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Adsorption Kinetic and Isotherm of Solution Pair of Methylene Blue and Crystal Violet by Algae-Silica-Magnetite Hybrid Adsorbent on *Porphyridium* sp. Algae

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Abstract. Algae-silica-magnetite hybrid (PSM) from *Porphyridium* sp. algae has been successfully synthesized using precursor tetraethyl orthosilicate (TEOS) and coating with magnetite particles (Fe_3O_4) via a sol-gel process. The resulting adsorbent was applied for adsorption of solution pair of methylene blue (MB) and crystal violet (CV). The result of the analysis using the Infrared Spectrometer (IR) showed that in the PSM adsorbent there is an organic groups derived from *Porphyridium* sp. algae while silanol and siloxane group derived from silica matrix. In addition, surface morphology analysis results using Scanning Electron Microscopy With Energy Dispersive X-Ray (SEM-EDX) showed PSM surface has more heterogeneous than algae-silica hybrid (PS). The adsorption of solution pair of MB and CV by PSM was done under the experimental conditions of adsorbent of 0.1 g, interaction pH of 8, contact time of 90 min, and adsorbate concentration of 0.5 mmol L^{-1}. The adsorption kinetics data indicate that it tends to follow the pseudo second order model with a correlation coefficient (R^2) of 0.989 and 0.965 respectively. While, the adsorption isotherm model tends to follow Freundlich model.

Keyword: *Porphyridium* sp. algae, adsorption, methylene blue, crystal violet.

1. Introduction

The development of the industrial field has a negative impact on the environment, as the increase in pollution is occurring in the water environment mainly from the disposal of dyes. The type of dye used by industrial plants when they are thrown into waters without being processed first can cause damage to animals and microorganisms located in those waters [1]. Its long term exposure can cause vomiting, nausea, anemia and hypertension in living things [2]. The dyestuff have complex chemical structures and stable that they are difficult to decompose [3]. The most widely used dyestuffs are methylene blue (MB) and crystal violet (CV) which each have molecular formula $C_{16}H_{18}C_1N_3S$ and $C_{25}H_{30}N_3Cl$ which it is a basic substance with good solubility but mutagenic, toxic, and difficult to degrade [4,5].

Method that can be used to process liquid waste such as MB and CV are method is adsorption, because it is simple, relatively inexpensive, process and cause no side effects for the environment as well as living beings [6,7]. Another advantage of the adsorption method is that it can reduce the concentration of excess dyestuffs in the waste [8]. Algae biomass has been proven from various studies can be effective for absorbing dyestuffs. Nevertheless, algae biomass still has a low lack of its type weight, it needs to be immobilized with silica matrix [9]. As well as coated with magnetic particles in order for the formed adsorbent to be magnetized so as to increase capacity, selectivity and

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adsorption rate [10]. In this research, the PSM was synthesized using *Porphyridium* sp. algae hybrid with tetraethyl orthosilicate (TEOS) and coated by magnetite particles through a sol-gel process. The results of PSM adsorption research in MB and CV solution pairs are effective enough and it can be applied to reduce wastes that use harmful dyes before being discharged into the environment.

2. Experimental methods

2.1. Materials

The material used consisted of tetraetil ortosilikat (TEOS); distilled water; HCl; NH_3; NaOH; $FeSO_4{\cdot}4H_2O$; $FeCl_3{\cdot}6H_2O$; MB; CV; $CuSO_4{\cdot}5H_2O$; ethanol purchased from Merck Co., Inc. (Germany). *Porphyridium* sp. biomass was obtained from the Lampung Sea Cultivation Bureau (Balai Besar Pengembangan Budidaya Laut Lampung, Indonesia). Fe_3O_4 particle manufacture was synthesized by the same method on previous research [9]. Success of the synthesis of PS and PSM adsorbents can be seen from the results of analysis of the infrared spectrometer (IR) Prestige-21 Shimadzu, Japan. And Scanning Electron Microscopy with Energy Dispersive X-Ray (SEM-EDX) (Zeiss MA10, Germany).

