Performance column adsorption of methylene blue using composite spent coffe ground-copper ferrites (SCG/CuFe$_2$O$_4$)

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Abstract. Composite Spent Coffe Ground-Copper Ferrites (SCG/CuFe$_2$O$_4$) synthesized by the method of precipitation. Copper nitrate, Ferri nitrate, SCG and sodium hydroxide mixed and stirred at 80$^\circ$C for 5h, then calcined at 600$^\circ$C for 2 h. The purpose of this research is to determine capacity adsorption SCG/CuFe$_2$O$_4$ to adsorb Methylene Blue (MB) with a column system. Approximately 0.5 g of SCG/CuFe$_2$O$_4$ were packed in to the column. Infusion tube filled with 250 mL MB 20 mg.L$^{-1}$ was adjusted to pH 10, streamed into the column with flow rate 0.8 mL/min and 1.2 mL/min. The results obtained show that the faster the flow rate, the adsorption capacity (q0) and Thomas constant (kTh) MB increase. The highest q0 and kTh values were obtained at a flow rate of 0.8 L / min at 80.13 mg/g, 0.0028 L/mg. min. Desorption of CuFe$_2$O$_4$ with 0.1 M HCl solution show with 3 times elution, all MB bound to the adsorbent can be removed.

1. Introduction

In the processing of coffee fruit into coffee beans produced by products in the form of 29% coffee pulp, 12% coffee husk, 1% coffee fiber [1],and for one ton coffee beans produces six hundred fifty kg of spent coffee grounds(SCG)[2] while Mussatto [3] reports that coffee entrepreneurs around the world annually produce six billion tons of SCG. Considering that the by-product waste from coffee is quite large, if it is not treated properly it will rot and pollute the environment.

The content of organic compounds, nitrogen, phosphorus and potassium in coffee SCG is quite high and very suitable to be used as vermicompost, soil amendment and the presence of metal binding groups like phenolic compound, tannin, caffeine and can be used as an adsorbent [4]. SCG has been used for adsorbing tetracycline [5], ion Ni$^{2+}$ [6], MB [7].

Recently, magnetic nanomaterial with nanosized pores and high surface area, have been studied as adsorbent for wastewater treatments. Anjali et al [12] reported that the magnetic coffee waste showed a high adsorption capacity for ion Pb$^{2+}$ at 25˚C was 41.15 mg/g. The equilibrium adsorption data fitted best with Langmuir isotherm model, and study showed the adsorption followed pseudo-second order kinetics indicating chemisorption. Man [13] report that adsorption capacity of composite nano zero valent iron-SCG (NZVI-SCG) is greater than the adsorption capacity of NZVI. The results of study show that the adsorption capacity of NZVI on ion Pb$^{2+}$ Cd$^{2+}$, As$^{3+}$, and As$^{5+}$ in aqueous solution are 173.3 mg/g,107 mg/g, 71.4 mg/g and 28.2 mg/g., while the adsorption capacity of NZVI-SCG on ion Pb$^{2+}$ are 937.9 mg/g, 643 mg/g for ion Cd$^{2+}$,134mg/g for ion As$^{3+}$ and 53 mg/g for ion As$^{5+}$. Dong et al
[14] using SCG to produce Fe-Biochar with pyrolysis method use of N₂ and CO₂. This adsorbent using removal arsenic in synthetic water at pH from 4 to 9, and the contact time was 6 h. The results showed that with increasing pH the adsorption capacity of Fe-biochar decreased. At pH 5, adsorption capacity of Fe-Biochar N₂ was 19 mg/g and at pH 8 are 4.9 mg/g, meanwhile for Fe-Biochar-CO₂ the adsorption capacity at pH 5 was 10 mg/g and at pH 8 are 4.8 mg/g. Results of comparative study, show that the adsorption capacity of Fe-Biochar N₂ is greater than Fe-Biochar CO₂. This is related to the surface area, where the surface area of Fe-Biochar N₂ are and surface area Fe-Biochar CO₂ are . Moreover, until now there is no reported study where magnetic coffee waste have been used for fixed bed column studies. Hence this study reports on the adsorption behavior of SCG-CuFe₂O₄ in a fixed bed column for removal of MB. The adsorption properties of MB including effect of flow rate and mass adsorbent were evaluated.

2. Method and Experiment

Composite Spent Coffe Ground-Copper Ferrites (SCG/CuFe₂O₄) were synthesized by a sol gel method. Copper nitrate, ferri nitrate, and citric acid mixed and stirred at 80°C for 60 min. Then add 2% (b/v) PVA and SCG to the solution and continuously stirred at 80°C for 24 h. After that, drying with oven. The dried powder was calcined in a muffle furnace at temperatures 500°C. The resulting product is characterized by SAA.

