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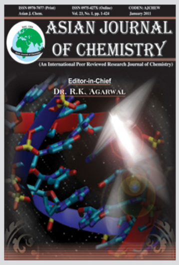

Application of Durian Peel (*Durio zibethinus Murray*) for Removal of Methylene Blue from Aqueous Solution

SIEW-TENG ONG[1,*], PEI-SIN KENG[2], MENG-SEAP VOON[3] and SIEW-LING LEE[4]

[1]Department of Chemical Science, Faculty of Science, Universiti Tunku Abdul Rahman, Jalan Universiti, Bandar Barat, 31900 Kampar, Perak, Malaysia
[2]Department of Pharmaceutical Chemistry, International Medical University, No. 126, Jalan 19/155B, Bukit Jalil, 57000 Kuala Lumpur, Malaysia
[3]Department of Science, Faculty of Engineering & Science, Universiti Tunku Abdul Rahman, Jln Genting Kelang, Setapak, 53300 Kuala Lumpur, Malaysia
[4]Ibnu Sina Institute for Fundamental Science Studies, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia

*Corresponding author: Fax: +60 54661676; E-mail: ongst@utar.edu.my; ongst_utar@yahoo.com

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The sorption characteristics of durian (*Durio zibethinus Murray*) peel in the removal of methylene blue from aqueous solutions under batch and continuous flow conditions were studied. The limitation in batch studies can be overcome by carry out flow tests using columns to obtain design models that would be applicable to commercial systems. Two well-known isotherm models, Langmuir and Freundlich were chosen for the fitting of experimental data. The sorption process conformed to Langmuir isotherm with the maximum sorption capacity of 49 mg/g at 25 ºC. Mathematical models were employed to analyze and explain experimental data obtained. Increase in the column bed depth yielded longer service time while increase in influent concentration and flow rate resulted in faster breakthrough.

Key Words: Adsorption, *Durio zibethinus Murray*, Methylene blue, Batch study, Column study.

INTRODUCTION

The main industrial sources that generate coloured waste include textile, ceramic, paper, printing and plastic industries. Due to the large amount of dyes used in the process of washing and finishing coloured products, the production of effluents contaminated with dyes is unavoidable. However, if the waste-water containing dye is untreated and released to the natural waterways, it would pose a serious threat to the natural aquatic ecosystem. Discharge of coloured effluents not only perturb the photosynthetic activity, but might also be toxic and carcinogenic to the aquatic life[1,2].

Conventional technologies for colour removal from industrial effluents include biological treatment, coagulation, ozonation, electrochemical processes, nanofiltration and activated carbon adsorption[3]. Amongst all, the sorption process by activated carbon is one of the most efficient techniques but drawback such as high capital and problems with the spent carbon limits its large-scale application.

Thus, a cost saving method of removing dye from waste-water is to take advantage of inexpensive adsorbent which does not require any expensive pretreatment[4]. Waste products from certain industrial and agricultural operations, natural materials and biosorbents are considered to be an economical alternative for dye removal in wastewater[5].

Durian (*Durio zibethinus Murray*) is a very important tropical fruit crop in Southeast Asia. Durian, which only one third of it can be consumed, would produce a lot of solid waste, especially during the durian season. Therefore, it is of great interest to utilize this waste material as an economical sorbent for dye removal. In this paper, we report the results obtained from isotherm and column studies on the removal of methylene blue using durian peel (DH).

EXPERIMENTAL

Sorbates: The cationic dye methylene blue (CI = 52015) was purchased from Sigma-Aldrich Chemical Company and used as received without further purification. Synthetic dye solution of methylene blue with the concentration of 1000 mg L^{-1} was prepared as stock solution and subsequently diluted when necessary.

Sorbents: durian peel used throughout the experiment was collected from a local supermarket in Kuala Lumpur, Malaysia. The durian peel collected was washed several times with tap water to remove any dirt or durian's flesh. The durian peel was cut into tiny pieces which are *ca.* 5-8 cm long and then sun dried. The dried durian peel was then ground to pass through a 1 mm sieve and used for the adsorption studies.

Sorption isotherm: Equilibrium studies were performed by agitating 0.1 g of durian peel with 20 mL of dye solution at various methylene blue concentrations (ranging from 25-200 mg/L). The amount of dye adsorbed at equilibrium, can be calculated with the equation:

$$q_e = \frac{C_o - C_e(V)}{W} \quad (1)$$

where: C_0 = initial dye concentration (mg/L), C_e = equilibrium dye concentration (mg/L), V = volume of dye used (mL), W = weight of sorbent used (g).

