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Adsorption and Photodegradation of Methylene Blue by Allophane and Nanocomposite Bismuth Oxyiodide-Allophane

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This study examines the ability of allophane as an adsorbent and photocatalytic capability of nanocomposite bismuth oxyiodide (BiOI)-allophane in removal of methylene blue dye. Adsorption was performed by using 50 mg of allophane from volcanic soil of mount Gamalama. The adsorption results showed that the optimum contact time is 10 min with adsorption percentage 91.81%. The percentage of adsorption decreases with increasing contact time and reaches equilibrium at about in 120 min. The initial concentration of methylene blue has an effect on the adsorption percentage. This is evidenced by the increased adsorption percentage of 73.35, 78.78, 82.12, 87.81 %, respectively for concentrations of 20, 50, 80 and 100 ppm. The photodegradation test results showed an excellent photocatalytic ability of BiOI-allophane composites. Using direct sunlight for 45 min, the percentage of photodegradation is 99.46 %. Increased contents of allophane in BiOI-allophane nanocomposite increases the photocatalytic ability.

Keywords: Methylene Blue, Adsorption, Photodegradation, Allophane, Bismuth oxyiodide, Nanocomposite.

INTRODUCTION

The rapidly growing industrial development has an effect on the quality of the environment. In the process of industries produce pollutants that can degrade environmental quality. One of the environmental pollutants comes from dye waste of textile industry. Methylene blue is considered as carcinogenic, mutagenic and non-biodegradable because of the presence of benzene groups which is difficult and need a longer time for degradation [1-3]. Hence, it is necessary to decompose first before being discharged into waters [4,5].

The textile industry uses only about 5 % dye in the process, while the remaining 95 % will be wasted as dye wastes [6]. Several methods have been studied to overcome methylene blue contaminants, such as adsorption and photodegradation. Adsorption is the simplest and most frequently used method in industry because it is easy to operate and low cost [7,8]. The use of photocatalysts is also an effective method for decomposing the carcinogenic and non-biodegradable dyes [9,10].

Cipta *et al*. [11] have reported the separation of allophane from the volcanic soil of mount Gamalama volcano. The allophane from the volcanic soil of mount Gamalama is shaped like an irregular ball, with a constituent mineral in the form of silica-alumina and has surface of area 125.158 $m^2 g^{-1}$ [11,12]. Allophane is possible to use as an adsorbent because it has large surface area. The nanocomposite bismuth oxyiodide (BiOI)-allophane from the volcanic soil of mount Gamalama has the ability to absorb visible light [12]. Based on these findings, this study examines the ability of allophane and BiOI-allophane nanocomposite in the removal of methylene blue contaminants. Allophane will be used as an adsorbent in the methylene blue adsorption process while BiOI-allophane nanocomposite as a photocatalyst to decompose methylene blue.

EXPERIMENTAL

The adsorption process is carried out by adding 50 mg of allophane into various concentration of methylene blue (20, 50, 80, 100 and 200) ppm. The mixture was stirred for 45 min then separated the solution by using centrifugation. The solution was then measured using UV-visible spectroscopy. BiOI and nanocomposite BiOI-allophane are synthesized according to the reported procedures [12]. The photodegradation process was performed using methylene blue with a concentration of 20 ppm with a direct sun radiation time of 45 min. The pH of solution is allowed to correspond to pH of methylene blue solution. The results of photodegradation were then measured by UV-visible spectroscopy.

RESULTS AND DISCUSSION

Adsorption of methylene blue was performed by using allophane from Gamalama volcanic soil as an adsorbent,while the photodegradation process is carried out using BiOI-allophane composite under direct sunlight for 45 min. Table-1 shows the results of methylene blue adsorption onto allophane, based on variation in initial concentration of methylene blue.

TABLE-1
REMOVAL OF METHYLENE BLUE BY USING ALLOPHANE (VARIOUS METHYLENE BLUE INITIAL CONCENTRATION)

Initial concentration (ppm)	C_e (ppm)	C ads. (ppm)	Ads. (%)
20	5.3298153	13.4564644	73.35092
50	10.6068600	39.3931398	78.78628
80	14.3007920	65.4353562	82.12401
100	12.1899740	86.8073879	87.81003
200	77.0976250	118.2058050	61.45190

It is found that the percentage of adsorption increased when initial concentration increases. The percentage of adsorption then decreased to 61.45 % for an initial concentration of 200 ppm. The decrease in adsorption percentage is due to saturation of the allophane adsorbent.

The effect of contact time on the adsorption of methylene blue by allophane is shown in Table-2. The effect of contact time was tested by adsorption for 10, 30, 90,120 and 180 min. The optimum adsorption was shown at contact time of 10 min, *i.e.* 91.81 %. The percentage of adsorption decreased gradually from 30, 90, 120 min and remained constant at 180 min, respectively at 87.74, 85.96, 85.70 and 85.70 %. This means that methylene blue adsorption process in allophane occurs quickly followed by a slow desoption process. The adsorption process at contact time 120 min indicating the occurrence of equilibrium is shown by the constant adsorption percentage 85.70%. The amount of active site on the surface of the adsorbent is proportional to the surface area. When the active site on the surface of the adsorbent has been saturated by a certain amount of adsorbate then the addition of adsorption contact time can no longer increase adsorption and even tend to decrease. By using the adsorption data, adsorption isotherms were determined which resulted in compatibility with Freundlich isotherms. The methylene blue adsorption isotherm graph is shown in Fig. 1 with a value of R^2 = 0.99 which means that the adsorption process takes place on heterogeneous and multilayer surfaces.

