Methylene Blue Removal Using Developed Material From Volcanic Ash Soils

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Abstract: Indonesia's textile industry has been increased dramatically in the last several years. As a tropical country, Indonesia provides an adsorbent material abundant in nature which can adsorb dyestuff. One of alternative adsorbent material available abundantly in Indonesia is volcanic ash soil. However, the capabilities of volcanic ash soil removing dyestuff in water were low. Therefore, the development of material is necessary to enhance the adsorption capacity. In this research, enhancing the adsorption ability of volcanic ash soil was done by adding alkaline solution with concentration of 0.5, 1.5 and 3.0 mol/L, respectively. The ability of developed materials from soil to adsorb methylene blue (MB) dye was tested in different adsorbent dose and contact time. The result showed that developed material had a higher adsorption capacity of methylene blue than volcanic ash soil. The optimum adsorption condition was obtained at 0.15 g of adsorbent dose for 24 hours of contact time where volcanic ash soil, A1, A2 and A3 were able to adsorb methylene blue dye (100 mg/L) with adsorption capacity of 5.72, 6.99, 6.90 and 6.16 mg/g, respectively. In addition, developing materials from soil also had better regeneration ability than soil through the fenton process.

Index Terms: adsorption, volcanic ash soil, developed material, regeneration, textile industry, methylene blue, waste management.

1 INTRODUCTION

Nowadays, the most promising industry in global market is textile [1]. Indonesia is one of country that has huge concern in developing the textile products for attracting international tourism. Increasing the textile products can cause greater used of dyes and produced high amount of undesirable dyestuff waste. Methylene blue dyes are categorized as one of the dyes in textile industry which contaminates the aquatic environment [2]. If dyestuffs waste are contained in aquatic system, it will produce many negative impact for environmental health because of their toxicity and difficult to be degraded by microorganism [3]. One of method that commonly applied for dye wastewater treatment is adsorption [4]. This method is easy to apply without needing a lot of solvents. There are many adsorbent materials which potentially adsorbed dyestuff waste with high adsorption capacity such as activated carbon [5] and composite material [6]. However, these materials are difficult to apply on an industrial scale because of the limitation of source. Therefore an alternative adsorbent material is needed with abundant availability in nature. In this research, volcanic ash soil was used as alternative adsorbent material for methylene blue removal considering that Indonesia have a lot this material with abundant availability. Volcanic ash soil commonly contained many negative charges which depends on ratio of silanol and aluminol group in this material [7]. The negative charge makes soil has the ability to adsorb methylene blue as cationic dye. However, the capabilities of volcanic ash soil to remove organic content in water are quite low [8], therefore, development of material is needed to enhance the adsorption capacity. Several parameters was included such as adsorbent doses and adsorption time.

2 EXPERIMENTAL SECTION

2.1 Materials

Volcanic ash soil materials were obtained from Bogor Agricultural University area without further purification. This soil was dried for one day to remove water content. All chemicals used were purchased from inorganic chemistry laboratory, Bogor Agricultural University.

2.2 Material Development Process

Materials development were conducted by mixing soil with alkaline solution (0.5, 1.5 and 3.0 mol/L) in a closed polypropylene vessel. The mixed was stirred for 1 hour and heated at 100°C for 24 hours. Solid phases obtained were rinsed for several times with destilled water after it was separated from liquid phases. The rinsing results were heated again at 100°C for 12 hours.

2.4 Adsorption Test

Methylene blue stock solution was prepared by diluting the standard methylene blue solution (500 mg/L). Before the adsorption test measured, the maximum wavelength of methylene blue dye was determined spectrophotometrically in range 400–700 nm using spectrofotometer UV-VIS.

2.4.1 Adsorbent Dose Effect

Adsorbent dose effect for methylene blue adsorption was investigated by mixing different mass of developed material (25, 50, 100, 150 and 200 mg) with 10 mL of dye (100 mg/L). The mixed-solution was shaked several times each hour for 24 hours to homogenize the solution. The liquid phase was separated and the methylene blue concentrations were analyzed using spectronic 20D at the maximum wavelength.

2.4.2 Time Adsorption Effect

The optimum adsorbent dose obtained was mixed with 10 mL of methylene blue solution (100 mg/L) for 30, 60, 180, 360 and 720 and 1440 minutes. Methylene blue concentration was determined after the adsorption process.

2.5 Material Regeneration

The most important parameter to apply adsorbent materials is their reusability. After adsorption process using optimum adsorbent dose (t=24 h), solid and liquid phases in solution were separated using centrifuge. About 1 mL of hydrogen
peroxide (6.5 mol/L) was mixed with the solid phase for 24 hours.

