blue ions and OH^- ions for the available binding sites on the adsorbent surface. This causes the H^+ ions to react with the anionic groups on the adsorbent surface, thus reducing the amount of methylene blue ions that can be bound. At low pH (less than 5), methylene blue ions can enter the pore structure of the adsorbent, while at high pH (more than 7), methylene blue zwitter ions tend to form larger aggregates (dimers), making it more difficult to enter the adsorbent pore. The larger aggregation of methylene blue zwitter ions can be caused by electrostatic attraction interactions between ionic groups and monomers.

Determination of Optimum Time

In this study, adsorption tests were carried out with time variations which aimed to determine the optimum time of the Fe_3O_4-ihau fruit peel powder composite in adsorbing methylene blue dye. The following graph of the optimum time effect is presented in Figure 5.

Based on the results obtained in Figure 5, it can be seen that the optimum time required to adsorb methylene blue dye by Fe_3O_4-ihau fruit peel powder composite occurs at 75 minutes with an adsorption capacity of 11.1469 mg/g. Based on this data, the longer the contact time, the greater the increase in adsorption, until it reaches a maximum at a certain point.

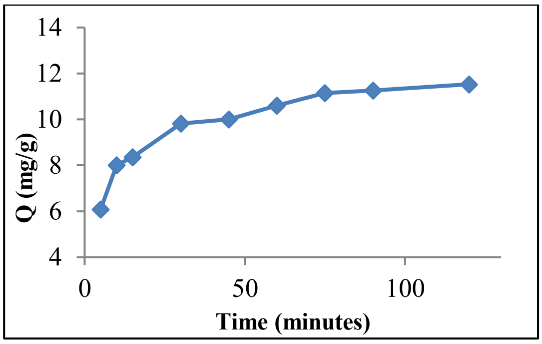

Figure 5. Effect of Time Variation on the Amount of Methylene Blue Adsorbed by Fe_3O_4-Ihau Fruit Peel Powder Composite

In the second stage, a rapid release of adsorbed substances occurs as the adsorbent pores become saturated. These two stages contribute to the prolonged duration of the adsorption process. Generally, the adsorption rate increases initially and then gradually decreases until it reaches equilibrium. This is because many pores are available for the adsorbate at the beginning of the process, but this number decreases over time. The remaining pores on the adsorbent surface become difficult to fill due to the repulsive forces between the adsorbate molecules in the solid and bulk phases.

Determination of the Adsorption Capacity of Concentration Variation

In this study, the maximum adsorption capacity of methylene blue dye solution was determined using a concentration variation, which aims to show the ability of Fe_3O_4-ihau fruit peel powder composite in adsorbing methylene blue dye.

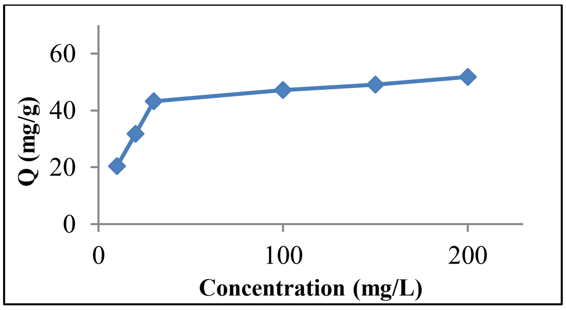

Figure 6. Effect of Concentration Variation on the Amount of Methylene Blue Adsorbed by Fe_3O_4-Ihau Fruit Peel Powder Composite

Based on the results obtained in Figure 6, it can be seen that the increase in the adsorption capacity of methylene blue dye adsorbed by Fe_3O_4-ihau fruit peel powder composite increases as the concentration of methylene blue dye solution increases, with the highest amount of methylene blue dye adsorbed at 43.1905 mg/g at a concentration variation of 30 mg/L. Based on Hayu et al. (2022), the initial dye concentration influences the occupancy of active sites on the adsorbent. At low initial dye concentrations, the adsorbent's active sites are sufficient to adsorb a small number of dye molecules. In contrast, at high initial dye concentrations, the limited number of active sites on the adsorbent cannot effectively increase the removal of dye molecules, resulting in a higher proportion of dye molecules remaining in the solution and a decrease in the adsorption capacity. Based on the calculation results, the maximum adsorption capacity of methylene blue dye by the adsorbent composite Fe_3O_4-ihau fruit peel powder is 43.7267 mg/g.

