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Removal methylene blue from aqueous solution using silica aerogel prepared from bagasse ash

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Abstract. One important component in the manufacturing industry is coloring substance. Methylene blue (MB) is one of the coloring substances commonly use industry. The frequent use of the substance may result in the accumulation of methylene blue in the environment and thus creates an environmental waste that is dangerous for living. To control the condition of the environment, efforts to minimize the accumulation of methylene blue with the least possible negative effect in the manufacturing industries need to be made. Synthesized silica aerogel, the bagasse-ash-based solid, originated from sugar factory can be a simple and cheap solution to the problem. This study is intended to discuss the use of silica aerogel as an adsorbent of methylene blue. The influence of experimental factors such as contact time, initial MB concentration, and the temperature was investigated. The adsorption equilibrium was represented with Langmuir and Freundlich isotherm models. Langmuir equations were found to have the correlation coefficient value in good ($R^2 = 0.9998$). Adsorption of MB onto silica aerogel followed pseudo second order kinetics. The thermodynamic parameters such as the change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were determined and the negative values of ΔG° indicated that the process of removal was spontaneous at all values of temperatures. The adsorption process was spontaneous and exothermic nature.

1. Introduction

Today there has been an increasing demand for coloring substances for industry such as textile, cosmetics, as well as the food industry. This condition might finally result in the excessive amount of coloring waste which might destroy the environmental condition of the area. The effort to remove the waste from the environment before it reaches waters will be an urgent need. Otherwise, it would make further serious environmental destruction such as loss of vegetations and the failure of photosynthesis process in the deep sea due to the lack of sun rays reaching the place [1]. A simple and cheap method to overcome the problem is an adsorption process.

Researchers have successfully developed adsorbent to overcome such coloring waste [2-5]. Nazriati et al [6] develop silica aerogel extracted from bagasse ash, a neglected solid waste, obtained at the sugar industry. This silica aerogel with the surface area of 1114 m²/g and pore volume of 2.16 cm³/g, possesses a characteristic of a very good adsorbent. This paper is intended to study the possible potential value of silica aerogel as an adsorbent of coloring substance by using methylene blue.



2. Materials and Methods

The materials used in the research are Bagasse ash obtained from PG. Kreet II Baru, a cane sugar mill in Malang Indonesia. Sodium hydroxide (p.a Merck), hydrochloric acid 37% (p.a Merck), ammonium hydroxide (p.a/Merck), cation exchange resin, trimethylchlorosilane(p.a, Merck), hexamethyldisilazane (p.a, Merck) filter paper Whatman-41, methylene blue (Sigma), universal indicator (Merck) and demineralized water.

Silica aerogel Synthesis was adopted from Nazriati et al [6] with silicic acid composition: TMCS: HMDS (1: 0.03: 0.06). The resulted synthesized silica aerogel was then applied as an adsorbent to adsorption methylene blue (MB) from a solution.

The stock solution MB (100 mg/L) was prepared by carefully weighing the needed MB that it was then put into a volumetric flask to be dissolved in demineralized water until it reached the intended level as shown by the mark. The following step was taking a certain amount of MB solution to be liquefied and was used as the adsorbate. The adsorption process was conducted by batch using 25 ml MB solution plus 0.01g silica aerogel in which the variety of contact time, initial concentration of MB solution, and temperature. During the adsorption process, the materials were mounted on the shaker with a speed of 150 rpm. In order to separate the filtrate from the adsorbent, the concentration was mounted on the centrifuge for 10 minutes, and the residual MB that remained in the filtrate was measured using a spectrophotometer on the MB's maximum wavelength of ($\lambda_{\max} = 665 \text{ nm}$). Where the amount of MB adsorbed by the adsorbent was calculated with the formula of:

$$\%removal = \left(\frac{C_o - C_e}{C_o} \right) \times 100 \quad (1)$$

$$q_e = \left(\frac{C_o - C_e}{M} \right) \times V \quad (2)$$

In which q_e is the amount of MB adsorbed by the adsorbent in the equilibrium, C_o is the initial concentration of MB and C_e is the equilibrium concentration of MB, V is a volume of MB used in the adsorption process, and M is the mass of the adsorbent.