2.2. Preparation of PSM adsorbent

Mixing solutions between 5 mL TEOS, 2.5 mL of distilled water, and 0.1 g of magnet particles stirred for 30 min yields a PSM adsorbent. At the time the mixing process takes place, added HCl 1M until pH of the solution becomes 2 (solution A). In the beaker of different plastic glasses, blended between 0.1 g *Porphyridium* sp. biomass and 5 mL of ethanol, which are stirred for 30 min (solution B). Then, solutions A and B are mixed until gel is formed. The resulting gel is left for 24 hours, cleaned by water and ethanol to neutral pH, and then drained in an oven at 40 °C. Dry materials are ground and deprived through a 200 mesh sieve. on the synthesis of the PS adsorbent is performed with the same procedure, but in the absence of the addition of the magnetic particle [10].

2.3. Adsorption Experiments

A batch method is a yag method used to perform adsorption process on PS and PSM adsorbent, using a solution pair of MB and CV as much as 25 mL on pH = 8. Batch adsorption experiments were carried out to estimate the efficiency of PS and PSM for the removal of solution pair of MB and CV from the contaminated water. In this process, a contact time and concentration of solution pair of MB and CV before and after adsorption processes is specified using UV-Vis Spectrophotometer (Agilent Cary 100, U.S.A.) at a wavelength of 591 (CV) and 664 nm (MB). The concentration of solution pair of MB and CV adsorbed per unit mass of adsorbent and the percentage solution pair of MB and CV adsorbed was determined using Eqs. (1)-(2):

$$q = \frac{(C_o - C_t)}{m} \times V \qquad (1)$$

$$\text{Adsorption \%} = \frac{C_o - C_t}{C_o} \times 100 \qquad (2)$$

Where C_o is concentration in the initial state, C_e is concentration at equilibrium, C_t is concentration at a certain time t of solution (mg L^{-1}), m is the mass of adsorbent (g), V is the volume of the solution (L), q is the number of solution adsorbed per unit mass (mg g^{-1}) [11].

3. Results and discussion

3.1. Characterization of adsorbent

Infrared Spectrometer (IR) characterization is performed to indicate the success rate of adsorbent creation through functional cluster identification present in the adsorbent. In Figure 1(a), shows the IR spectrum results of PS. The wavenumber region 2931.80 cm^{-1} indicates the presence of an aliphatic group ($–CH_2$). The wavenumber at 3425.58 cm^{-1} indicates the presence of O-H vibration, and the wavenumber at 1049.28 cm^{-1} is an asymmetry vibration of the siloxane group (Si–O–Si). While the wavenumber at 856.39 cm^{-1} explains the presence of siloxane groups from Si–O and 432.05 cm^{-1} indicates the vibration of Si–O. In Figure 1(b) shows the IR spectrum results of PSM. The PSM spectrum appearing peaks relatively similar to PS and a peak emerges wavenumber 462.92 cm^{-1} indicated a magnetite group from Fe–O stretch vibration [12,13]. The characterization uses Scanning Electron Microscopy With Energy Dispersive X-Ray to show success levels through surface morphology and constituent elements. On the Figure. 2 can be seen that the surface morphology of PSM adsorbent is more heterogeneous than PS because of the presence of magnetic particles [14], the result of such characterization amplified with EDX power indicating the presence of elements from the Fe an O magnet.

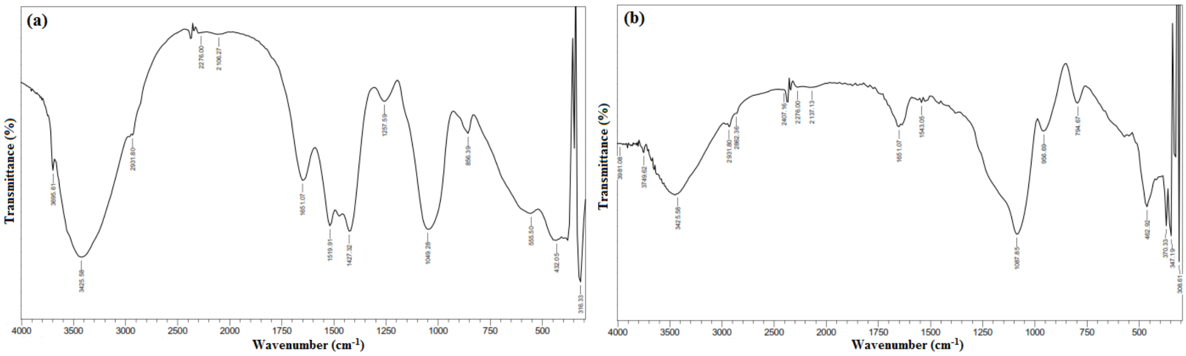

Figure 1. IR images of the (a) PS and (b) PSM.

