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Original Research Paper

Removal of Methylene Blue from Dye Wastewater Using River Sand by Adsorption

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ABSTRACT

Removal of methylene blue (MB) from aqueous solutions by river sand using batch and column techniques was investigated. It was observed that the maximum removal of MB was achieved at pH 4, 45 minutes contact time and 500 g/L dosage adsorbent river sand. Adsorption data were better fitted to the Langmuir isotherm. Pseudo second-order kinetics was most suitable to explain the kinetic study. The removal of methylene blue by column adsorption of river sand was ranged between 29.01% and 99.99%. It was found that the adsorption of methylene blue by river sand was more conformed to the model Thomas. In different flow rates study, flow rate of 10 mL/min in the column adsorption can better remove the methylene blue. This study shows that the river sand cannot undergo desorption.

INTRODUCTION

Global freshwater quality is declining due to anthropogenic activities and this is particularly true for the discharge of pollutants from various industries to the water bodies. One of the main sources of water pollution is from the dyes production industries and other industries associated with dyes and pigments (Sharma & Kaur 2011).

Dyes are widely used in industrial sectors such as textile, electroplating, printing, etc. Globally, the total use of dyes in textile industries is more than 10^7 kg/year and 90% of dyes are used in fabric manufacturing. This causes more than 1000 t/year of dyes released by the textile industries worldwide (Rastogi et al. 2008). The dyes released by industries poses a significant harm to the environment by polluting freshwater ecosystems, thus can cause serious impacts on human health and aquatic ecosystem (Ghaedi et al. 2013). Dye is not easily removed by conventional water treatment processes due to its complex molecular structure (Kushwaha et al. 2014). Many methods and treatment processes such as coagulation-flocculation, electrochemistry and adsorption are used to remove dyes from effluent industries. Adsorption is a simple model, low-cost and efficient method that is widely used in dye removal from water (Han et al. 2011).

One of the most widely used adsorbents is activated carbon due to its high adsorptive properties. However, activated carbon is not easily and economically available because of its expensive cost that hinders its application at a large scale (Özacar & ķengil 2006, Rafatullah et al. 2010). Therefore, many studies have been conducted to find out inexpensive alternative adsorbent (Rafatullah et al. 2010). This paper aims to determine the river sand as a potential low-cost and easily available adsorbent in removing the MB from aqueous solution. The adsorption by river sand was compared with sea sand and desorption of used river sand was also investigated.

MATERIALS AND METHODS

Materials: River sand used as adsorbent for dyes treatment was collected from Sungai Semenyih and BaganLa-lang, respectively. Nitric acid and sodium hydroxide were used to adjust the pH, while hydrochloric acid, sodium chloride and sulphuric acid were used in desorption of river sand. The absorbance of methylene blue (MB) was measured using Spectrophotometer DR/2700 at wavelengths of 665 nm. For batch study, conical flask was sealed and kept in rotary shaker and peristaltic pump was used to perform different flow rates in the column study.

Methods: ***Batch study***: Batch experiment was carried out to determine the optimum parameters, adsorption isotherm and adsorption kinetics. In the study of optimum pH, 40 g of river sand was mixed with 100 mL MB solution in conical flask. The pH of the MB solution was adjusted in the range of pH 2-10 by adding nitric acid or sodium hydroxide. The conical flasks were placed at rotary shaker at 150 rpm for two hours. To determine the optimum contact time,

the conical flasks with 100 mL MB solution and 40 g river sand were withdrawn at predetermined time intervals from the rotary shaker. In the experiment to determine the effect of adsorbent sand dose in adsorption of MB, various amounts of adsorbent in the range of 5.0 g to 50.0 g were mixed with 100 mL MB solution and shaken at 150 rpm for two hours. Dye concentrations after shaking and filter were measured using a spectrophotometer. Langmuir model and Freundlich model were used to determine the adsorption isotherm, whereas pseudo first-order model, pseudo second-order model, Elovich model and intra-practical model were used to evaluate the adsorption kinetics.

***Column study*:** Comparison of the adsorption of MB by river sand was performed and the effect of different flow rates in adsorption column was studied. To compare the adsorption by river sand, 150 g river sand was packed in the column and the MB solution was pumped into the column at flow rate of 3 mL/min by peristaltic pump. The effluents were collected at different time intervals to measure the concentration of MB. To study the effect of flow rate, different flow rates in range of 3 mL/min to 10 mL/min were applied.

***Regeneration studies*:** To regenerate the column, hydrochloric acid, sodium chloride and sulphuric acid were pumped through the used river sand separately. The effluents were collected at different time intervals to measure the concentration of MB.