3. Results and Discussions

3.1. The effect of contact time

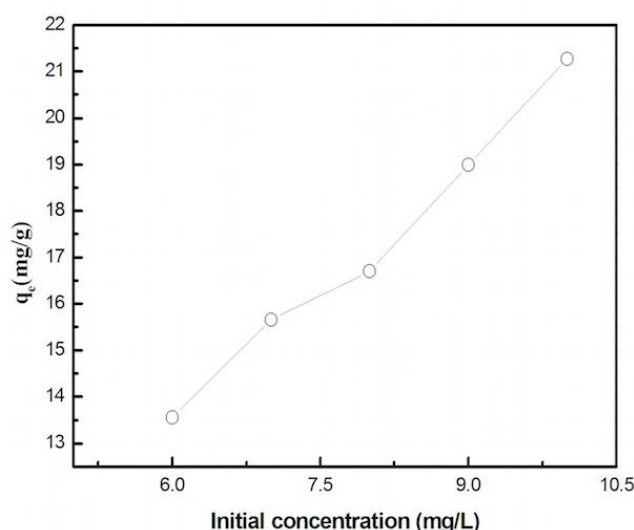
A test on bagasse ash based silica aerogel as an adsorbent of methylene blue is first carried out to study the influence of time variable (contact length) on the rate of adsorption capacity of the adsorbent on methylene blue. In this test two variables are identified: MB solution of 7 mg/L as the dependent variable and contact length as an independent variable. The independent variable was manipulated in terms of time between 0 to 120 minutes in length. The result of the test is depicted in Table 1. Table 1 indicates that silica aerogel adsorption capacity increases in line with the contact time length of the adsorption. The data shows the highest adsorption capacity of 15.685 mg/g with the adsorbed methylene blue is 89.474%. Beyond the 90-minute contact length, however, the figures remain constant. Therefore, the next variation is done at 90 minutes contact time.

Table 1. The data percentage of adsorbed methylene blue in different contact time

Time (minute)	Concentration (mg/L)		Removal of MB (%)	q_t (mg/g)
	C_0	C_t		
15	7	1.129	83.869	14.677
30	7	0.981	85.988	15.048
45	7	0.928	86.740	15.179
60	7	0.833	88.107	15.419
75	7	0.789	88.722	15.526
90	7	0.737	89.474	15.658
120	7	0.737	89.474	15.658

3.2. The effect of the initial concentration

The issue is the question of whether there is any effect of initial concentration MB on the absorption capacity of silica aerogel. To answer this question a test was conducted using various initial MB concentrations of 6, 7, 8, 9, and 10 mg/L. The result of the test indicates that the adsorption capacity increase in line with the increases of MB initial concentrations, as indicated in Figure 1.

**Figure 1.** The effect of MB initial concentration

It is depicted in Figure 1 that the higher the MB initial concentration the higher the MB adsorption capacity is likely to be. This could possibly due to the increase of the driving force as a result of mass transfer that occurs along with the change from the solution phase to the solid phase. This force increases proportionally to the increase of the adsorbate initial concentration. In addition, the increase of methylene blue initial concentration may cause increased competition among adsorbent so as to cause a higher adsorption capacity.

3.3. The effect of temperature

The effect of temperature was observed within the range of 313-333 K. Table 2 shows that the adsorption capacity decreases when the temperature increases from 313-333 K. The effect of temperature on MB adsorption capacity is then used to determine the parameter of the adsorption that covers adsorption thermodynamic and adsorption isotherm, each of which covers (ΔG° , ΔH° , dan ΔS°) for the thermodynamics, and Langmuir and Freundlich for the isotherm respectively.

3.4. Thermodynamic Adsorption.

Free energy (G°) is reserved energy available to conduct action, enthalpy (H°) is defined as calorie change occurring at constant pressure, whereas entropy (S°) is defined as a measurement of a random system. The thermodynamic parameter may be determined based effect of temperature as shown in Table 2.

Table 2. Effect of temperature on the adsorption capacity

C_0 (mg/L)	C_e (mg/L)			Adsorbed Methylene Blue (%)			q_e (mg/g)		
	313 K	323 K	333 K	313 K	323 K	333 K	313 K	323 K	333 K
6	0.488	0.522	0.722	91.866	91.308	87.959	13.780	13.696	13.194
7	0.904	0.962	1.067	87.081	86.261	84.757	15.239	15.096	14.833
8	1.096	1.306	1.517	86.304	83.672	81.041	17.261	16.734	16.208

As shown in Table 2, there is a constant relationship between various temperature conditions, methylene blue concentration, and adsorption capacities: that is the higher the temperatures the lower the adsorption capacity is likely to be. This indicates that the adsorption process likely occurs exothermically. This can be further justified by looking at the thermodynamic value of ΔH° . The calculation of ΔH° begins with the calculation of ΔG° value using the following formula:

$$K_c = \frac{C_a}{C_e} \quad (3)$$

$$\Delta G^\circ = -RT \ln K_c \quad (4)$$

The value of ΔH° and ΔS° can be determined by means of van't Hoff curve. The curve that links between $\ln K_c$ and $1/T$. The linear relationship between $\ln K_c$ and $1/T$ is shown in the following equation.

$$\ln \ln K_c = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (5)$$

$$\ln \ln K_c = \frac{-\Delta H^\circ}{R} \left(\frac{1}{T} \right) + \frac{\Delta S^\circ}{R} \quad (6)$$

This formula can be used to determine thermodynamic adsorption parameter as indicated in Table 3.

