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Methylene Blue Adsorption Isotherm on *Spirulina* sp. Microalgae Biomass Coated by Silica-Magnetite

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Abstract. In this study, it has been performed modification of *Spirulina* sp. algae biomass with silica (HAS) coated with magnetite particles (HASM) and its adsorption test on a solution of methylene blue dye (MB) in solution. The identification of functional groups from HASM adsorbent was studied using infra-red (IR) spectrophotometer, the degree of crystallinity of the material was determined by X-ray diffraction (XRD), while the morphology and HASM constituent elements were analyzed by Scanning Electron Microscopy-Energy-Dispersive-X-Ray (SEM-EDX). The HASM adsorption isotherm of MB solution was studied by applying adsorption experiments using the batch method. The concentrations of MB dye in the adsorption process were analyzed by a UV-Vis spectrometer. Adsorption of 100 mg L⁻¹ MB dye solution by HASM adsorbent at pH of 6 with a contact time of 60 minutes resulted in an adsorbed MB amount of 90.90 mg g⁻¹. The adsorption isotherm model of the MB dye solution in the HASM adsorbent tends to follow the model of Freundlich adsorption isotherm. The adsorbent HASM is the effective adsorbent to absorb MB dye in solution.

Keywords: *Spirulina* sp., adsorption, silica coated magnetite.

1. Introduction

Increasing industrial development has an influence on the environment, such as diverting pollution from chemicals both containing organic and inorganic [1]. The main problem with this chemical pollution is the difficulty of decomposing these compounds, so that it will have a negative impact on the environment. One of the non-biodegradable organic compounds in the environment is textile dyes. Textile dyes are generally made from azo mixture and derivatives of benzene groups. The benzene groups are very difficult or need a long time to degrade. Azo compounds if too long in the environment, will be a source of disease because they are carcinogenic and mutagenic [2].

One textile dye that pollutes the environment is methylene blue. Methylene blue dyes are textile dyes made from azo substances and from azo benzene groups [3]. Therefore, it is necessary to do an effective alternative to reduce the concentration of MB from the remnants of dissolved dyes and also from impurities obtained from natural fibers to avoid environmental pollution more widely [4].

To reduce pollution, several techniques have been used, including coagulation, complexation, ion transfer, and adsorption techniques. From these methods, the adsorption method is the most widely used method to reduce the influence of environmental pollution [5]. This adsorption method has several advantages among others, the process is very simple, the costs used are quite cheap, and environmentally friendly [6].

The adsorption process is one of the waste treatment techniques that is expected to be used to reduce metal concentration or excessive organic composition [7]. The adsorbents commonly used in the adsorption process are activated carbon, silica gel, alumina, and zeolite. Recently, researchers have collected the processing of wastes contaminated with coloring agents and heavy metals using bacteria, fungi, yeast and algae [8]. Biomass is usually used as biosorbent because it is available in large quantities, mostly biochemically, very effective, and relatively stable. Absorption of substance molecules by algae biomass can occur through interaction with functional groups such as hydroxyl, carboxylic, amino and phosphate [9].



Recently it has been developed, the use of alternative adsorbents originating from nature because it is more economical, for example algal biomass. Some types of algae have received attention because of their high ability to adsorb ions or molecules through the existed functional groups in algal biomass and their use as biosorbents which can be reused for waste processing in solution. However, biomass also has several disadvantages, namely low density, easily damaged due to decomposition of other microorganisms, and difficult techniques to use in columns as adsorbents [10].

Therefore, it is necessary to make modifications to overcome the disadvantages of using algae as an adsorbent. One matrix that is often used in the processing of algal biomass is silica. Silica gel is an inorganic solid that has a surface active side such as silanol (-Si-OH) and siloxane (Si-O-Si) groups which can chemically bind to functional groups found in algal biomass and it has large surface area.

To further increase the adsorption ability of modified algae-silica biomass, silica-magnetite coating techniques were carried out [11]. Silica coating techniques with magnetite particles are used so that the adsorbent has a large capacity and selectivity for adsorbates adsorbed and separation of adsorbates can be used quickly [12]. Using this technique, it is expected that silica-*Spirulina* sp. algae hybrids with magnetite can produce adsorbents that are effective against MB and environmentally friendly because they have no by products such as suspended solids. In addition, using this technique cannot damage the structure so that the immobilization process of *Spirulina* sp. on silica matrix is expected to maintain the activity of functional groups provided in *Spirulina* sp. algae [13].