RESULTS AND DISCUSSION

Effect of pH: pH is a very important parameter in the adsorption process, especially in dye adsorption. pH of the medium will control the magnitude of the electrostatic charge generated by the dye molecules. Therefore, the adsorption rate will vary with the pH (Önal et al. 2006). Fig. 1 shows that the removal of methylene blue varies in pH and the optimum pH to remove methylene blue by using river sand is pH 4. Removal of methylene blue is higher from pH 4 to pH 10 due to the presence of H^+ ions competing with the cation dye during adsorption (Yamin et al. 2007).

Effect of contact time: Fig. 2 shows the effect of contact time on the removal of methylene blue with river sand. Removal of methylene blue increases from 2 minutes to 45 minutes and almost equilibrium from 45 minutes to 105 minutes. During the adsorption process, the surface of the adsorbent will adsorb dye molecules and will become full. Thus, the adsorbent cannot adsorb more dye molecules at the end (Crini 2008).

Effect of adsorbent dose: The removal of methylene blue adsorption increases with the dose of sand in range of 23.05 % to 71.93% as shown in Fig. 3. As the adsorbent surface increases and the adsorption sites for the interaction of adsorbent and solute increases (Salleh et al. 2011). Optimal dose of adsorbent to remove methylene blue sand was 500 g/L which has 71.93% removal.

Adsorption isotherms: There are a number of formulas used to analyse isotherm equilibrium absorption experiments. Langmuir and Freundlich isotherm models are the most commonly used (Crini 2008). Linear form of Langmuir model is $\frac{1}{q_e} = \frac{1}{K_L C_e q_m} + \frac{1}{q_m}$, where C_e is equilibrium concentration of adsorbate in solution (mg/L), q_e is the amount adsorbed per unit mass of adsorbent (mg/g) and K_L is Langmuir constant (L/mg) (Ansari et al. 2013). Linear form of Freundlich model is $\log q_e = \log K_F + 1/n \log C_e$ where q_e is adsorbed per unit mass of adsorbent (mg/L), K_F is adsorption capacity [(mg/g) $(mg/L)^n$] and $1/n$ is adsorption intensity (Gao et al. 2013).

The isotherm constants and correlation coefficients were calculated from the linear Langmuir and Freundlich plots by plotting $1/q_e$ vs. C_e [Fig. 4 (a)] and $\log q_e$ vs. $\log C_e$ [Fig. 4 (b)] and represented in Table 1. By comparing the correlation coefficients R^2, it can be deduced that the experimental equilibrium adsorption data are well described by the Langmuir equation compared to the Freundlich model. This indicates that the adsorption occurs at specific homogeneous sites within the adsorbent; adsorbate interactions are negligible and the adsorbent surface will be saturated after monolayer adsorption (Han et al. 2011).

Adsorption kinetics: The mechanism of adsorption and potential rate controlling step can be described by four kinetic models that include pseudo first-order kinetic equation, pseudo second order, Elovich equation and intra-particle diffusion model (Zou et al. 2006). The pseudo first-order kinetic is given by:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad ...(1)$$

Where q_e and q_t are the adsorption capacity (mg/g) at equilibrium and time t, K_1 is rate constant pseudo first-order kinetic equation (min^{-1}). The linear form of pseudo second-order kinetic is given as:

$$\frac{t}{q_t} = \frac{1}{(K_2 q_e^2)} + \frac{t}{q_e} \quad ...(2)$$

Where K_2 is rate constant pseudo second-order kinetic equation (g $mmol^{-1}$ min^{-1}). q_e and q_t are the adsorption capacity (mg/g) at equilibrium and time t. The values of the constants K_2 and q_e can be obtained from the intercepts and the slope of the linear plot of t/q_t versus t. Elovich equation is given by:

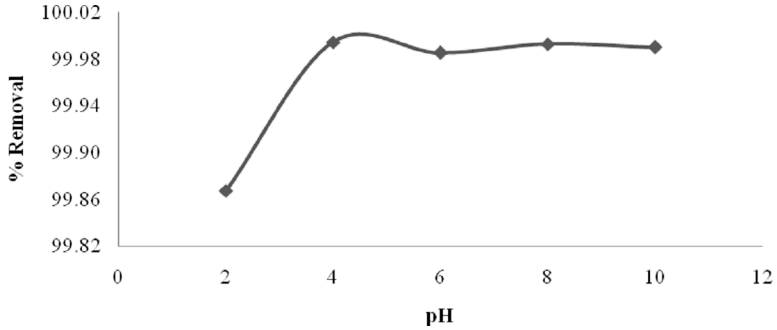

Fig. 1: The effect of pH to remove MB.