Column filled with granular SCG-CuFe₂O₄ as much as 0.5 g. Infusion tube filled with 250 mL MB 20 mg.L⁻¹ was adjusted to pH 10, passed through a column at flow rate 0.8 mL/min, 1.2 mL/min. Effluent were collected from the column exit at different time intervals and MB concentration were analyzed using spectrophotometer (Shimadzu 160A). Operation of the column was stopped when the ratio concentration MB after and before adsorption (Ce/Co) = 0.95. The relationship time with Ce/Co described with breakthrough curve.

In this research, two variables that can influence the adsorption process have been carried out, namely the effect of the adsorbent weight and the effect of the adsorbate flow rate. Two variations of weight were used to influence the weight of the adsorbent, namely 0.3 g and 0.5 g. The flow rates were varied at 0.8 mL/min and 1.2 mL/min and 14 L/min. In this condition, the concentration of MB dye used was 20 ppm with an adsorbent weight of 1.0 g. For a flow rate of 1.2 mL/min the MB flow was stopped at 120 min. Whereas for the flow rate of 0.8 mL/min the flow was stopped at 200 min, that is, when the MB concentration in the effluent was the same as the MB concentration in the influent.

The SCG-CuFe₂O₄ adsorbent containing MB, obtained from the adsorption results, was used for the desorption process. A total of 50 mg of adsorbent resulted from the adsorption was added to 20 mL of 0.1 M NaOH. Stirring with a magnetic stirrer 10; 20; 30; and 40 minutes, then filtered. Measure the absorbance with a UV-Vis spectrophotometer at λ = 660 nm.

3. Result and Discussion

3.1. Effect of flow rate

The results of the flow rate variation are shown as a breakthrough curve that illustrates the relationship between Ct / Co and t, where Ct is the MB in effluent concentration and Co is the MB in influent concentration. While t is the adsorption time. The results of the data obtained from the adsorption process are presented in a breakthrough curve. Below is a breakthrough curve for the effect of the flow rate. From the breakthrough curve, it can be seen that the shape of the curve gets steeper as the flow rate increases, because the time to achieve the breakthrough and exhaustion conditions is faster.

The faster the flow rate, meaning the faster the interaction time between the adsorbent and the adsorbate, this causes the qb and qe values to decrease with increasing flow rate speed. At the highest flow rate, MB flows faster so that its distribution between the adsorbent pores is not optimal. As a result, the effluent leaves the column before equilibrium occurs [6]. From these data, it can be concluded that the flow rate of 0.8 mL/min has a better adsorption capacity than the flow rate of 1.2
mL /min. This is because at a flow rate of 0.8 mL / min MB has a longer contact time with the adsorbent so that the distribution and balance between each adsorbent can be better reach.

![Flow rate curve](image1)

**Figure 1.** Flow rate curve (a) 0.8 mL /min (b) 1.2 mL /min

3.2. Effect Mass Sorbent

In the effect of the weight of the adsorbent, two variations of weight were used, namely 0.5 grams and 1.0 grams. In these conditions the MB concentration used was 20 ppm with a flow rate of 0.8 mL / minute. For 0.5 gram adsorbent weight MB flow was stopped at 160th minute. Meanwhile, for adsorbent weight 1.0 gram, MB flow was stopped at 240 minutes. The data obtained during the adsorption process is presented in the form of a breakthrough curve. Following are the breakthrough curves for the 0.5 g and 1.0 g adsorbent weights.

![Mass sorbent curve](image2)

**Figure 2.** Mass sorbent curve (a) 0.5 g (b) 1.0 g

In accordance with Figure 2 above, the more adsorbent used means the more amount of MB that can be absorbed, and the longer it takes for the adsorbent to adsorb the adsorbate until it is saturated. Likewise, the adsorption capacity at breakthrough and exhaustion conditions, the values of $q_b$ and $q_e$ increased with increasing adsorbent weight.

This means that it is heavy adsorbent 1.0 g indicates more active parts that bind to the adsorbate the better it is shown from the value of the large adsorption capacity. At the adsorbent weight of 0.5 g and
with the same flow rate, the MB does not have enough time to disperse into the adsorbent properly, so that the \( q_b \) and \( q_e \) values are smaller. From the breakthrough curve, it can be seen that the curve shape for the adsorbent weight of 0.5 g is steeper than the adsorbent weight of 1.0 g, which means that the time to reach the breakthrough condition is faster. From these data it can be concluded that 1.0 g of adsorbent weight has the ability to better distribute MB so that the adsorption process can be maximized.