Control experiments without sorbent was carried out to ascertain that the sorption was by the sorbent and not the wall of the container.

Column study: Column studies were performed using a glass column of 1.0 cm internal diameter. The flow rate of the eluant was controlled by using a peristaltic pump.

Effect of bed-depth: The effect of bed depth on the methylene blue sorption was tested by packing the column to 2.5, 6.0 and 9.0 cm, corresponding to 0.5, 1.5 and 2.0 g of durian peel, respectively, while maintaining the influent concentration at 2.5 mg/L with the flow rate of 10 mL/min.

Effect of flow rate: The flow rate of the eluant was varied from 7, 10 and 15 mL/min while the bed depth was fixed at a height of about 6.0 cm using 1.5 g of durian peel. The feed concentration of methylene blue remained constant at 2.5 mg/L.

Effect of influent concentration: The effect of different influent concentrations on the breakthrough was studied using dye concentrations of 1.0, 2.5 and 5 mg/L. The column was packed to a height of about 6.0 cm using 1.5 g of durian peel. The flow rate was maintained and regulated at 10 mL/min.

Techniques: For both studies, the dye concentrations were analyzed using a Perkin Elmer Lambda 35 UV-VIS spectrophotometer. All measurements were made at the wavelength corresponding to maximum absorption for methylene blue, λ_{max} = 664 nm. Dilutions were carried out when measurement exceeded the linearity of the calibration curve.

RESULTS AND DISCUSSION

Sorption isotherm: Sorption isotherm is an important parameter because it shows how the adsorption molecules distribute themselves between the liquid and solid phase when the adsorption process reaches an equilibrium state. The equilibrium data of the sorption of methylene blue was fitted into both Langmuir and Freundlich equations. The Langmuir and Freundlich linear plots of methylene blue-durian peel systems are shown in Figs. 1 and 2, respectively. The Langmuir isotherm can be represented in the equation below:

$$\frac{C_e}{q_e} = \frac{1}{Q_o K_L} + \frac{C_e}{Q_o} \quad (2)$$

whereas the linear form of Freundlich isotherm model can be represented as:

$$\log q_e = \frac{\log C_e}{n} + \log K_f \quad (3)$$

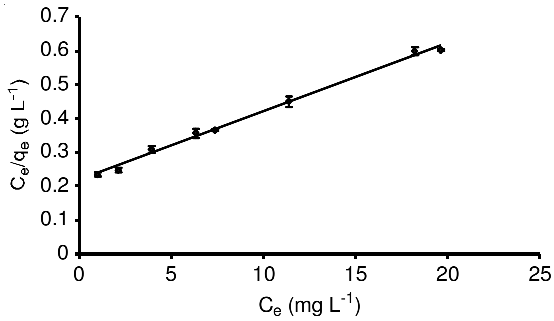

Fig. 1. Langmuir isotherm on sorption of methylene blue by durian peel

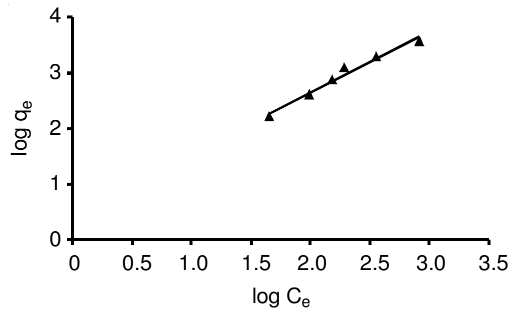

Fig. 2. Freundlich isotherm on sorption of methylene blue by durian peel

where C_e = equilibrium liquid phase dye concentration (mg L^{-1}), q_e = amount of dye adsorbed at equilibrium (mg g^{-1}), Q_o = maximum adsorption capacity (mg g^{-1}), K_L = adsorption equilibrium constant (L mg^{-1}), n = Freundlich constant for intensity and K_f = Freundlich constant for adsorption capacity. The straight line plot (Fig. 1) suggests the applicability of Langmuir isotherm which assumes there is monolayer coverage and constant sorption energy on the sorbent surface.

