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Adsorption of Remazol Brilliant Pink (Red 3BS) dye onto Leucaena Leucocephala Shell Based Activated Carbon: Batch Study

H. Masitah[1*] and S. Nor Azzahra[1]

[1]School of Environmental Engineering, Universiti Malaysia Perlis, Kompleks Pusat Pengajian Jejawi 3, 02600 Jejawi, Perlis.

ABSTRACT

Adsorption of remazol brilliant pink (Red 3BS) dye from aqueous solution onto activated LLS adsorbent was investigated in a batch study. Adsorption isotherm and kinetics study were carried out by considering the effects of various parameter such as adsorbent dosage (0.2 g - 2.0 g) initial concentration (25mg/L-125mg/L) and contact time (10 min - 180 min), also effect of solution pH (2 - 12). Equilibrium data were fitted to Langmuir and Freundlich isotherm models. The equilibrium data were best described by Langmuir isotherm with the maximum adsorption capacity 2.945 mg/g. Furthermore, the kinetic model applied to pseudo-second-order, which has the best fitted data. The result of this study showed the potential of low cost of LLS agricultural waste material to adsorb the reactive dye pollutant containing in wastewater system.

Keywords: Adsorption, Isotherms, Kinetics, Leucaena Leucocephala Shell, Reactive Red 3BS.

1. INTRODUCTION

Water pollution remain as main issue in Malaysia where the source of pollution is caused by the effluent discharge from textile industries which generates abundance of dyestuffs. Over 10000 different types of dyes are used in industries for textile dyeing, leather dyeing and colouring processes (Daoud *et al.*, 2017). Due the process, more than 50% reactive dye lost through hydrolysis which later contribute to water bodies and waste stream contamination. The effluent containing reactive azo dye is very difficult to remove from conventional wastewater treatment method due to the sulfonic acid group which make the dyes water soluble (Mogens and Ujang, 2004).

Adsorption is considered to be an important phenomenon in most natural physical, biological and chemical process. Due to their flexibility, low energy consumption and cost effective technology, it has been recognized for wastewater treatment method in industries in these current days. Activated carbon is a universal adsorbent mostly applies in the industry for dye removal due to its adsorption capacity. It has been proved as a great potential adsorbent because it's unique characteristic such as large surface area, well-developed pore structure and has various chemical nature on the surface However, the activated carbon used in the industry application are quite expensive (Karthikeyan and Rajendran, 2010).

As the alternative approach, agricultural waste with high carbon content, low cost and available throughout the year are preferable by products to do research on the adsorption of dye. Generally, *Leucaena Leucocephala* shell (LLS) waste are widely available and has large quantities throughout the year. It also has been found the significant in term economic value as the adsorbent for dye removal as it provides great surface area and gain more porosity (Rajendran, *et al.*, 2015). Hence,

*Corresponding Author: *masitah@unimap.edu.my*

this study investigated the adsorption of Red 3BS dye onto activated LLS adsorbent in a batch mode study. To specify, the aim of this study focus on to prepare, characterize the LLS, evaluate the adsorption study, and also evaluate the adsorption isotherm and adsorption kinetic study of remazol brilliant pink (Red 3BS).

2. MATERIAL AND METHODS

2.1 Adsorbate: Remazol Brilliant Pink (Red 3BS)

Remazol brilliant pink (Red 3BS) dye as shown in Figure1 is a reactive azo dye. The dye was selected as adsorbate without further purification in this research study. The aqueous solution was prepared by dissolved the solute of Red 3BS dye into the deionized water without any pH adjustment. The maximum absorbance wavelength of dye is 542nm. The general properties of Red 3BS dye presented in Table 1.

Table 1 General characteristic of remazol brilliant pink (Red 3BS) dye

Remazol Brilliant Pink (Red 3BS)	
Chemical Index (C.I)	C.I. 239
Class	Reactive azo dye
Molecular weight	1085.84
Maximum wavelength, λmax(nm)	542

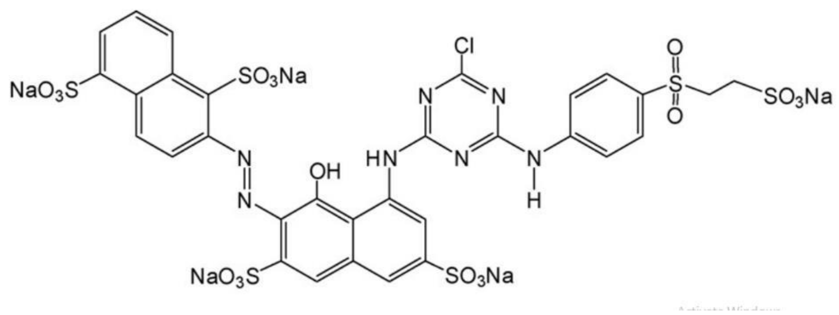

Figure 1. Remazol brilliant pink (Red 3BS) (Asouhidou *et al.*, 2009).