3 RESULT AND DISCUSSION

3.1 The Maximum Wavelength of MB
Before the adsorption process, the maximum wavelength of methylene blue solution was determined using methylene blue solution with concentration of 5 mg/L. The maximum wavelength obtained was 664 nm as shown in Fig. 1.

3.2 The Effect of Adsorbent Dose
One of important parameter for wastewater treatment using adsorption method is the amount of adsorbent dose. In this research, the effect of adsorbent dose was conducted to know the suitable amount of adsorbent that can adsorb methylene blue dye. This process was investigated in a test tube with ambient temperature for 24 hours of contact time. The adsorption efficiency (%) of dye was calculated using the following equation.

\[
\text{Adsorption efficiency} \, (\%) = \left[ \frac{(C_0 - C_e)}{C_0} \right] \times 100\%
\]

Where \(C_0\) is initial methylene blue concentration in solution (mg/L) and \(C_e\) is concentration of methylene blue after equilibrium state (mg/L). The effect of adsorbent dose for MB adsorption was showed in Fig. 2. The results explained that the use of A1 adsorbent about 25 mg was able to adsorb methylene blue dye in high adsorption capacity and no significant changed with the use of adsorbents as much as 50–200 mg (Fig. 3). However, the optimum adsorbent doses of volcanic ash soil, A2 and A3 were obtained at 150 mg with adsorption efficiency of 81.20, 97.76 and 87.44%, respectively.

3.3 The Effect of Contact Time
The different of adsorption time can provide information regarding the equilibrium state of the adsorbent material. The optimum contact time can be known by determining the adsorption capacity value of methylene blue in equilibrium state. The uptake of methylene blue was adsorbed onto the soil and developed material (\(q_e\) mg/g) was calculated according to following equation:

\[
q_e = \frac{V(C_0 - C_e)}{m}
\]
where $V$ is the volume of methylene blue solution (L) and $m$ is adsorbent mass (g). The relation between the adsorption capacity of methylene blue dye and the contact time is shown in Fig. 4. The adsorption curve for each adsorbent has a different adsorption rate for methylene blue dye. It was noted that the different alkaline concentrations showed a significant effect on the structure of the material surface and affects the active side.

![Figure 4. The relation between contact time and adsorption capacity of methylene blue](image)

The adsorption capacity of methylene blue using soil and A3 was increased with increasing the contact time from 30–60 minutes. After 60 minutes the adsorption of the dye showed nearly constant curve with slight changes in the adsorption capacity reflecting the equilibrium stage. Meanwhile, the adsorbent of A1 and A2 had a faster adsorption ability compared to soil and A3 and there were in a equilibrium state starting from 30–1440 minutes. It can be expressed that optimal conditions have been reached at 1440 hours of contact time for methylene blue adsorption. The uptake capacity of volcanic ash soil, A1, A2 and A3 were 5.72, 6.99, 6.90 and 6.16 mg/g, respectively for 1440 min.

### 3.4 Material Regeneration

The most important parameters for application of adsorbent materials is their regeneration ability. The regeneration of developed material was carried out by fenton reaction using hydrogen peroxide followed heating process. This is possibly because developed material from volcanic ash soil contains $\text{Fe}^{3+}$ ion from $\text{Fe}_2\text{O}_3$ [10]. The $\text{Fe}^{3+}$ ion can react with hydrogen peroxide to produce $\text{Fe}^{2+}$ ion and hydroxy radical. Then, it will be generated when $\text{Fe}^{2+}$ ions react again with hydrogen peroxide. Methylene blue molecules adsorbed on the surface of adsorbent material will be removed by hydroxy radical into MB molecular fragments, $\text{CO}_2$ and $\text{H}_2\text{O}$, therefore, the developed material can be regenerated through heating process. The effect of fenton reaction to the solution shown in figure 5.

![Figure 5. The effect of fenton reaction to the solution containing soil, A1, A2 and A3 (from left to right): (a) before and (b) after hydrogen peroxide is added](image)

In addition, the regeneration of A2 and A3 by fenton reaction occurs faster than soil and A1 because of the alkaline concentration effect. Regenerated material can also be used again to adsorb methylene blue dye.

### 4 Conclusion

Developing material from volcanic ash soil in order to enhanced the adsorption capacity of methylene blue dye has been successfully carried out by adding alkaline solution to the soil. The optimum condition for methylene blue adsorption was obtained at 150 mg for 24 hours. The adsorption capacities of soil, A1, A2 and A3 were 5.72, 6.99, 6.90 and 6.16 mg/g, respectively for 1440 min.

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### REFERENCES


