Preliminary study of dye removal from aqueous solution using elephant dung activated carbon

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Abstract. Dyes are widely used in various industries. It is significant to remove dye from wastewater before discharge. Adsorption onto activated carbon is more than beneficial than the other traditional methods as a result of its high adsorption capacity for coloured particle. The main objective of this study is to prepare activated carbon from elephant dung (EDAC). The adsorption performance of EDAC was studied by conducting batch adsorption experiments. The adsorption data are correlated with Langmuir and Freundlich under various conditions methylene blue (MB) concentration and contact time. The optimum dosage of EDAC was found to be 100 mg. EDAC adsorption was fitted with Langmuir model. The calculated maximum adsorption capacity was 18.98 mg/g. A dimensionless separation factor (RL) indicated a favourable adsorption of MB onto EDAC. The study indicates that EDAC could be employed as a cost-effective alternative adsorbent for removing MB from wastewater streams. EDAC also was cheap, more eco-friendly and effective waste utilization.

1. Introduction

Dyes are widely used in various industries, for example, textile, paper and leather to produce its colour properties [1]. The increasing existence of dyes in the aqueous bodies is one of the most significant environmental issues [2]. The textile industries discharged the highest amount of dye effluent (54%), which found more than half of dye effluents being in the environment around the world [1]. Dyes also affect photosynthetic activity owing to reduced light penetration, leading to disturb the ecosystem [2]. Dye effluents existing in water sources are undesirable as vital water for animals and humans’ daily activities [3]. Therefore, it is important to apply some colour removal treatment methods to decrease the harmful effects before releasing the dye effluents into water bodies. There are the dye treatment from wastewater methods including anaerobic decolourisation, chemical oxidation, reverse osmosis, ion exchange, adsorption and biological treatment methods [4]. Among these techniques, adsorption onto activated carbon has been demonstrated to be the most effective
process to remove colour because of its initial cost, uncomplicatedness of design, easy operation and insensitivity to toxic constituents [5]. Adsorption onto activated carbon is more than beneficial than the other traditional methods as a result of its high adsorption capacity for both organic and inorganic substrates, especially, for coloured particle [4]. Nevertheless, application of commercial activated carbon for colour adsorption has some limitations due to its high cost and regeneration problem. The challenges have been explore some effective, cheaper and easily available alternatives adsorbents. Previous studies demonstrated alternatives low cost activated carbons prepared from natural products such as sun flower stalks, corn cobs and barley husk, rice husk, modified saw dust, peanut hulls, peanut shells, pineapple stem and orange peel [6]. These activated carbons derived from various natural materials are broadly used as adsorbents because of their high adsorption capacity, large surface area and micro-porous structure, which a result of their chemical and thermal stability.

Elephant dung is available in large quantities in the Thai Elephant Conservation Center (Lampang province, Thailand). Elephant dung is used to produce biogas, paper, paper products and fertilizer. However, it is encounter elephant dung to become extremely valuable products. Therefore, use of elephant dung as a bio-sorbent will undertake to verify to be the potential utility of low-cost activated carbon from elephant dung waste for dye treatment from aqueous solution.

In this study, elephant dung waste was chosen as the raw material to manufacture activated carbon by carbonization and chemical activation processes. The adsorption performance of elephant dung activated carbon was studied by synthesized wastewater. The adsorption data were associated with the Langmuir and Freundlich models.

2. Method

2.1 Preparation of elephant dung activated carbon

Elephant (Elephas maximus) dung was collected from Thai Elephant Conservation Center, Lampang province, Thailand. The dung was dried by sunlight for a week and dried in a hot air oven at 103 °C for 24 hours. The preparation method was modified from the previous study [4]. The dried material was as activated by concentrated sulfuric acid (36 N) (1:2) for 12 hours. The acid was then detached by repeatedly washing with a large quantity of deionized water. It was then dried in a hot air oven at 103 °C for overnight. The elephant dung activated carbon (EDAC) was ground and sieved with apertures of 250 µm and stored in an air tight container for adsorption studies.

2.2 Preparation of dye solution

The adsorption studies were obtained with color of methylene blue (MB), supplied by Fisher Scientific and used without further purification. This dye has an empirical formula of C_{16}H_{18}ClN_{3}O_{3}S, molecular weight of 373.896 g/mol. The dye solution of 1000 mg/L was prepared from methylene blue for single solution which was dissolved in deionized water and adjusted to 1000 mL for the concentrated stock solution. The concentration of MB was analysed by Hitachi U-2900 spectrophotometer using wavelength of 665 nm for measuring its colour concentrations.

2.3 Equilibrium studies and effect of dye concentration, contact time and EDAC dosages on dye removal

Batch adsorption experiments were carried out at room temperature by varying the different initial dye concentrations (10, 20, 30 and 40 mg/L). The dye solutions of 50 mL were obtained to a series of 250 mL Erlenmeyer flasks with a desired dose of adsorbent (EDAC). The batch experiment was conducted without any pH adjustment. The Erlenmeyer flasks were then shaken by incubating shaker at a constant agitation speed (100 rpm). The samples were withdrawn from the shaker at determined time intervals, and the supernatant liquid portions were centrifuged by centrifuge machine at 8000 rpm for 20 minutes and analysed for remaining dye concentration using spectrophotometer. For the adsorbent dosage study, 0.02-0.10 g of EDAC was introduced into a series of 250 mL Erlenmeyer flasks.
containing 50 mL of different concentrations (10, 20, 30 and 40 mg/L) of MB solution. The samples were withdrawn, centrifuged and estimated for remaining dye concentration spectrophotometrically.