2.2 Preparation of *Leucaena leucocephala* Shell (LLS) Activated Carbon

The collected *Leucaena leucocephala* shell (LLS) was washed with distilled water to remove any impurities and dried in an oven at 110 °C for 24 hours. After dried, it was cut into small pieces and were ground. Next, the sample was chemically activated by impregnating with 0.1 M solution of $ZnCl_2$. After impregnated, the sample was washed with plenty of distilled water to remove the chloride residual. Then it was dried at 110 °C to remove the moisture content. The sample was activated and carbonized in a muffle furnace under continuous nitrogen flow at 500 °C for 1 hour. Finally, the activated carbon sample was sieved to get uniform particular size in range 150-200μm. The powdered *Leucaena leucocephala* shell (LLS) activated carbon then stored in bottle.

2.3 Batch Equilibrium Studies

The adsorption experiment was carried out at 30°C of room temperature in a batch mode to examine the optimum result of Red 3BS dye adsorption onto LLS activated carbon under a various condition such as the effect of adsorbent dosage, the effect of initial concentration and contact time, and the effect of pH (2-12). To run the experiment, all the working aqueous solution of the dye were filled with 100ml in the 250mL of Erlenmeyer conical flask. The prepared working solution that had been added with adsorbent and were shaken under constant speed 150 rpm of agitation rate at the present time interval. After shaken, it was then filtered and the concentration of residual Red 3BS dye was measured by using the beam UV spectrophotometer of U-2810 model. The adsorption capacity for each effect of adsorbent dosage were investigated by calculating The amount of adsorption at equilibrium time *t*, *q*e (mg/g), is calculated by

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{1.0}$$

where C_0 and C_t (mg/L) are the liquid-phase concentrations of dye at initial and any time *t*, respectively; *V* the volume of the solution (L); *W* is the mass of dry adsorbent used (g).

To conduct the study on the effect of adsorbent dosage, the parameter factor was design by varying the dosage from 0.2g - 1.0g with initial concentration 25mg/L and was shake for 3 h. The effect of initial concentration contact time was conducted by adding 1g of adsorbent into 25 - 125mg/L of dye and agitated for 10 -180min. The effect of initial pH from range value 2 to 12 were conducted by adding 1.0gram adsorbent into 75mg/L of Red 3BS concentration, which agitated for 3 h.

2.4 Batch Kinetic Studies

The procedures of kinetic experiments are basically identical to those of equilibrium tests. The aqueous samples were taken at present time intervals, and the concentrations of dye were similarly measured. The amount of adsorption at time *t*, *qt* (mg/g), is calculated by

$$q_t = \frac{(C_0 - C_t)V}{W} \tag{2.0}$$

where C_0 and C_t (mg/L) are the liquid-phase concentrations of dye at initial and any time *t*, respectively; *V* the volume of the solution (L); *W* is the mass of dry adsorbent used (g).

3. RESULTS AND DISCUSSION

3.1 Effect of Adsorbent Dosage

Figure 2 shows the graph on the effect of adsorbent dosage for adsorption of Red 3BS dye onto activated LLS adsorbent. Under the effect of adsorbent dosage study, several dosage parameter was investigated, such as 0.2g, 0.4g, 0.6g, 0.8g and 1.0g. The different adsorbent dosage was tested on 25mg/L initial concentration of reactive Red 3BS dye and 100mL volume of solution were kept constant. To undergo adsorption process, it was all agitated under 150rpm speed for 3 hours.