A comparison study on the maximum adsorption capacity of methylene blue onto various low-cost sorbents[6-11] was compiled and shown in Table-1. Amongst all, the activated carbon prepared by several low-cost sorbent has been shown to be the most efficient sorbents in removing methylene blue. However, this method still suffers from several drawbacks such as relatively high operating costs and problems with regeneration of exhausted carbon. Although durian peel do not possess high sorption capacity as compared to activated carbon, they are, however, still capable to remove an appreciable amount of methylene blue. Besides, durian peel is considerably cheaper and therefore serves as an attractive alternative for the removal of dyes in solution.

TABLE-1
COMPARISON OF THE SORPTION CAPACITY OF MB ONTO VARIOUS LOW-COST SORBENTS

Sorbent	Maximum sorption capacity, q_0 (mg/g)	Author
Bamboo (AC)	454	Hameed *et al.*[6]
Coconut husk (AC)	434	Tan *et al.*[7]
Vetiver roots (AC)	423	Altenor[8]
Castor seed shell	158	Oladoja *et al.*[9]
Rice husk	41	Vadivelan and Kumar[10]
Hazelnut shell (AC)	8.8	Aygun *et al.*[11]
Apricot stone (AC)	4.1	Aygun *et al.*[11]
Walnut (AC)	3.5	Aygun *et al.*[11]
Almond shell (AC)	1.3	Aygun *et al.*[11]
Durian peel	49	Present study

The Freundlich isotherm assumes that as the adsorbate concentration increases so does the concentration of adsorbate on the sorbent surface. This expression is characterized by the heterogeneity factor, n and the Freundlich isotherm can be used to describe heterogeneous surface with a non-uniform distribution of heat adsorption over the surface. A graph of log q_e *versus* log C_e was plotted (Fig. 2). The K_F and n values were calculated to be 2.625 and 0.907, respectively. The correlation coefficient, R^2 value is 0.9885. The n value obtained shows that the adsorption process is favourable[12].

Both Langmuir and Freundlich models appear to provide reasonable fittings for the sorption data of methylene blue on durian peel. Applicability of both isotherms to sorption of dyes by agricultural wastes, activated carbons prepared from wastes and treated spent bleaching earth have been reported previously[13-17].

Effect of bed depth: Effect of bed depth on the breakthrough curves of methylene blue is depicted in Fig. 3. The breakthrough curve shifted to the right as the bed depth increase from 2.5-9.0 cm (Fig. 3) which means that the breakthrough time increases as the bed depth increases. An increase in bed depth increases the surface area of the biosorbent which provides more binding sites for the adsorption[18,19]. Besides, a higher bed depth will also increases the contact time of methylene blue with durian peel in the column and resulted in higher removal efficiency. Similar trend was reported for the adsorption of reactive black 5 by polysulfone-immobilized *Corynebacterium glutamicum*[20], dye from textile wastewater in a fixed-bed column by surfactant modified zeolite[21] and adsorption of Congo red by EDA rice husk[7]. The BDST model states that bed-depth and service time of a column bears a linear relationship. This model ignores the intraparticle mass transfer resistance and external film resistance which means the dye is adsorbed onto the surface of the sorbent directly. These assumptions enable the BDST model to provide useful modeling equations for the changes in the system parameters[22]. The BDST model is express as:

$$t = \frac{N_o}{C_o U} Z - \frac{1}{kC_o} \ln\left(\frac{C_o}{C_t} - 1\right) \quad (4)$$

where t = service time to breakthrough (min), N_o = sorption capacity (mg/g), C_o = initial dye concentration (mg/L), C_t = effluent concentration (mg/L), U = linear flow rate (cm/min), Z = bed depth (cm), k = rate constant of sorption (L/mg min).

The sorption capacity, N_o and the rate constant, k was calculated from the slope and y-intercept of the BDST plot, respectively and the results are presented in Table-2.

TABLE-2
BDST CONSTANTS

C_t/C_o	N_o	k	R^2
0.1	33.34	0.031	0.9193
0.2	57.32	0.011	0.8978

From the values, it is notice that as the C_t/C_o value increases, the N_o value increases, whereas the k value decreased. A similar trend was reported by Han and co-workers[4] in the adsorption of Congo red by column mode using rice husk.