The photodegradation of methylene blue using nanocomposite BiOI-allophane showed better results than adsorption. This is showed by the greater percentage of optimum degradation (99.46 %) (Table-3). Photodegradation process was done only by using direct sunlight for 45 min. The ability of BiOI to decompose photodegradation increases with increasing amount of allophane in nanocomposite (Fig. 2). The highest photocatalytic ability is shown by the nanocomposite with a total 1.5 g of allophane (99.46 %). This is because the presence of allophane increases the nanocomposite surface area. The percentage of photodegradation degradation by BiOI is lower than that of nanocomposite BiOI-allophane, which is attributed due to low absorption of BiOI. The presence of allophane enhances the nanocomposite absorption of methylene blue which ultimately increases the ability to degrade methylene blue. The photodegradation mechanism that occurs through two stages *i.e.*, methylene blue adsorption by allophane followed by decomposition by BiOI. The photocatalytic mechanism of BiOI to decomposed methylene blue under direct sunlight [13] takes place by following equations:

$$BiOI + h\nu \longrightarrow BiOI\ (e^- + h^+) \quad (1)$$

$$O_2 + e^- \longrightarrow O_2^{\bullet-} \quad (2)$$

$$O_2^{\bullet-} + e^- + 2H^+ \longrightarrow 2^{\bullet}OH \quad (3)$$

$$H^+ + O_2^{\bullet-} + {}^{\bullet}OH + \text{Methylene blue} \longrightarrow CO_2 + H_2O \quad (4)$$

TABLE-2
REMOVAL OF METHYLENE BLUE BY USING ALLOPHANE (VARIOUS CONTACT TIME)

Contact time (min)	C_e (ppm)	C ads. (ppm)	Ads. (%)
10	8.496042216	95.25065963	91.81078
30	12.717678100	91.02902375	87.74161
90	14.564643800	89.18205805	85.96134
120	14.828496040	88.91820580	85.70702
180	14.828496040	88.91820580	85.70702

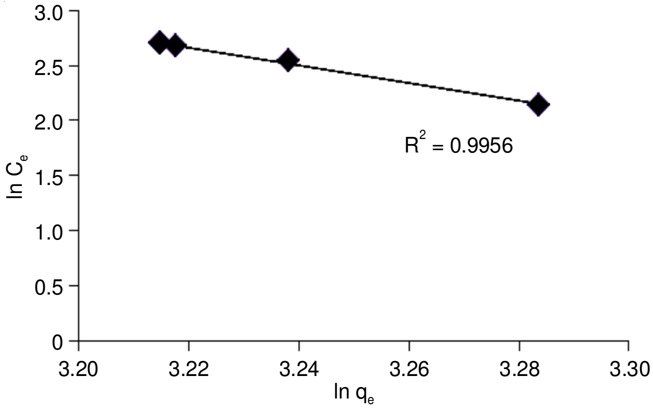

Fig. 1. Freundlich isoterm adsorption

TABLE-3
PHOTODEGRADATION OF METHYLENE BLUE

Sample	C_o (ppm)	C_e (ppm)	Degradation (%)
BiOI	20	0.512928760	97.43536
0.25 g Allo/BiOI	20	0.249076517	98.75462
1.00 g Allo/BiOI	20	0.206860158	98.96570
1.50 g Allo/BiOI	20	0.106596306	99.46702

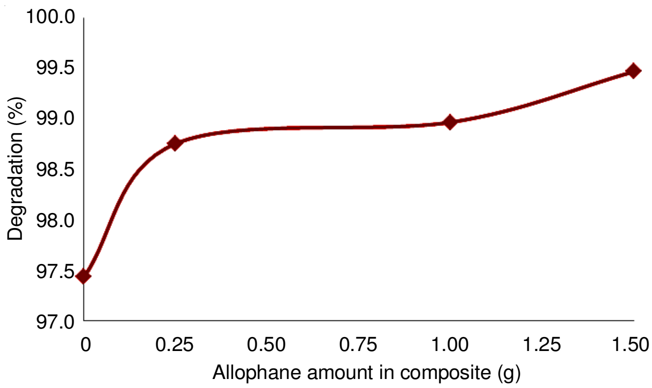

Fig. 2. Effect of amount of allophane on photodegradation of methylene blue

Conclusion

Allophane has showed highest methylene blue adsorption (91.81 %) at initial concentration of 20 ppm and 10 min contact times. The increase in the initial concentration of methylene blue affects the percentage of adsorption. Nanocomposite BiOI-allophane can work as photocatalysts to decomposed methylene blue under direct sunlight. The highest percentage of degradation (99.46 %) was acheived by nanocomposite BiOI-allophane containing 1.5 g of allophane.

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