3.3. Adsorption Kinetics Model

The Thomas kinetics model to study the heterogeneous adsorption process in a flowing system [7]. Thomas's kinetic model is expressed by the equation:

\[
\ln \left[ \frac{C_e}{C_t} - 1 \right] = \frac{k_{Th}q_0}{Q} - k_{Th}C_0t \quad \text{.........(1)}
\]

Where \( C_t \) is the concentration of effluent leaving the column (mg/L) at time \( t \), \( C_0 \) is the initial concentration before entering the column (mg/L), \( Q \) is the flow rate \( v \) (L/min), \( w \) is the mass of the adsorbent in the column (g), \( k_{Th} \) is the Thomas rate constant (L/min. g), \( q_0 \) is the adsorption capacity of the adsorbent (mg/g).

From the Thomas equation, the values for \( k_{Th} \) and \( q_0 \) are obtained. These two values are used to create a predictive breakthrough curve based on Thomas's adsorption theory. The following is the breakthrough curve of the experimental results and based on the results of calculations from the Thomas adsorption model. The \( k_{Th} \) and \( q_0 \) values of the experimental results are shown in Table 2 below.

| No | Variable | \( k_{Th}(\text{L/mg/min}) \) | \( q_0(\text{mg/g}) \) |
|----|----------|------------------|------------------|
| 1  | 0.8      | \( 4 \times 10^{-4} \) | 91               |
| 2  | 1.2      | \( 7 \times 10^{-4} \) | 66               |
| 3  | 0.5      | \( 4 \times 10^{-4} \) | 66               |
| 4  | 1.0      | \( 2 \times 10^{-4} \) | 99               |

It can be seen from Table 2 above, that the \( k_{Th} \) value is inversely proportional to \( q_0 \). The greater the \( k_{Th} \) value, the smaller the \( q_0 \) value. For the effect of adsorbent weight, the increase in the amount of adsorbent is proportional to the increase in the value of \( q_0 \). However, with the influence of flow rate, the faster the flow rate, the smaller the \( q_0 \) value. By using the \( k_{Th} \) and \( q_0 \) values that have been obtained, it is used to make a predictive breakthrough curve based on Thomas's adsorption theory. The following is the breakthrough curve from the experimental results and based on the calculation results according to the Thomas adsorption model. From the curve equation, there are only two adsorption that meet the criteria of the Thomas adsorption model, namely at a flow rate of 1.2 mL/min with an adsorbent weight of 1.0 g and at Flow rate of 0.8 mL/min with adsorbent weight 0.5 g, as shown in Figure 3 and Figure 4 below.
Figure 3. Curva breakthrough experimental results and prediction results with Thomas mode at a flow rate of 1.2 mL/min and adsorbent weight 1.0 g. (a) blue and (b) red Thomas's prediction results

3.4. Desorption Methylene Blue
From Figure 4 it can be seen that the amount of MB that is desorbed is very different significantly. The amount of MB that was desorbed was quite high and subsequently increased significantly. The amount of MB desorbed increased over time until it reached the maximum amount of MB desorbed at \( t = 50 \) minutes, 96% and did not change after that time. This shows that sodium hydroxide can be used for desorption of MB.

Figure 4 Effect of time on desorption MB

4. Conclusion
The experimental results show that in the breakthrough condition the increasing weight of the adsorbent, adsorption time, volume of adsorbate, so that the \( q_b \) and \( q_e \) values obtained are also greater. Optimal adsorption occurred at an adsorbent weight of 1.0 gram at a flow rate of 0.8 mL/min and concentration 200 ppm MB with \( q_b \) and \( q_e \) of 25.92 mg/g and 15.68 mg/g, respectively. Conversely, if adsorbate flow rate increases, the adsorption time, adsorbate volume, and the value of \( q_b \) and \( q_e \) will be smaller. The optimal adsorption occurred at an adsorbate flow rate of 0.8 mL/min at 1.0 gram of adsorbent weight and 400 ppm gram of MB with \( q_b \) and \( q_e \) of 25.92 mg/g and 15.68 mg/g, respectively. The Thomas adsorption model is suitable for the adsorbent weight conditions of 0.5 gram with a flow rate of 0.8 mL/min and a flow rate of 1.2 mL/min with an adsorbent weight of 1.0 gram.
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