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ORIGINAL ARTICLE

Kinetic and Equilibrium Studies for Dye Adsorption onto Sugarcane Bagasse and Rice Husks

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KEYWORDS

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ABSTRACT: The textile industry discharges large quantities of highly colored wastewater from industrial processes using chemical components. Many dyes are designed to be chemically stable so that they are difficult to decolorize due to their complex structure and synthetic origin. The dye waste is subsequently released directly to water bodies during the textile finishing process. This improper released has adverse effects on the environment and may reduce photosynthesis in aquatic plants. Even though adsorption techniques have been widely used to remove textile dye from waters, the kinetic models used to describe the adsorption of textile dye onto a porous material is still not yet fully understood. This study investigated different applications of absorbent from sugarcane bagasse (SB) and rice husks (RH) in removing color from aqueous solution and the application of kinetic model for adsorption of color from aqueous solutions onto SB and RH. A batch study was carried out under various mass of adsorptions and contact time with constant with the initial concentration of aqueous solution was 400ADMI. The data obtained from batch experiments showed that the removal of RH (93%) was more efficient than SB (49%). This study also advanced the understanding on the kinetic adsorption study of RH and SB to prove that the adsorbents have potential to reduce dye from synthetic solution. The contribution of this study in the removal of significant dye pollutants from industrial wastewater will require future assessment in a prospective wastewater treatment facility setting.

INTRODUCTION

The color of effluent released into the receiving water has become a major environmental problem in recent years[1]. Textile, pulp, and paper effluent discharges often impart color to the receiving waters for miles downstream from the source[2]. Manufacturing industries for coloring and many other industries that use dyes and pigments produce wastewater that is high in color and organic content[3]. The excessive application of dyes can give a negative impact. For example, if chemicals that are used to produce synthetic dyes find their way into water bodies, it will affect human health and the environment[4]. These compounds, when ingested or even in contact with human skin, cause adverse effects ranging from hormone disruption in children to cancer in employees in factories and people who drink polluted water[5,6].

Many investigations in recent years focused on the treatment of synthetic dye using kinetic adsorption model, which are pseudo-first order (PFO) and pseudo-second-order (PSO)[7-9]. Furthermore, the adsorption has potential as one of the most efficient methods of wastewater treatment as well as eliminating organic contaminants in synthetic dyes production[10]. Due to a clear and simple design, adsorption has more advantages

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compared to other treatment methods, which require low investment in terms of management and operation costs[11]. Although many adsorption models have been used in removing dye from wastewater, the use of the adsorption kinetic model and comparison with SB and RH need to be verified[2]. This study sought to compare the different applications of adsorbents from SB and RH in removing the dye concentration from synthetic wastewater and the use of kinetic for adsorption of dye from aqueous solutions onto SB and RH.

MATERIALS AND METHODS

Materials

The SB and RH were collected from Pontian, Johor and Ipoh, Perak, respectively. These materials were first cleaned with tap water to clean the dirt on the material. The samples were dried under sunlight. Then, they were rinsed with distilled water to wash off unwanted substance on the adsorbent. This followed by drying in an oven for 3 to 4 hours at 105°C. The SB was taken out from the oven and cut into small pieces before grinding it using grinder mixer. The purpose of grinding the SB is to ease the sieving process to obtain enough adsorbent for the batch experiments[12].

Preparation aqueous solution

Synthetic dye aqueous solution was prepared by dissolving 0.001g of methylene blue into 1L of deionized water in a volumetric flask[13].

Batch experiment

Each sample of dye solution 150ml mixed with adsorbent were shaken using an apparatus called orbital shaker at constant speed of 170 rpm in conical flask. The HACH DR 6000 Spectrophotometer was used to determine the concentration of the retained dye. Each sample was analyzed by measuring the intensity of light passing through the samples according to HACH Method 10048 which is ADMI Weighted Ordinate Method[14]. The data of the light intensity was recorded for 10 flasks of the sample at different times up to 5 days until equilibrium condition.

RESULTS AND DISCUSSION

The effect of contact time for sugarcane bagasse

The effect of time was conducted to find the optimum time where the removal efficiency is the highest and at equilibrium state. In this study, the experiments for the effect of contact time were observed for up to 5 days as it is considered to be the maximum time to allow a proper absorption to occur. Table 1 shows the removal efficiency, E (%) for 2 g of SB and tested on 150 mL of synthetic dye 400ADMI.