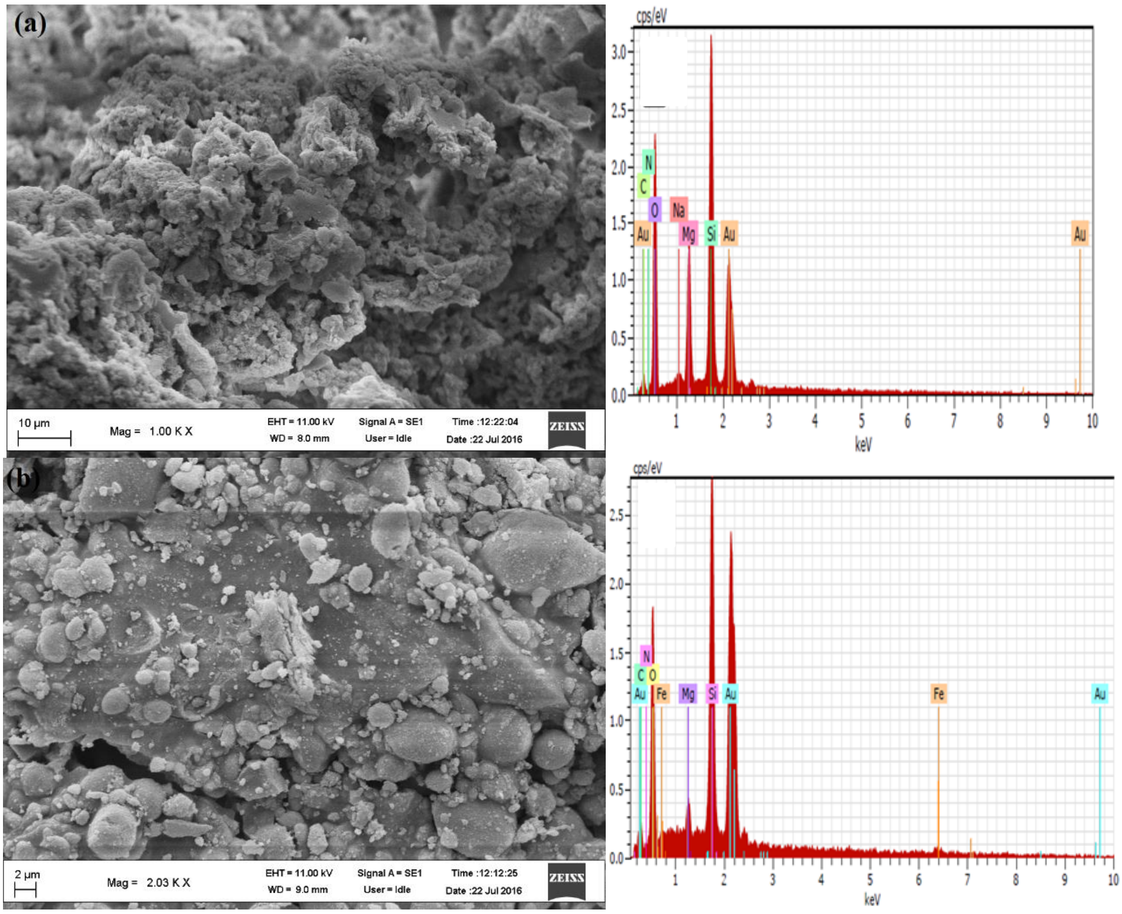

Figure 2. SEM micrograph and EDX images of (a) PS and (b) PSM.