2. Experimental details

2.1. Synthesis HASM

Solution (A) 5 ml of TEOS mixed with 2.5 ml of distilled water added 0.1 g of magnetite put into a plastic tube, then added a few drops of HCl 1 M to pH 2. Solution (B) as much as 0.4 g of *Spirulina* sp. algae biomass mixed with 5 ml ethanol stirred with a magnetic stirrer until the solution is homogeneous. Both solutions are mixed until a gel is formed [14]. The wet gel formed is left to stand for 24 hours then washed with ethanol and distilled water until pH 7, dried using freeze dry, then crushed with a grinding tool [15].

2.2. Isotherm Adsorpsi

An amount of 50 mg of HAS and HASM adsorbents with optimum concentration was put into 5 different plastic containers. Then added 20 ml of solution with different concentrations (0, 25, 30, 100, 200, and 300 mg L⁻¹) with optimum stirring time. The optimum pH was made using citrate buffer solution with pH range of 3.0 - 6.0 for the acidic pH and the phosphate buffer solution with pH range of 7.0-9.0 for the alkaline pH. After stirring, the adsorbent and solution were separated using centrifugation. The filtrate obtained was analyzed by UV-Vis spectroscopy at the maximum wavelength of MB 664 nm.

3. Results and discussion

3.1. Characterization Spektroskopi IR

In Figure 1(a), it can be observed that the IR spectra of magnetite have an absorption band at wave number 547.78 cm⁻¹ which is a characteristic absorption of magnetic particles (Fe₃O₄). The absorption band in the wave number area 3441.01 cm⁻¹ originating from the hydroxyl group (-OH), at the wave number region 1627.920 cm⁻¹ is the carbonyl group. In Figure 1(b), it can be observed that IR spectra of *Spirulina* sp. algae biomass. There is an absorption peak of 3000 cm⁻¹ wavenumber which is a stretching region N-H which overlaps with O-H. In the absorption area of 2931.80 cm⁻¹ shows the stretching C-H vibration of (-CH₂) aliphatic and in the absorption area 1658.78 cm⁻¹ showed asymmetric carbonyl.

In Figure 1(c), it can be observed that the IR spectra of HAS show that the peak at wave number 1087.85 cm⁻¹ symmetrical vibration absorption of O atoms from the siloxane (Si-O-Si) functional group. The presence of a siloxane group reinforced by absorption at wave number 794.67 cm⁻¹ is a symmetrical stretching vibration of Si-O and a peak at 455.20 cm⁻¹ has a bending vibration of Si-O from a siloxane group (Si-O-Si). At wave number 3441.01 cm⁻¹, a wide band of sharp absorption peaks appears which is the -OH stretching vibration of a silanol (Si-OH) group. The absorption band area of 2931.80 cm⁻¹ shows stretching vibrations C-H of (-CH₂) aliphatic derived from organic groups

in the biomass of *Spirulina* sp algae. This shows that the process of immobilizing algae biomass with silica as a matrix has been successfully carried out. In the absorption area 1658.78 cm^{-1} showed asymmetric carbonyl.

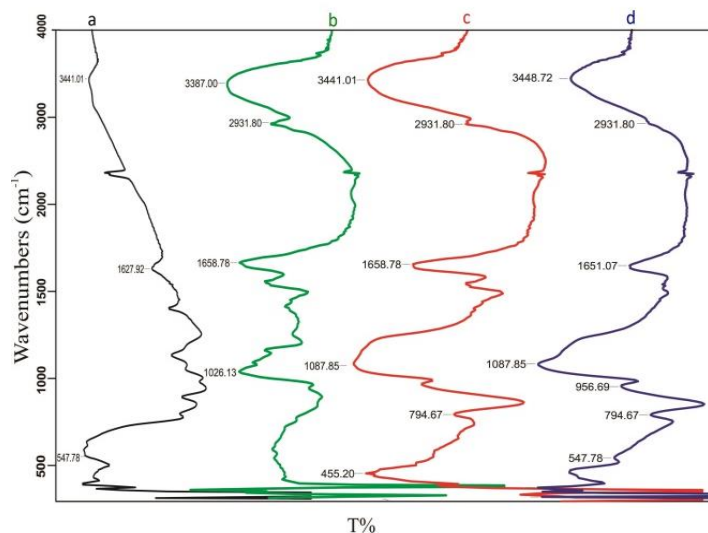


Figure 1. Spectra IR (a) Magnetite, (b) Biomassa algae *Spirulina* sp., (c) HAS, and (d) HASM