Effect of flow rate: Effect of flow rate on the breakthrough curves of methylene blue are shown in Fig. 4. The highest flow rate, 15 mL/min shows an earlier breakthrough time, whereas the lowest flow rate 7 mL/min shows a longer retention time of dye in the sorbent before the sorbent is

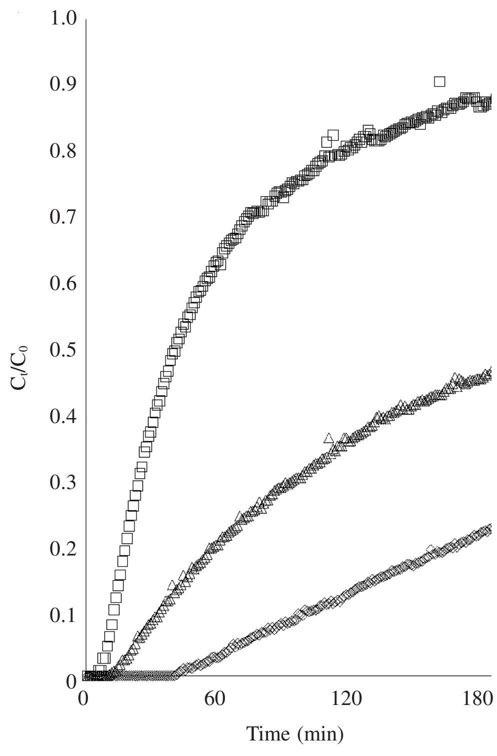

Fig. 3. Effect of bed depth on the breakthrough curve

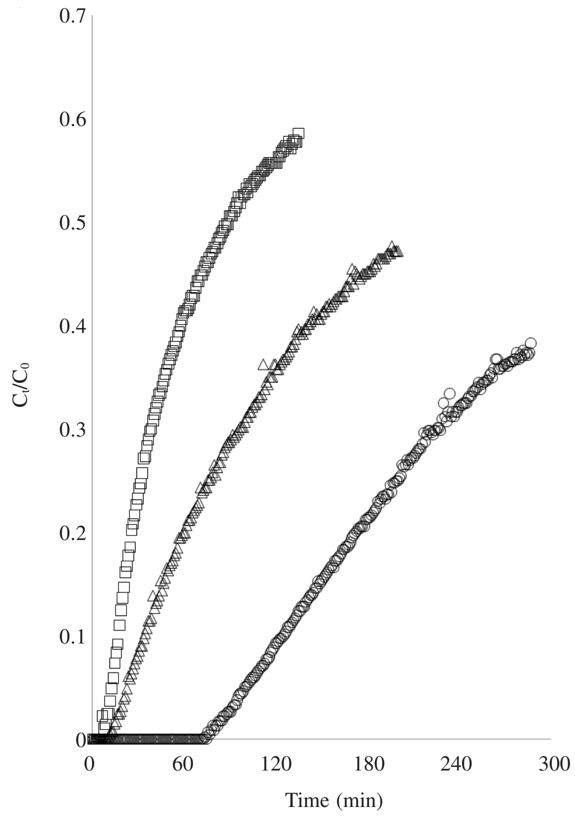

Fig. 4. Effect of flow rate on the breakthrough curve

exhausted. This phenomenon can be explained by the insufficient residence time of dye molecules in the packed column which will lead to a decrease in the diffusion rate of the solute into the pores of the durian peel[18].

Mathematical modeling: The experimental data obtained from the effect of flow rate was used to calculate the column performance and applied to Clark mathematical model, which incorporates the Freundlich equation. The equation of the Clark model is:

$$\frac{C_t}{C_o} = \left(\frac{1}{1+Ae^{-rt}}\right)^{1/n-1} \quad (5)$$

where: C_t = effluent concentration at time t (mg/L), C_o = influent concentration (mg/L), A = Clark equation constant, r = Clark equation constant (min^{-1}), n = Freundlich constant.

For a particular adsorption process on a fixed bed, the constants A and r can be determined by using the non-linear regression analysis of the Clark model to predict the breakthrough curve. Fig. 5 shows the predicted and experimental breakthrough curves obtained at various flow rates using Clark model. As depicted in Fig. 5, deviation was observed at higher flow rate. By using the same model, the column performance was evaluated. Form the calculated values obtained, flow rate appeared to have a great effect on the breakthrough of methylene blue, whereby a higher percentage of methylene blue removal was observed at slower flow rate.