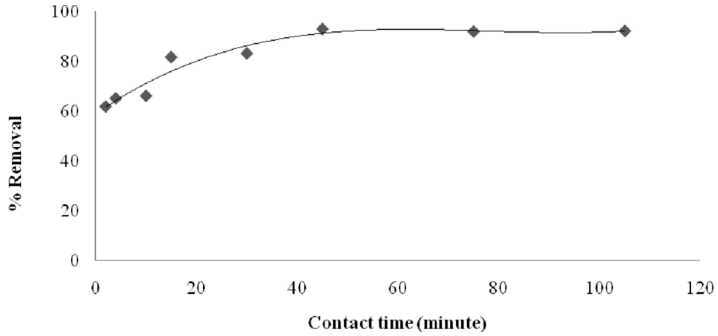

Fig. 2: Effect of contact time to remove MB.

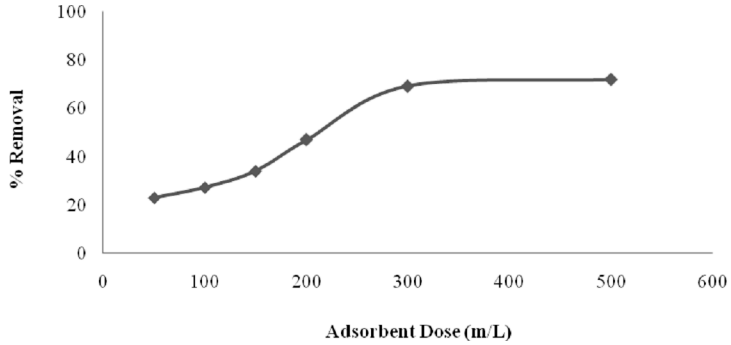

Fig. 3: Effect of adsorbent dose to remove MB.

$$q_t = \frac{\ln(\alpha\beta)}{\beta} + \frac{1}{\beta}\ln t \quad ...(3)$$

Where α is initial rate (mmol g^{-1} min^{-1}) and β is related to the surface coverage and activation energy (mmol g^{-1}). The constants can be obtained from the slopes and intercepts straight line q_t against ln t (Zou et al. 2006). The linear form of intra-particle diffusion model is represented by:

$$q_t = k_t t^{0.5} + c \quad ...(4)$$

Where c is the intercept and k_t is the rate constant of intra-particle diffusion model (mg/g $min^{-1/2}$) (Azhar et al. 2013).

The result indicates that the experimental data fit well with the pseudo second-order kinetic model with the highest R^2 ($R^2 = 0.999$) compared to other models (Table 2). This suggests that the adsorption process is controlled by chemical adsorption involving power sharing of valence electrons between methylene blue and adsorbent (Krishni et al. 2013).

Column study: Effluent breakthrough curves are important for the design of the adsorption column. There are various kinetic models which have been developed to predict the dynamic adsorption column including the Thomas model, Bohart-Adams and Yoon-Nelson model (Han et al. 2009). Thomas model assumes that the adsorption-desorption ki-

Table 1: The isotherm constants and correlation coefficients of Langmuir and Freundlich model.

Model	Parameter
Langmuir	
$\mathbf{q_m}$(mg/g)	5.889
K_L(L/mg)	20.585
R^2	0.610
Freundlich	
n	1.129
K_F (mg/g)(mg/L)^n	228.402
R^2	0.570

Table 2: Kinetic constants and correlation coefficients of models.

Adsorption Kinetic Model	R^2
Pseudo first-order	
K_1 (minute^{-1})	0.107
q_e (mg/g)	0.602
R^2	0.806
Pseudo second-order	
K_2 (g m mol^{-1} minute^{-1})	0.176
q_e(mg/g)	2.360
R^2	0.999
Elovich	
β(g mmol^{-1})	4.241
α(mmol g^{-1} minute^{-1})	60.608
R^2	0.892
Intra-particle	
C	1.492
K_i(mg/g minute$^{-1/2}$)	0.094
R^2	0.828

Table 3: Constants and correlation coefficients for fixed-bed models for adsorption on river sand and sea sand.

Fixed-bed column adsorption model	River sand
Thomas	
K_T (mL/minit.mg)	2.67×10^{-5}
q_e(mg/g)	6.134
R^2	0.677
Yoon - Nelson	
K_{YN} (1/minit)	0.0267
q_e(mg/g)	6.134
$t_{0.5}$ (minit)	306.70
$q_{e(exp)}$(mg/g)	0.783
R^2	0.677
Adams-Bohart	
K_{AB} (1/minit.mg)	2.67×10^{-6}
N_0(mg/L)	7209.29
R^2	0.677

netics of Langmuir and no axial dispersion. The linear form of Thomas model is given by:

$$\ln\left(\frac{Co}{Ct}-1\right)=\frac{kThqex}{Q}-kThCot \qquad ...(5)$$

Table 4: Thomas model parameters using linear regression analysis under different flow rate.