The extent of MB removal by EDAC was calculated to fit with the Langmuir and Freundlich model as shown in equation (1) and in equation (2), respectively [7, 8].

\[
1/Q_e = (1/K_Lq_m)1/C_e+1/q_m
\]  

(1)

Where; \(Q_e\) is the uptake of dye, \(C_e\) is the concentration of dye in wastewater, \(q_m\) represents the mass of dye adsorbed over mass if adsorbent for a complete monolayer, \(K_L\) is the Langmuir constant, and \(C_e\) is the equilibrium concentration

\[
Q_e = K_F C_e^{1/n}
\]  

(2)

Where; \(Q_e\) is the uptake of dye, \(C_e\) is the concentration of dye in wastewater, \(K_F\) is represents the Freundlich constant related to adsorption capacity and \(n\) is the Freundlich constant related to adsorption intensity (\(n>1\)). The linearized form of Freundlich isotherm can be written as in equation (3)

\[
\log Q_e = \log K_F + (1/n)\log C_e
\]  

(3)

3. Result and discussion

Batch equilibrium studies

Considering on the R² values achieved, the goodness-of-fit for the batch equilibrium studies to the isotherm models found that the R² of Langmuir model is more than that of Freundlich model according to R² at 0.9894 and 0.9411, respectively, as shown in Figure 1. For Langmuir isotherm, the essential feature of Langmuir isotherm model can be expressed in terms of a dimensionless separation factor (\(R_L\)), given by the following equation [9]

\[
R_L = 1/(1+b_1C_0)
\]  

(4)

where, \(C_0\) is the initial dye concentration (mg/L). \(R_L\) indicates the type of isotherm to be either unfavourable (\(R_L>1\)), linear (\(R_L=1\)), favourable (0<\(R_L<1\)) or irreversible (\(R_L=0\)). In this study, the \(R_L\) values were found in the range of 0.019-0.072, which lie between 0 and 1 for all dyes, hence suggesting a favourable adsorption of dyes onto EDAC. The Freundlich isotherm constant (mg/g) (\(K_F\)) and adsorption intensity (\(n\)) were 9.028 and 2.490, respectively. Since the \(1/n\) value, it was showed that \(1/n\) being greater than 1 one indicates cooperative adsorption [10] and \(1/n\) is a heterogeneity parameter, if \(n\) lies between one and ten, this mark a favourable sorption process [11] as shown in Table 1.
Figure 1. (a) Langmuir adsorption isotherm and (b) Freundlich adsorption isotherm of MB dye removal using EDAC

Table 1. Langmuir and Freundlich adsorption isotherm constants and regression correlation coefficients ($R^2$) for MB dye

| Isotherm model | $R^2$ |
|----------------|-------|
| Langmuir       | 0.9894|
| $K_L = 1.279$  |       |
| $q_m = 18.975$ |       |
| Freundlich     | 0.9411|
| $K_f = 9.028$  |       |
| $n = 2.490$    |       |

Effect of initial MB concentration, EDAC dosage and contact time

The ability of EDAC to remove MB at different initial concentrations (10-40 mg/L) is presented in Figure 2. After 120 minutes contact time, no difference was recorded in the amount of MB uptake; to the contrary, a decrease was observed in removal, i.e. desorption was occurring at longer contact times. As higher concentrations resulted in increased removal efficiency, this suggests an association with higher availability of active binding sites present on the surface of EDAC [7].
The effect of EDAC dosage (20 -100 mg), it is clear from the results that removal efficiencies of dyes increases with increase in the dosage of EDAC and reaches saturation after a particular amount of EDAC for all the dyes studied as shown in Figure 3. This is caused by the fact that, increase in adsorbent dose, increases the number of adsorption sites on the surface of the adsorbent [12]. It is noticeable that adsorbent dose increasing, the removal efficiency of EDAC increases; however, the removal efficiency was low with increase in initial dye concentrations from 10 mg/L to 40 mg/L. This is due to the reason that adsorption sites remain unsaturated during the adsorption process [13-14]. The optimum dosage of EDAC was found to be 100 mg.

4. Conclusion
In this study, a preliminary study of the utility of elephant dung activated carbon (EDAC) for methylene dye found that EDAC could be effectively used as a low cost adsorbent for the removal of colour and dye molecules from aqueous solution. The optimum dosage of EDAC was found to be 100 mg. Furthermore, EDAC adsorption was fitted with Langmuir model. The calculated maximum
adsorption capacity was 18.98 mg/g. A dimensionless separation factor \((R_L)\) indicated a favourable adsorption of MB onto EDAC. Further studies should focus on effect of pH and temperature on dye removal. Economic analysis should also be completed in order to evaluate the feasibility of its use in the large-scale community.

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Acknowledgments
The authors gratefully acknowledge the financial support provided by Thammasat University under the TU New Research Scholar, Contract No.8/2561. We are also grateful to Thai Elephant Conservation Center in Lampang province, Thailand, who provided elephant dung for the study. We are thanks to Environmental Health Laboratory, School of Health Science, Mae Fah Luang University, Thailand to permit us to use laboratory facilities. In addition, we are grateful for TU Research Fund and Faculty of Public Health, Thammasat University that provided the financial support for our research presentation.