Table 3. Thermodynamic pdsorption parameter

T (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol)
313	-5.173		
323	-4.867	-14.0914	-28.515
333	-4.603		

Table 3 shows that the value of ΔG° turns to be negative as the temperature decreases, this is an indication that the methylene blue adsorption by silica aerogel occurs spontaneously at and tends to be better at low temperature. The negative value of ΔH° could indicate that the adsorption occurs exothermically, whereas the ΔH° value of -14.0914 kJ/mol (<80 kJ/mol) indicates that the adsorption occurs physically. Meanwhile, the negative value of ΔS° is an indication that there is a decreasing of the random adsorption process [7].

3.5. Adsorption Isotherm

The adsorption isotherm is the relationship between adsorption capacity and adsorbate concentration at a constant temperature. Two kinds of isotherm adsorption were tested in this study namely; Langmuir and Freundlich isotherm. While Langmuir isotherm was tested by making a curve showing the relationship between C_e/q_e and C_e using the following equation:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b_l} + \frac{C_e}{Q_0} \quad (7)$$

Freundlich isotherm was tested using a linear equation as follows:

$$\text{Log } q_e = \text{Log } K_f + \frac{1}{n} \log \log C_e \quad (8)$$

In which q_e is adsorption capacity, C_e is an adsorbent final concentration in the solution, K_f and n indicate the adsorption capacity of the adsorbent and the intensity of the adsorption. It is important to note that the value of K_f and n is determined from the linear relationship between $\log q_e$ and $\log C_e$. Isotherm adsorption was studied using data in Table 2. The results of the determination of the Langmuir and Freundlich adsorption isotherms are presented in Table 4.

Table 4. Parametric model of Langmuir and Freundlich adsorption isotherms

Temperature (K)	Langmuir isotherm			Freundlich isotherm		
	R^2	Q_0 (mg/g)	b_l (L/mg)	R^2	K_f	n
313	0.9694	20.8333	3.7209	0.8791	16.3192	3.9968
323	0.9916	19.5313	4.1967	0.9579	15.5776	4.7642
333	0.9998	20.4918	2.5026	0.9975	14.4810	3.6036

Table 4 shows that the Langmuir isotherm model provides a better correlation coefficient (R^2) than that of Freundlich. For that reason, the Langmuir model is used in this study. This may also justify that the surface of bagasse ash based silica aerogel is homogeneous.

3.6. Adsorption kinetics

The kinetic parameter is used to determine the speed of MB adsorption during the adsorption process based on contact time data. Kinetic adsorption model is determined using 15-90 minute-contact-time data. In order to determine the parameter it must be noted that the value of q_e and q_t is determined using the following equation:

$$q_e = \left(\frac{C_o - C_t}{M} \right) x V \quad (9)$$

Pseudo first order equation model is used to develop a curve of the relationship between time and $\log (q_e - q_t)$ so that k_1 value and adsorption capacity (q_e, cal) can be calculated using the following formula:

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2,303} t \quad (10)$$

The calculation of kinetics pseudo-second order is executed with the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \quad (11)$$

Table 5 presents the result of the calculation adsorption kinetic using the two models: pseudo first order and pseudo second order.

Table 5. Pseudo first and second order adsorption kinetic models

q_e (mg/g)	Pseudo first order model			Pseudo second order model		
	q_{ecal} (mg/g)	k_1 (min ⁻¹)	R^2	q_{ecal} (mg/g)	k_2 (g/mg.min)	R^2
15.658	1.0845	0.0352	0.9678	15.8983	0.0339	0.9999

Table 5 depicts the data that the value of the adsorption capacity resulting from pseudo-second-order model (q_{ecal}) is close to the value of the adsorption capacity at the time of the experiment (q_e) namely 15.8983 mg/g. This indicates that the adsorption process of methylene blue using silica aerogel can be well explained using the pseudo-second-order model. This statement is also justified by the fact that the correlation coefficient value (R^2) of the pseudo-second model is closer to 1 compared to that of pseudo-first order [8].

4. Conclusions

To sum up, the following points may be highlighted. First, the adsorption capacity of silica aerogel toward methylene blue is optimum at the 90 minute contact time reaching the figure of 15.658 mg/g. Second, silica aerogel's adsorption capacity toward methylene blue increases in line with the increasing of the initial concentration of the adsorbate. Third, the mechanism of the adsorption tends to follow the Langmuir isotherm adsorption model ($R^2=0.9998$) and pseudo-second-order model of kinetic adsorption with the calculated capacity of 15.8983 mg/g. Finally, the negative value ΔG° indicates that the adsorption process occurs spontaneously and exothermically as indicated by the negative value of ΔH° (-14.0914 kJ/mol).

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