Q (mL/minute)	C_0 (mg/L)	q_e (mg/g)	k_T (mL/minute.mg)	R^2
3	1000	6.134	2.67×10^{-5}	0.677
5	1000	3.445	1.13×10^{-4}	0.655
8	1000	3.292	1.87×10^{-4}	0.671
10	1000	3.374	2.43×10^{-4}	0.821

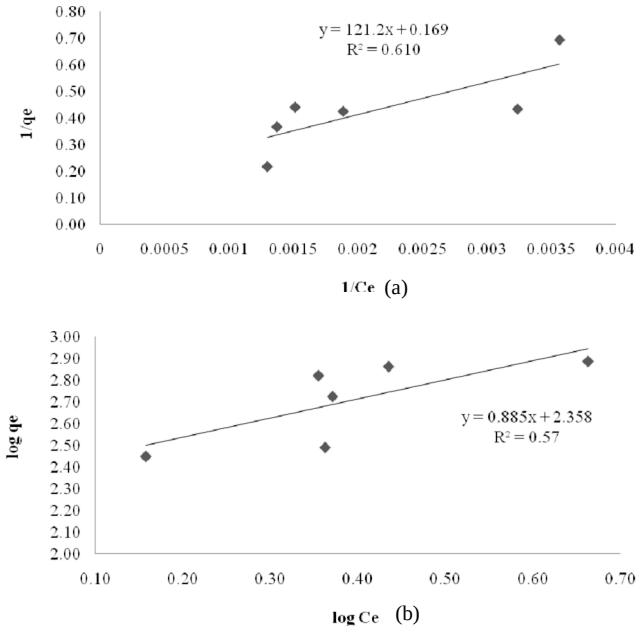

Fig. 4: Plot linear of (a) Langmuir model and (b) Freundlich model

Where k_{Th} (mL/min.mg) is model Thomas constant, q_e (mg/g) is predicted adsorption capacity, x (g) is adsorbent mass, Q (mL/min) is influent flow rate, C_0 (mg/L) is influent concentration and C_t (mg/L) is effluent concentration. Linear equation of Yoon-Nelson model is given by:

$$\ln\frac{Ct}{Co-Ct}=kYNt-TkYN \qquad ...(6)$$

Where k_{YN} (min^{-1}) is constant, T (minute) is time for 50 % breakthrough of adsorbent (Saadi et al. 2013).

Bohart-Adams model establish the basic equations that describe the relationship between C_t/C_o and t in a continuous system (Ahmad & Hameed 2010). This model is based on the assumption that the adsorption rate is proportional to both the concentration of the absorbing species and the remaining capacity of the adsorbent (Saadi et al. 2013). The linear equation is given by:

$$\ln\left(\frac{Ct}{Co}\right)=kABCot-kABNo\frac{Z}{Uo} \qquad ...(7)$$

Table 5: Yoon-Nelson model parameters using linear regression analysis under different flow rate.

Q (mL/minute)	C_0 (mg/L)	q_e (mg/g)	$t_{0.5}$ (minute)	k_{YN} (1/minute)	R^2	$q_{e(exp)}$ (mg/g)
3	1000	6.134	306.70	0.027	0.677	0.783
5	1000	3.445	103.35	0.113	0.655	0.873
8	1000	3.292	61.725	0.187	0.671	1.314
10	1000	3.359	50.387	0.243	0.821	1.709

Table 6: Bohart-Adams model parameters using linear regression analysis under different flow rate.

Q (mL/minute)	C_0 (mg/L)	k_{AB} (l/minute.mg)	N_0 (mg/L)	R^2
3	1000	2.67×10^{-6}	7209.287	0.677
5	1000	1.0×10^{-4}	4266.500	0.662
8	1000	1.60×10^{-4}	4352.525	0.652
10	1000	2.10×10^{-4}	4419.239	0.813

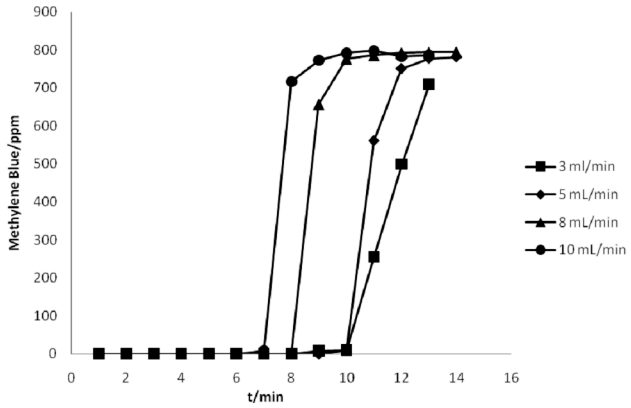

Fig. 5: Breakthrough curve of methylene blue column adsorption using river sand at different flow rates.