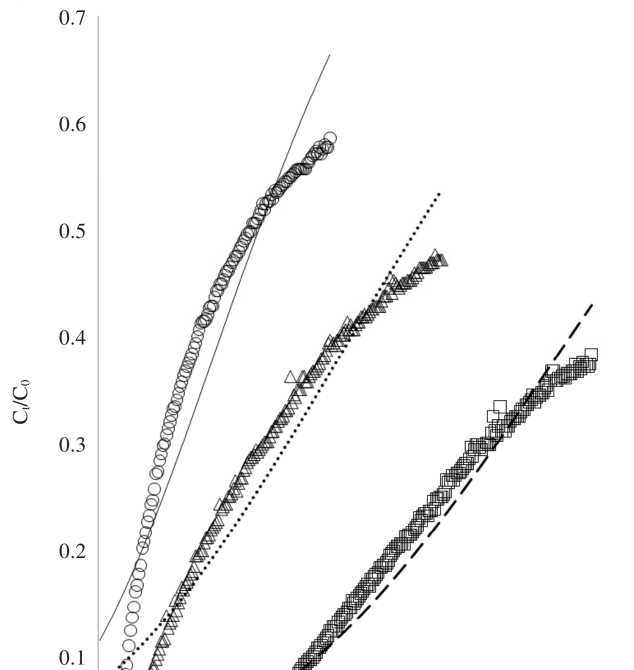

Fig. 5. Comparison of experimental and Clark model predicted breakthrough curves

Effect of influent concentration: Effect of influent concentrations on the breakthrough curves of methylene blue are shown in Fig. 6. The breakthrough curve was shifted to the right side of the graph as the concentration decreases. A sharp breakthrough curve was obtained at a higher dye concentration because as the dye concentration increases, the sorption sites experience a higher exhaustion rate. Similar trend was observed in the breakthrough point of the adsorption of textile wastewater onto modified zeolite[23].

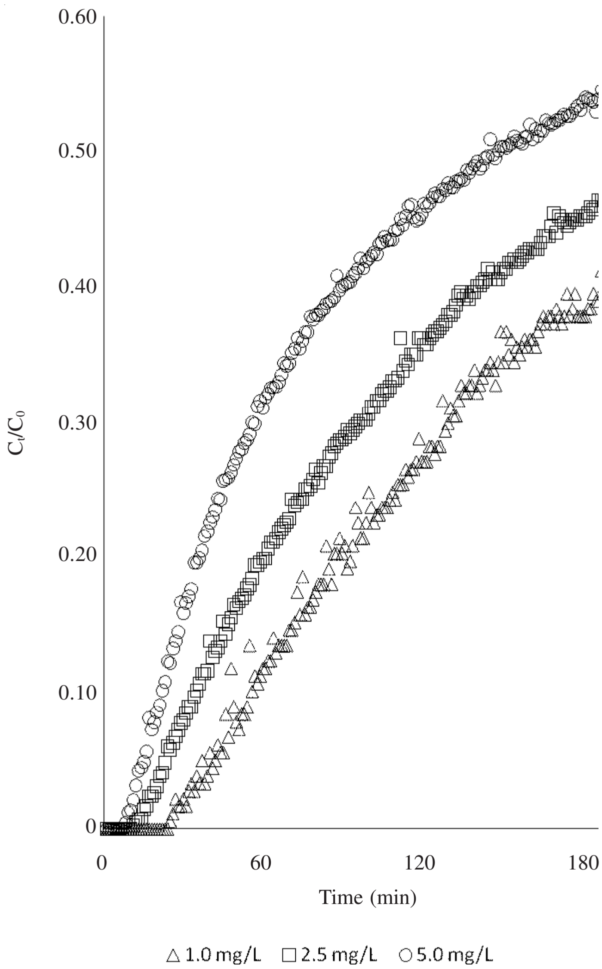

Fig. 6. Effect of influent concentration on the breakthrough curve

Conclusion

Durian peel was found to be a good low-cost sorbent in the removal of methylene blue from aqueous solution. The isotherm study showed that equilibrium sorption data of methylene blue on durian peel conform to both Langmuir and Freundlich isotherm models. Based on the Langmuir isotherm analysis, the maximum sorption capacity was determined to be 49 mg/g. In column studies, the column performance was found to be bed-depth, flow rate and influent concentration dependent. Generally, decreasing influent concentrations and increasing bed depths increased the service time of the column. The column capacity was evaluated using BDST model and the plot generated a straight line but with some deviation. The flow rate data was fitted into the Clark model and results showed that a lower flow rate yielded a higher percentage removal of methylene blue.

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