In Figure 1(d), it can be observed that the IR spectra of HASM, it is known that the absorption band at wave number 2931.80 cm^{-1} is a stretch of C-H stretching vibration of $(-\text{CH}_2)$ aliphatic originating from the organic group biomass *Spirulina* sp. This is not much different from the HAS spectra in the absorption indicating that the immobilization process of algal biomass with silica matrix and coating with magnetite particles has been successfully carried out. At wave number 547.78 cm^{-1} which is a characteristic absorption of magnetic particles (Fe_3O_4). The absorption band at the wave number area 3448.72 cm^{-1} originating from the hydroxyl group $(-\text{OH})$, in the wave number region 1651.07 cm^{-1} is the carbonyl group.

3.2. Characterization SEM-EDX

The differences in surface morphology is displayed in Figure 2 between (a) magnetite and (b) HASM, the magnetite shows the presence of granules of magnetite while in HAS it is more homogeneous because of the presence of silica, and HASM in the material appears homogen but there are still magnetite granules derived from Fe_3O_4 . The EDX data in Figure 2(a) shows the presence of Fe and O elements derived from Fe_3O_4 and in Figure 2(b) it is known that the results of elemental analysis using EDX show the presence of C, O, Si, and Fe elements derived from *Spirulina* sp. algae biomass, matrix silica and Fe_3O_4 . This supports the results of characterization using XRD, which indicates that the HASM material was successfully synthesized from HAS and magnetite.

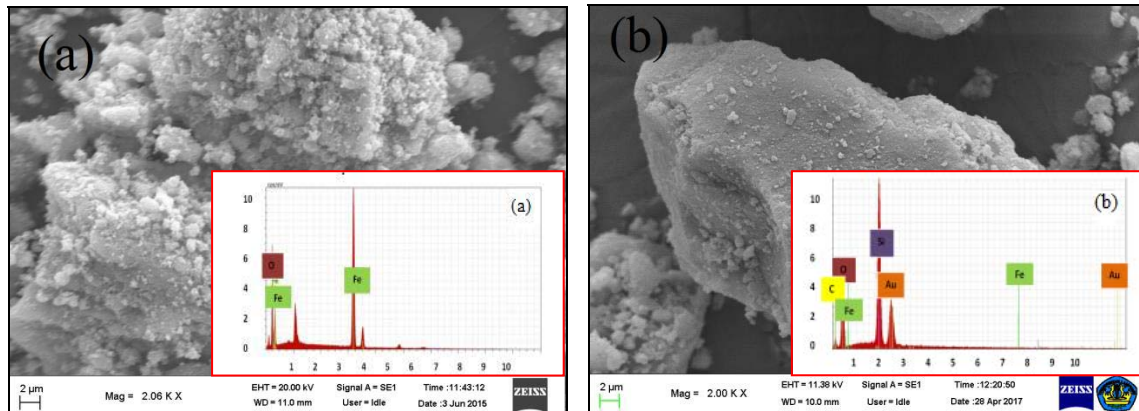


Figure 2. Results of the 2000x SEM-EDX characterization (a) magnetite and (b) HASM

3.3. Adsorption

3.3.1. Adsorption kinetics

The adsorption rate of the adsorbent to MB acts to determine the optimum conditions of interaction of the MB solution and its equilibrium state to the adsorbent. In the plot of the amount of MB adsorbed against the interaction time of Figure 3(a) shows that the MB adsorption by HAS and HASM varies to reach the optimum time at each time of 15; 30; 60; 90; and 120 minutes. From Figure 3(b) shows that adsorption takes place quickly in the initial stage on the outer surface of the adsorbent followed by a slower internal diffusion process which is a step from determination of rate.