Table 1. The removal efficiency based on different contact times

Time (min)	Initial Concentration, C_o (mg L^{-1})	Final Concentration, C_f (mg L^{-1})	Removal Efficiency, E(%)
0	400	0	0
30	400	246	34
60	400	231	35
120	400	230	43
180	400	226	44
240	400	215	44
420	400	208	45
1440	400	203	46
2880	400	200	47
4320	400	199	48
5760	400	198	49

Figure 1 shows the effect of time on removal percentage. Based on Figure 1, there is a steady increase in removal efficiency starting from 48% until it reaches the highest at 49%. When the time increase, the removal percentage increase. The optimum time was recorded at 4320 minutes where the removal efficiency at constant rate it indicates that the equilibrium time at 4320 minutes.

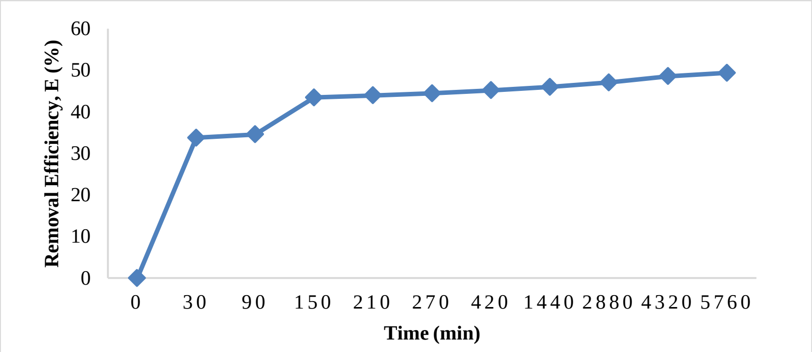

Figure 1. The effect of contact time on removal efficiency

The effect of contact time for rice husks

The experiment effect of time is conducted to find the optimum time where the removal efficiency is the highest and reach the equilibrium state. In this study, the experiments on the effect of contact time are observed for up to 5 days as it is considered to be the maximum appropriate time to allow proper absorption to occur. Table 2 shows the removal efficiency, E (%) for removing dye using 2g of RH adsorbent and tested on 150ml of synthetic dye 400ADMI. The highest removal efficiency of RH from synthetic dye solution is 93% starting 1440 minutes.

Table 2. The removal efficiency based on different contact times

Time (min)	Initial Concentration, C_o (mg L^{-1})	Final Concentration, C_f (mg L^{-1})	Removal Efficiency, E (%)
0	400	0	0
30	400	50	88
60	400	47	88
120	400	42	90
180	400	39	90
240	400	32	92
420	400	32	92
1440	400	30	93
2880	400	29	93
4320	400	29	93
5760	400	28	93

Based on Figure 2, the equilibrium state starts from 88% and reaches the highest removal efficiency at 93%. The removal percentage also increase with time giving the optimum time recorded at 1440 minutes where the removal efficiency at constant rate it indicates that the equilibrium time at 1440 minutes

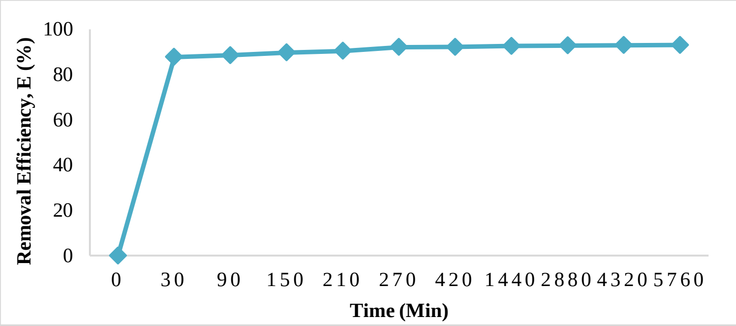

Figure 2. The effect of contact time on removal efficiency

Adsorption kinetics

The experimental data were applied to the pseudo-first order (PFO) and pseudo-second order (PSO) equations in order to evaluate the kinetics of the adsorptions of synthetic dye onto SB and RH. The PFO and PSO equation is expressed in Table 3.

Table 3. Kinetic Models Equation Application

Kinetic models	Linear form
pseudo-first-order (PFO)	$\ln(q_e - q_t) = \ln(q_e) - k_1 t_i$
pseudo-second-order (PSO)	$\frac{t_i}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t_i}{q_e}$

Linear plots of ln (q_e-q_t) versus contact time, t_i (min) and t_i/q_t versus contact time, t_i (min) were plotted to understand the applicability of the intraparticle diffusion[15], PFO and PSO models for the dye adsorption onto two adsorbents. The values of C, k_1, R^2, and all kinetics correlation coefficient values are defined from equations[16].

The linearity of the plots (R^2) demonstrates that the intraparticle diffusion and PSO kinetic models play a significant role in the uptake of the dye by SB and RH. In addition, the experimental q_e values can obtained from the intercept of linear plots of PSO kinetics for adsorption of synthetic dyes onto SB and RH[7].