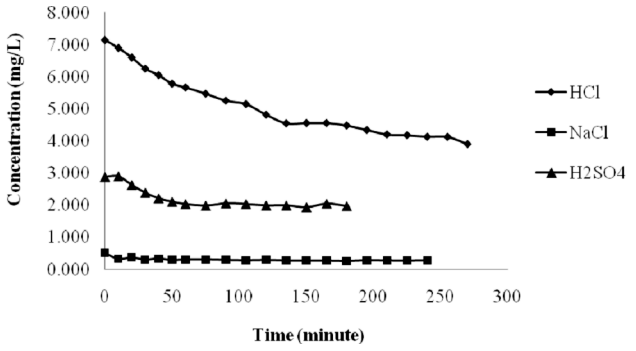

Fig. 6: Desorption of river sand by HCl, NaCl, and H_2SO_4.

Where k_{AB} (1/min.mg) is constant, z (cm) is depth of column, N_0 (mg/L) is maximum ion adsorption capacity per unit volume of the column and U_0 (cm/min) is the linear velocity of the influent solution (Saadi et al. 2013).

Thomas model and Yoon-Nelson model are fitted well with the experiment data of fixed-bed column adsorption by river sand, with $R^2 = 0.677$ for both the models. Table 3 shows the constants and correlation coefficients for fixed-bed models for adsorption on river sand and sea sand.

Effect of flow rate: When the flow rate increases from 3 mL/minute to 10 mL/minute, the breakthrough time has rapidly decreased from 90 minutes to 30 minutes (Fig. 5). This indicates that breakthrough occurred more rapidly with increasing flow rate. Time is getting short for saturation when higher flow rates. Increasing the flow rate will result in increased flow turbulence, and resistance in the external surface of the adsorbent decreases, and reduce the residence time. Thus, less time is needed to reach a breakthrough and saturation (Karimi et al. 2012).

Evaluation of Thomas model parameter: Constant of Thomas model (k_{TH}) and adsorption capacity can be determined by linear equation of Thomas model. Linear regression results and values of R^2 are listed in Table 4, where values of R^2 range from 0.6765 to 0.8209. Table 4 shows that the constant increased with flow rate. This is due to faster mass transfer at higher flow rates (Zhang et al. 2011).

Evaluation of Yoon-Nelson model parameter: Linear regression results and values of R^2 are presented in Table 5. It was observed that rate constant (k_{YN}) and time that is required for 50 % adsorbate breakthrough are decreased and increased, respectively. Calculated q_e is greater than experimental q_e. The experimental data are fitted well with the model. It can be concluded that both Thomas model and Yoon-Nelson model are appropriate models to describe fixed-bed adsorption.

Evaluation of Bohart-Adams model parameter: Linear regression results in Table 6 show that the constant of Bohart-Adams model is increased with the increasing flow rate. This indicates that the overall kinetic of the system is controlled by the external mass transfer (Baral et al. 2009). The Bohart-

Adams model is not appropriate to predict the breakthrough curve due to its lower value of R^2 compared to other models.

Desorption: Desorption experiment was conducted with hydrochloric acid, sodium chloride and sulphuric acid to desorb the MB from river sand (Fig. 6). From the experiment, it was observed that the highest desorption rate of MB is with hydrochloric acid. However, desorption of MB is still considered very low showing that the adsorption of MB by river sand is irreversible.

The adsorption of methylene blue by using river sand was investigated. Various factors such as pH, contact time and adsorbent dose were investigated. Langmuir model is the fittest for the experimental data. The most suitable model to describe the adsorption kinetics is pseudo second-order model. Thomas model is the most suitable model to describe the kinetics of the adsorption column of the sand. The rate of removal of methylene blue adsorption on a column depends on the flow rate. Column adsorption capacity increased with the flow rate. Regeneration of sand was used with hydrochloric acid (HCl), 2M sodium chloride (NaCl) and 2M sulphuric acid (H_2SO_4), 2M ineffective indicates that the adsorption is not reversible. It can be concluded that the adsorbent used in this study has the capacity of removing the MB from dye wastewater.

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