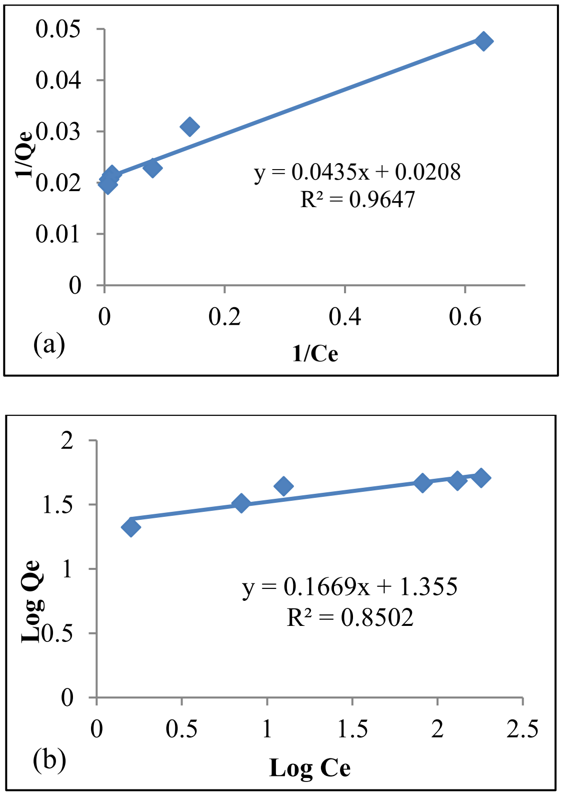

Figure 7. Curves of (a) Langmuir Isotherm, (b) Freundlich Isotherm

Figure 7 shows that the adsorption of Fe_3O_4-ihau fruit peel powder composite on methylene blue dye obtained results, namely, the Langmuir isotherm has an R^2 value of 0.9647, and the Freundlich isotherm has an R^2 value of 0.8502. Based on these results, the adsorption of methylene blue dye by Fe_3O_4-ihau fruit peel powder composite follows the Langmuir isotherm model because the R^2 value obtained is greater than the R^2 value in the Freundlich isotherm. This states that the adsorbed methylene blue dye only lasts one layer (monolayer), and the surface is homogeneous because each active site can only adsorb one molecule, besides being able to describe the equilibrium conditions between the surface and the solution that can be reversible (Amanda et al., 2021).

Determination of Adsorption Thermodynamics of Temperature Variation

In this study, adsorption tests were carried out with temperature variations, which aimed to determine the thermodynamics of adsorption using Fe_3O_4-ihau fruit peel powder composite against methylene blue dye. The following temperature effect graph is presented in Figure 8.

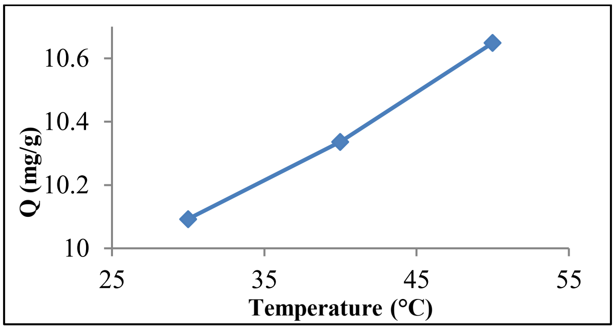

Figure 8. Effect of Temperature Variation on the Amount of Methylene Blue Adsorbed by Fe_3O_4-Ihau Fruit Peel Powder Composite

Based on the results obtained in Figure 8, it can be seen that the highest capacity obtained from adsorption by Fe_3O_4-ihau fruit peel powder composite to adsorb methylene blue dye occurs at 50 °C with a total capacity of 10.6487 mg/g. This shows that in the adsorption process with a fixed initial methylene blue dye concentration, the higher the adsorption temperature, the greater the adsorption capacity. So that, in accordance with the research of Maruthapandi et al. (2018), which states that the adsorption capacity at the initial concentration increases with increasing temperature, the calculation data obtained is as in Table 2.