3.2. Adsorption

3.2.1. Adsorption kinetics

Investigations about adsorption kinetics from PS and PSM in absorbing solution pair of MB and CV were investigated through the interaction of solutions at contact time ranging from 0-120 min. In Figure 3, it can be observed that in general adsorption in solutions pairs of MB and CV looks relative quickly. At contact time 15 min, the percentage of adsorption by the solution pair of MB and CV increases sharply in the PS and PSM adsorbent. Then the percentage of adsorption for the next contact time of 30-120 min was relatively constant. The longer the adsorption contact time, the greater the interaction between the adsorbent particles and the adsorbate can cause the greater number of adsorbates adsorbed. The kinetic model of the adsorption process of MB and CV solution pairs by PS and PSM adsorbents was determined using the data contained in Figure 3. The obtained data were analyzed by kinetics model of pseudo-first-order [Eq. (3)] and pseudo-second-order [Eq. (4)] [15.16] as follows:

$$\log(q_{e} - q_{t}) = \log q_{e} - \frac{k_{t}}{2.303} \times t \qquad (3)$$

$$\frac{t}{q_{t}} = \frac{1}{k_{2}{q_{e}}^{2}} + \frac{t}{q_{e}} \qquad (4)$$

Where q_e and q_t (mg g^{-1}) are the total adsorption capacity of pairs of dye solutions at t time and at equilibrium, respectively, k_1 and k_2 are first order and second order rate of constants. Experimental kinetics data and kinetic parameters are shown in Table 1. From the data contained in Table 1, it can be seen that kinetic models of MB and CV solution pairs by PS and PSM tend to follow pseudo-second-order kinetic models, shown with higher correlation coefficient values (R^2) compared to the kinetic model of pseudo-first-order. In Table 1, it can be seen also the adsorption constant rate (K) value of a pseudo-second-order is greater than that of the first-order. This is due to the presence of an active cluster from *Porphrydium* sp. and silica, also the presence of magnetite particles causes adsorbent to become magnetite. The particle layer of magnetite on silica as a matrix causes an increase in the rate of adsorbate adsorption in adsorbent [17-19].

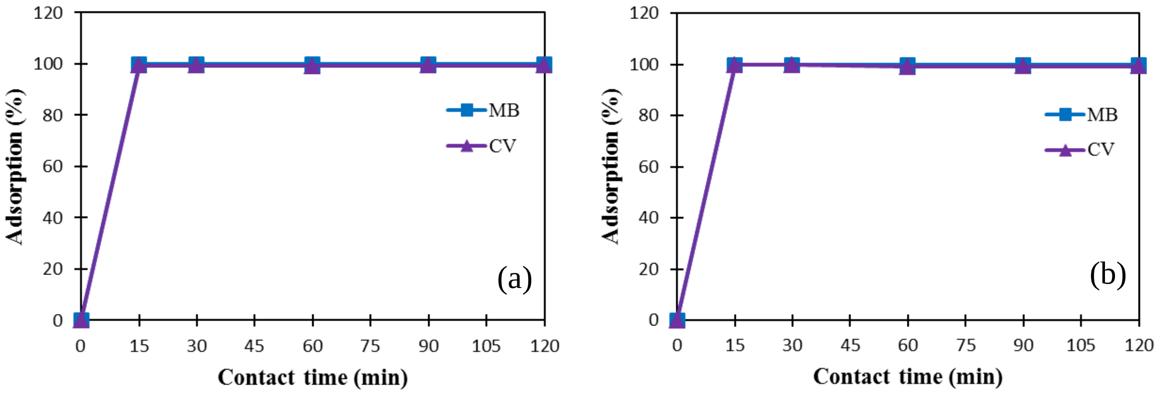

Figure 3. Effect of contact time on adsorption solution pair of MB and CV by (a) PS and (b) PSM.

Table 1. Comparation of Pseudo-first-order and pseudo-second-order parameters for the adsorption of solution pair of MB and CV by (a) PS and (b) PSM.

Adsorbent		Kinetics Model			
		Pseudo-first-order		Pseudo-second-order	
		K_1 (min^{-1})	R^2	K_2 ($g\ mg^{-1}\ min$)	R^2
PS	**CV**	0.019	0.309	5.455	0.984
	MB	0.018	0.309	1.392	0.994
PSM	**CV**	0.019	0.311	2.331	0.965
	MB	0.018	0.309	0.501	0.989