Pseudo first order for sugarcane bagasse

By using the PFO linear equation of $\ln(q_e - q_t) = \ln(q_e) - k_1 t_i$, it is possible to identify the important parameters presented in Figure 3. This equation can be expressed as:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t_i; \quad y = mx + c; \quad y = \ln(q_e - q_t); m = -k_1; x = t_i; c = \ln(q_e)$$

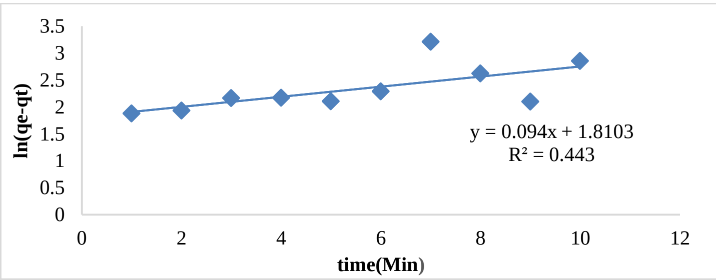

Figure 3. Pseudo First Order Figure of SB.

As shown in Figure 3, that the slope of plot ln (q_e - q_t) versus t_i is 0.094. The y-intercept of the kinetic model is 1.8103 which is equivalent to ln (q_e). By solving the ln (q_e) through exponential solution, the value of q_e is 7.625 mg/g. The value of q_e is the PFO constant or the adsorption capacity of the system. The R^2 determines the correlation coefficient of the adsorption system to the kinetic model[7]. In this case, the R^2 value for SB is lower which is 0.443 obtained from the linear model, it is indicate the PFO equation not really fitted for kinetic model for this analysis.

Table 4. Kinetic table of Pseudo First Order for SB

Solution	Amount (g)	q_e (mg g^{-1})	k_1 (min^{-1})	R^2	q_e (exp) (mg g^{-1})
Synthetic solution for SB	2	15.15	4.064×10^{-3}	0.0966	15.15
	4	7.625	9.501×10^{-3}	0.443	7.625
	6	4.917	-0.13	0.2727	4.917

The Table 4 shows for batch experiments of PFO for variety amount of adsorbent. As can be seen, 4 g SB adsorbent have the highest value of correlation coefficient, R^2 which is 0.443 compared to other adsorbent mass. The analysis result is important to show the chemisorption mechanism due to the sharing electron between adsorbent-adsorbate into a chemical bond[17].

Pseudo first order for rice husks

As shown in Figure 4, the slope of plot ln (q_e - q_t) versus t_i is 0.2849. The y-intercept of the kinetic model for RH is 0.0426 which is equivalent to ln (q_e). By solving the ln (q_e) through exponential solution, the value of q_e is 13.413 mg g^{-1}. The value of q_e is the PFO constant or the adsorption capacity of the system. The R^2 determines the correlation coefficient of the adsorption system to the kinetic model. The correlation coefficient, R^2, for RH obtained from the linear model is 0.8881.

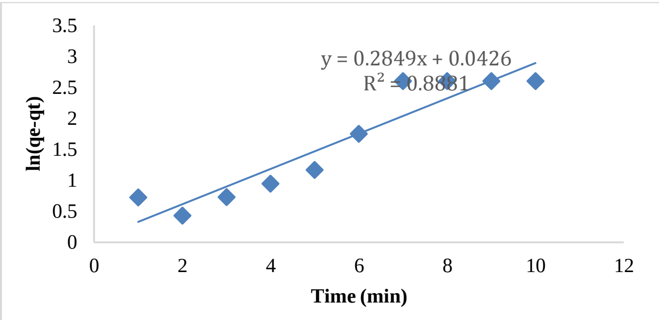

Figure 4. Pseudo First Order Figure of RH

Data in Table 5 batch experiments of PFO for RH shows that 4 g of RH adsorbent have the highest value of correlation coefficient, R^2, which is 0.8881 compared to the 2 g and 6 g of RH. The correlation coefficient, R^2 indicate that PFO kinetic model is successfully fitted with the adsorption kinetic of synthetic dyes onto RH compared to SB due to higher value of R^2.

Table 5. Kinetic table of Pseudo First Order for RH

Solution	Amount (g)	q_e (mg g^{-1})	k_1 (min^{-1})	R^2	q_e (exp) (mg g^{-1})
Synthetic solution for RH	2	28.175	4.462×10^{-4}	0.2155	28.175
	4	13.413	0.13	0.8881	13.413
	6	7.233	0.076	0.2504	7.233

Pseudo second order for sugarcane bagasse

The assumption for PSO kinetic model is the reaction rate of adsorption solute dependent on the active sites on the adsorbent surface corresponding to adsorption of solution. The PSO kinetic model is important to determine the adsorption capacity and initial solute uptake. Based on Figure 5, the slope is 0.0651 it is indicate the slope signifies the intensity of adsorption or heterogeneity of the adsorption [18].