Table 2. Thermodynamic Parameters of Adsorption

T (°C)	C_e	Q_e	$K_d = \frac{Q_e}{C_e}$	ln K_d	1/T (K)
30	0.9629	10.0927	10.4812	2.3496	0.0033
40	0.8656	10.3359	11.9406	2.4799	0.0032
50	0.7405	10.6487	14.3805	2.6659	0.0031

The results of measurements and calculations of adsorption thermodynamics, including a graph of the relationship between 1/T and In Kd on methylene blue dye solution by Fe_3O_4-ihau fruit peel powder composite, are shown in Figure 9.

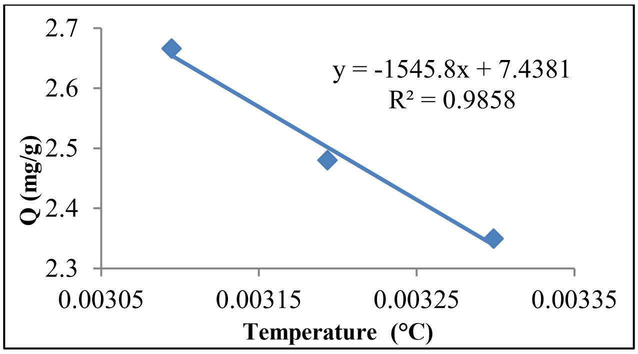

Figure 9. Relationship Curve of ln Kd and 1/T for Methylene Blue Adsorbed by Fe_3O_4-Ihau Fruit Peel Powder Composite

Figure 9 shows the data's linearity to the linear form of the van't Hoff equation (R^2 = 0.9858). Based on the regression equation on the curve, the thermodynamic parameters can be calculated so that the adsorption thermodynamic parameters will be obtained, namely the enthalpy value (ΔH°), entropy (ΔS°) and Gibbs free energy (ΔG°).

Table 3. Thermodynamic Result Data of Methylene Blue Adsorbed by Fe_3O_4-Ihau Fruit Peel Powder Composite

T (K)	Thermodynamic Parameters		
	ΔG° (J/mol)	ΔH° (J/mol)	ΔS° (J/K.mol)
303.15	-5921.872		
313.15	-6456.603	12851.781	61.840
323.15	-7162.314		

Based on the thermodynamic parameters of adsorption for methylene blue dye by Fe_3O_4-ihau fruit peel powder composite, the amount of ΔG° = negative value, ΔH° = 12851.781 J/mol and ΔS° = 61.840 J/K.mol. According to (Neolaka et al., 2019). The positive enthalpy (ΔH°) parameter value indicates that the methylene blue dye adsorption process occurs endothermically, where the adsorption capacity at the same initial concentration increases with increasing temperature, and the ΔH° value <20 kJ/mol indicates that the methylene blue dye adsorption process occurs by physisorption. While the positive entropy (ΔS°) value illustrates some structural changes in methylene blue that increase the randomness at the solid-liquid interface during the adsorption process, the adsorption process is spontaneous because the Gibbs free energy (ΔG°) is negative (Maruthapandi et al., 2018).

CONCLUSION

Based on the research, the results of the characterization of the Fe_3O_4- ihau fruit peel powder composite (*Dimocarpus longan* var. malesianus Leenh.) using FTIR, namely the presence of Fe-O and O-H groups, in SEM, obtained a surface that has denser pores than ihau leather powder and a rough texture because spherical magnetite material fills the pores. At the same time, XRD shows that the Fe_3O_4-ihau fruit peel powder composite has a diffraction peak that matches the magnetite pattern, indicating the composite's successful formation. The optimum condition of Fe_3O_4-ihau fruit peel powder composite in adsorbing methylene blue was obtained at pH 4, time 75 minutes, following the Langmuir isotherm with a maximum adsorption capacity of 43.7267 mg/g, and the adsorption process of methylene blue dye occurs spontaneously, endothermically, and by physisorption.

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