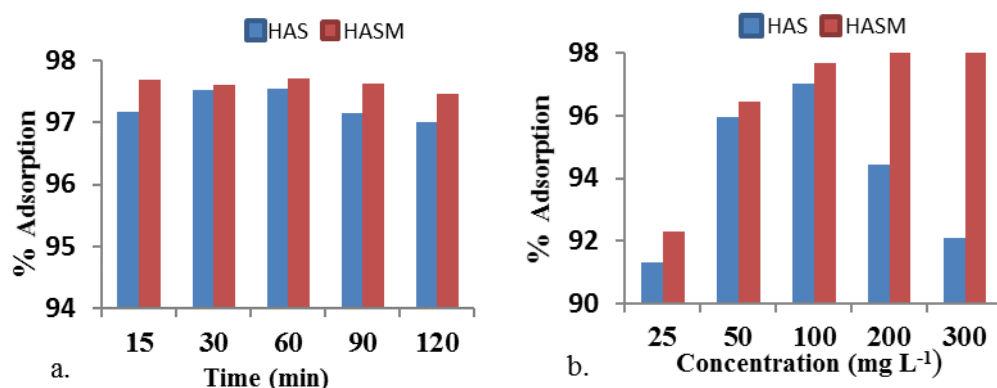


Figure 3. Influence of (a) interaction time and (b) concentration of MB adsorption by HAS and HASM.

The relatively short contact time can cause the adsorption process to be not optimal, this is because the adsorption speed is determined by the diffusion rate of the adsorbate species on the solids of the adsorbent. The longer the contact time of adsorption, the greater the collision frequency between the adsorbate particles and the adsorbent, so that it can cause greater amounts of adsorbed MB [16]. Then from the data contained in Figure 4 was analyzed using pseudo first order and second order kinetics [11, 14].

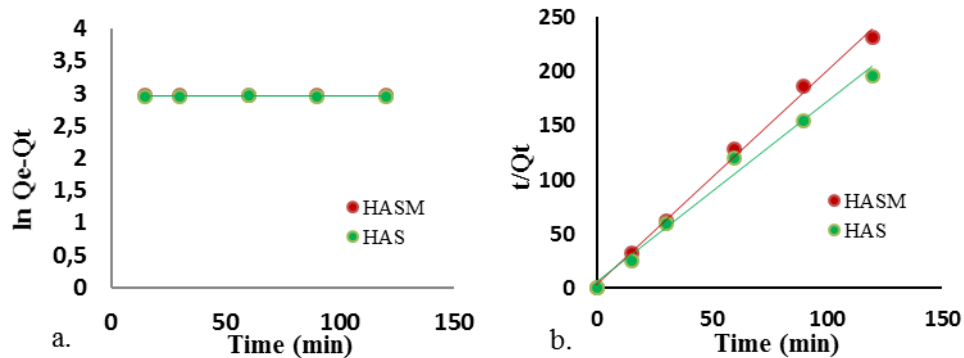


Figure 4. Kinetics of pseudo (a) first-order and (b) second-order MB dye on HAS and HASM

From Figure 4(a) it can be observed that the value of R_2 in the pseudo first-order kinetics equation for HAS and HASM is 0.307 and 0.308 respectively. This shows that the MB adsorption on HAS and HASM does not follow the pseudo first-order kinetics model. In addition to using pseudo first-order kinetics, analysis was also carried out using pseudo second-order kinetics. In Figure 4(b) it can be seen that the value of R_2 for each of the HAS and HASM adsorbents is 0.987 and 0.996, respectively. This indicates that the adsorption process in HAS and HASM tends to follow the pseudo 2 order kinetics model. In addition, from Figure 4 data shows that the k_2 value in the HASM material is greater than HAS. This indicates that HASM has a greater adsorption rate than HAS. The greater rate of adsorption rate on HASM compared to HAS was due to the magnetic properties of HASM which resulted in higher adsorption rates on HASM compared to HAS.

3.3.2. Adsorption Isotherm model

Concentration is one of the factors that determines optimum adsorption. In this study, a concentration variation of 0 - 300 ppm was used to determine the optimum concentration of MB absorbed. In Figure 3(b) it can be observed that adsorption increases with increasing concentration of MB. At the concentration of 300 ppm methylene blue, the amount of MB was adsorbed at HAS at 92.09% and at HASM at 98.03%.

The data contained in Figure 3(b) can be observed that the higher the initial concentration can be interacted with HAS and HASM adsorbents, the higher the amount of adsorbed metal (Q). Data were analyzed using the adsorption isotherm model. Adsorption isotherm is used to determine the interaction between the amount of adsorbed substance and the amount of adsorbent and the ability achieved by the adsorbent in adsorbing methylene blue. Adsorption isotherm is an important parameter in adsorption because it plays a role in determining the maximum conditions to produce optimal adsorption. In this study two patterns of adsorption isotherm equations were used, namely Langmuir and Freundlich isotherms on HAS and HASM.