3.2.2. Adsorption isotherm

The adsorption isotherm model of PS and PSM in absorbing the solution pairs MB and CV is done by varying the concentration from 0.1- 0.5 mmol L-1. In Figure 4, it can be seen that there is an increase in adsorption, the data contained in Figure 3 were analyzed using adsorption isotherm models of Langmuir [Eq. (5)] and Freundlich [Eq. (6)] [20,21] as follows:

$$\frac{1}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m} \qquad (5)$$

$$\log q_e = \log\ K_F + \frac{1}{n \log C_e} \qquad (6)$$

Where C_e (mg L^{-1}) is the equilibrium concentration of solution, q_e (mg g^{-1}) is the adsorption capacity of solution at equilibrium, q_m (mg g^{-1}) is the adsorbent monolayer adsorption capacity, and K_L is the equilibrium constant including the affinity of binding sites (L mg^{-1}). K_L and q_m can be determined from the linear equation plot of log $1/q_e$ vs $1/C_e$ which will produce a straight line with $1/q_m K_L$ as slope and $1/q_m$ as intercept. K_F ((mg g^{-1}) (L $mg^{-1})^{1/n}$) is the adsorption capacity factor and n is the adsorption intensity factor, with n values ranging from 1 to 10 [21].

Next, plot of log q_e vs log C_e will produce K_F and exponent of n. Langmuir adsorption isotherm model assumes that on the surface of the adsorbent, there are a certain number of active sites that are proportional to the surface area, the adsorbent surface is uniform, and the adsorption process is monolayer. In Table 2, showing the value of R^2 of the freundlich adsorption isotherm model higher than langmuir [22], this data is also supported with the value of Freundlich constants (n) of the PSM adsorbent showing its value greater than 1. The freundlich adsorption isotherm model proves that the adsorption occurring opens only through the active site, and also on heterogeneous adsorbent surfaces (multilayers), in the presence of magnetic particles on the adsorbent can increase the rate adsorption [12].

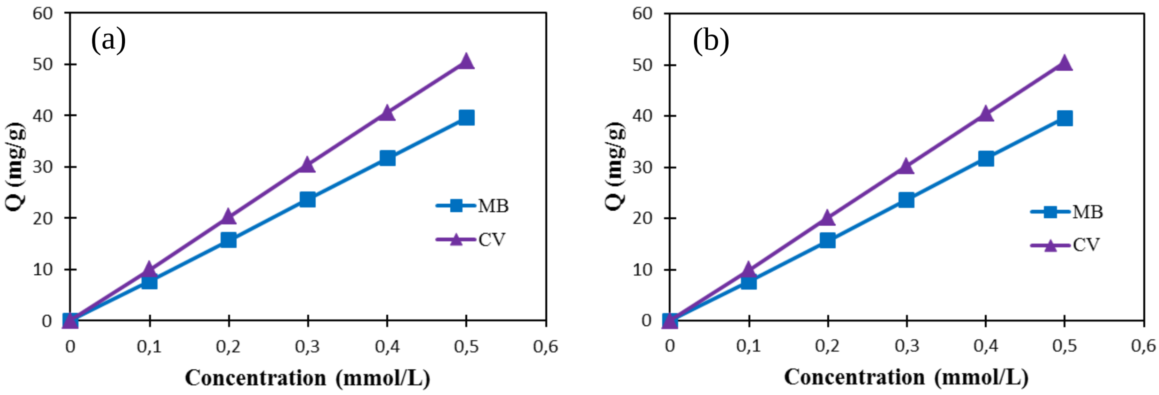

Figure 4. Influences of solutions concentration on adsorption of MB and CV by (a) PS and (b) PSM.

Table 2. Comparation of Langmuir and Freundlich parameters for the adsorption of solution pair of MB and CV by (a) PS and (b) PSM.

Adsorbent		Isotherm Model					
		Langmuir			Freundlich		
		n_m (mg/g)	K_L (L/mg)	R^2	n	K_F (mg/g) $(L/mg)^{1/n}$	R^2
PS	**CV**	112.359	0.323	0.618	1.419	27.283	0.820
	MB	2.066	0.722	0.627	0.104	2.755	0.829
PSM	**CV**	13.642	0.381	0.612	0.836	15.111	0.933
	MB	4.887	1.298	0.494	0.239	20.118	0.502

4. Conclusions

Based on the results of this study, the synthesis of PSM adsorbent was successfully created to remove MB and CV dyestuff in solution. The PSM adsorbent characterization results indicate the presence of an some active groups acting as active and adsorbents become magnetic so as to make the rate and adsorption capacity increase. Thus, these PSM are effective for removing MB and CV dyestuff in wastewater.

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