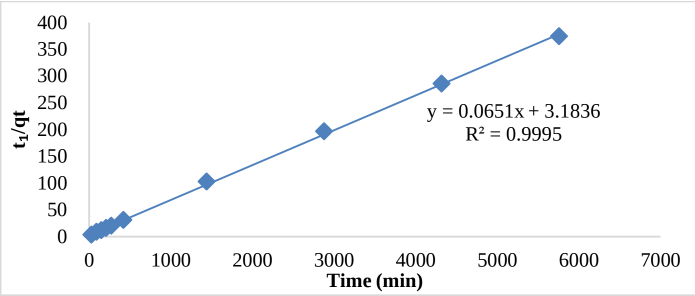

Figure 5. Pseudo Second Order Figure for SB

The y-intercept for the line is 3.1836 which is equivalent to $\frac{1}{k_2 q_e^2}$. The solving the y-intercept helps to identify the maximum adsorbent capacity,$k_2 q_{e^2}$, in which for this study which is 0.314 mg/g. By applying the value of $k_2 q_{e^2}$ into the equation, k_2 can be calculated and gave 1.369×10^{-3} (min^{-1}). In this study, the PSO model shows that the correlation coefficient, R^2, obtained is 0.9995. Based on the Table 6, the correlation coefficient, R^2, value near to 1 shows that the data has good fitting with PSO model.

Table 6. Kinetic Parameters PSO for the adsorption of synthetic dyes onto SB

Solution	Amount (g)	q_e (mg/g)	k_1 (min^{-1})	R^2	q_e (exp) (mg g^{-1})
Synthetic co/w SB	2	15.15	1.369×10^{-3}	0.9995	15.15
	4	7.625	2.033×10^{-3}	0.9985	7.625
	6	4.917	8.152×10^{-3}	1	4.917

Pseudo second order for rice husk

The PSO kinetic model is important to determine the adsorption capacity and initial solute uptake. From Figure 6, the slope of PSO linear plot is 0.0354, it is indicating the intensity of adsorption or heterogeneity of the adsorption.

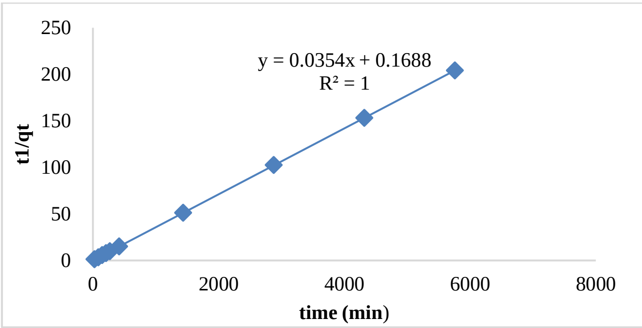

Figure 6. Pseudo Second Order Figure for RH

The y-intercept for the line is 0.1688 which is equivalent to $\frac{1}{k_2 q_{e^2}}$. Solving the y-intercept helps to identify the maximum adsorbent capacity, $k_2 q_{e^2}$for this study which is 5.924 mg g^{-1}. By applying the value of $k_2 q_{e^2}$ into the equation in Table 3, k_2 is 7.463×10^{-3} (min^{-1}). In this study, the R^2 obtained is 1; it is indicating that PSO kinetic model is fitted with the adsorption kinetic of synthetic dyes onto RH compare to SB due the higher value of R^2 with different adsorbent mass.

Table 7. Kinetic Parameters for the adsorption of synthetic dyes onto RH

Solution	Amount (g)	q_e (mg/g)	k_1 (min^{-1})	R^2	q_e (exp) (mg g^{-1})
Synthetic co/w RH	2	28.175	7.463×10^{-3}	1	28.175
	4	13.413	4.363×10^{-3}	1	13.413
	6	7.233	0.012	1	7.233

CONCLUSIONS

The RH and SB adsorbent have been proved to have potential to be used in wastewater treatment. The two materials are low-cost material and environmentally friendly. The findings from batch experiments showed that the removal of RH is more efficient compared to SB removal. Analysis of kinetic showed that the PSO kinetic model is well fitted for adsorption kinetic of synthetic dyes onto RH compared to SB. Hence, the result of the kinetic model proved that the adsorbents have the potential to reduce the dye concentration from aqueous solution. This study may also provide an insight into the application of this kinetic model adsorption process in the future. Hence, this study contributes eco-friendly and low-cost in removing the dye pollutant from industrial wastewater for future assessment in a prospective wastewater treatment facility setting.

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Conflict of interests

No conflict.

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