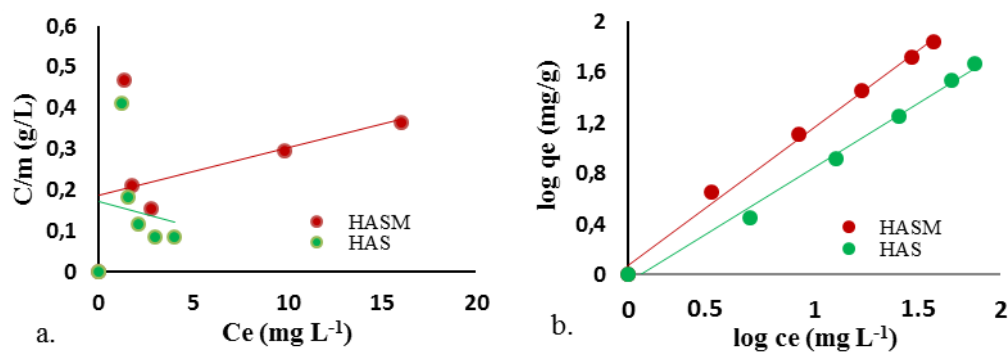


Figure 5. The linear equations of the adsorption isotherm models of the MB dye on the HAS and HASM adsorbent with the adsorption isotherm model of (a) Langmuir and (b) Freundlich

In the Langmuir isotherm it is explained that the adsorbent surfaces of HAS and HASM have active sites that are proportional to the adsorbent surface area [17]. Each active site has the same energy so that it can be said that the surface of the adsorbent is homogeneous. In addition to being analyzed using the Langmuir isotherm model, analysis was also carried out using the Freundlich adsorption isotherm model. Freundlich adsorption isotherm states that the surface of the adsorbent is heterogeneous [18]. This is because the affinity of each active site is not the same, so the adsorption on the most active sites is preferred.

Based on the data presented in (Table 1) it can be observed that the pattern of MB adsorption isotherms in HAS and HASM tends to follow the Freundlich adsorption isotherm. This is indicated by the correlation coefficient (R_2) in the Freundlich isotherm parameters greater than the Langmuir isotherm parameters found in (Table 1). The adsorption capacity (n_m) in HAS and HASM for MB is 83.33 mg g⁻¹ and 90.90 mg g⁻¹.

Table 1. Langmuir and Freundlich adsorption isotherm parameters

Adsorbent	Langmuir			Freundlich			$\Delta G^{\circ}_{\text{ads}}$ (kJ mol ⁻¹)
	n_m (mg g ⁻¹)	K_L (L mol ⁻¹)	R^2	n (mol g ⁻¹)	K_F (mg g ⁻¹) (L mg ⁻¹) ^{1/n}	R^2	
HAS	83.33	0.069	0.015	1.098	1.153	0.993	6.668
HASM	90.90	0.058	0.193	1.101	1.153	0.994	7.101

The value of K_L (adsorption equilibrium constant) on HAS for MB is 0.069 L mol⁻¹ and K_L on HASM for MB is 0.058 L mol⁻¹. The greater the K_L value, the greater the affinity of absorption by the adsorbent. The Langmuir isotherm explains that the adsorbent surface in this case HAS and HASM there are a number of active sites that are proportional to the adsorbent surface area. At each active site has the same energy so that it can be said that the surface of the adsorbent is homogeneous. In this study the MB adsorption process has adsorption energy of less than 20.92 k J mol⁻¹ so that it can be grouped to occur through physical interactions. However, the low adsorption energy does not indicate that adsorption only takes place in physics, but shows that chemical interactions play a role in adsorption in addition to physical interactions. The low adsorption energy can be caused by the binding mechanism of MB ions in HAS and HASM due to the large number of HAS and HASM functional groups that can bind MB ions and have different reactivity so that they can bind MB ions through physical and chemical interactions. Increased MB adsorption capacity in HASM is caused by reversible properties

4. Conclusions

The optimum amount of MB adsorbed by HAS and HASM adsorbents at pH 6 with a contact time of 60 minutes and tends to follow the pseudo-second-order kinetic model. Methylene blue adsorption isotherm by HAS and HASM tend to follow the Freundlich isotherm model with each adsorption capacity on HAS at 83.33 mg g⁻¹ while on HASM at 90.90 mg g⁻¹.

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