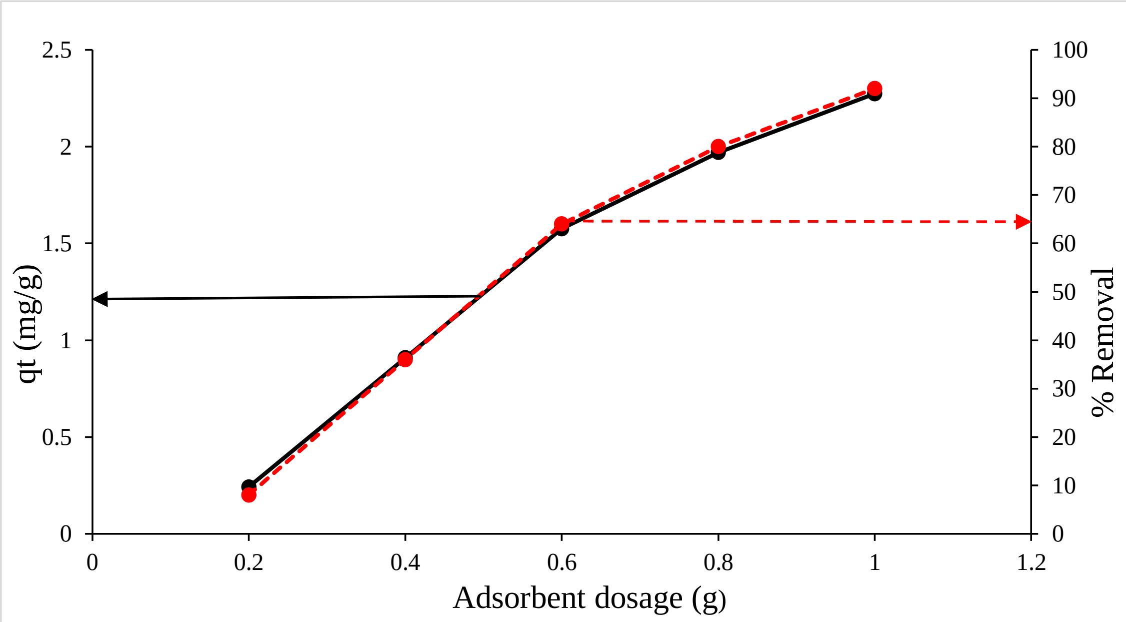

Figure 2. Effect of adsorbent dosage on the Red 3BS adsorption (C_0 = 25 mg/L, T = 30 ∘C).

The graph shows the trend of adsorption capacity efficiency, which as the adsorbent dosage increased, the amount of dye adsorbed also increased. The percentage removal of Red 3BS increased as the adsorbent dosage increased from 0.2g to 1.0g, which relatively explained to the result an increasing of adsorption capacity onto activated LLS adsorbent. This result's trend was similarly applied to the previous researcher's study based on malachite green dye removal using *Limonia acidissima* (wood apple) shell (Sartape *et al.* 2013). Further, it is clear that the 8% removal of reactive Red 3BS dye reflected to the least adsorbent dosage 0.2g adsorbed 0.242 mg/g indicates the lowest amount of dye uptake, while 88% removal of reactive Red 3BS dye removal reflected the highest adsorbent dosage 1.0g adsorbed 2.273 mg/g indicates the highest amount of dye uptakes. This is actually due to greater amount of adsorbent dosage enable greater surface site availability on the adsorbent, consequently increase the adsorption capacity (Almeida *et al.*, 2009). Results indicate that the specific surface area yield more adsorption with more unit weight of adsorbent. Hence, this study proved that as the amount of dosage increased, the amount of dye adsorbed also increased which can be supported from previous researcher study that investigate on methylene blue dye (Pathania *et al.*, 2017).

3.2 Effect of Initial Concentration

In this study, effect of initial concentration and contact time on adsorption of Red 3BS dye onto activated LLS adsorbent was investigated. The experimental parameter was carried in a batch mode with a series of initial concentration was varied into 25mg/L, 50mg/L, 75mg/L and 100mg/L and a set of contact time from 10 minutes to 180 minutes. The volume of sample solution was kept constant with the specification of time interval under 150rpm agitation rate. Figure 3. displayed the trend of adsorption capacity, q_t (mg/g) of different initial against contact time, t. From the graph, the optimum result for adsorption capacity for Red 3BS dye with concentration 25mg/L to 125mg/L was observed to approach equilibrium at the function of 180min contact time. The result clearly explained on the behaviour of adsorption phenomenon, which adsorption capacity increased with the extended contact time. At initial stages with the function of 10 minutes contact time, it show the rapid uptake of adsorption capacity, which later it become slower and potentially showing a gradual change to reach equilibrium where no more dye can be removed. This is because large number of surface sites were present at the initial stages. After at specific contact time, the surface sites are difficult to be occupied due to repulsion between the solute molecules of the solid and bulk phase (Ahmad and Alrozi 2011). In the present study, the equilibrium attainment was determined by the maximum uptake of each initial concentration (25- 125mg/L) which defined at 180 min of contact time.

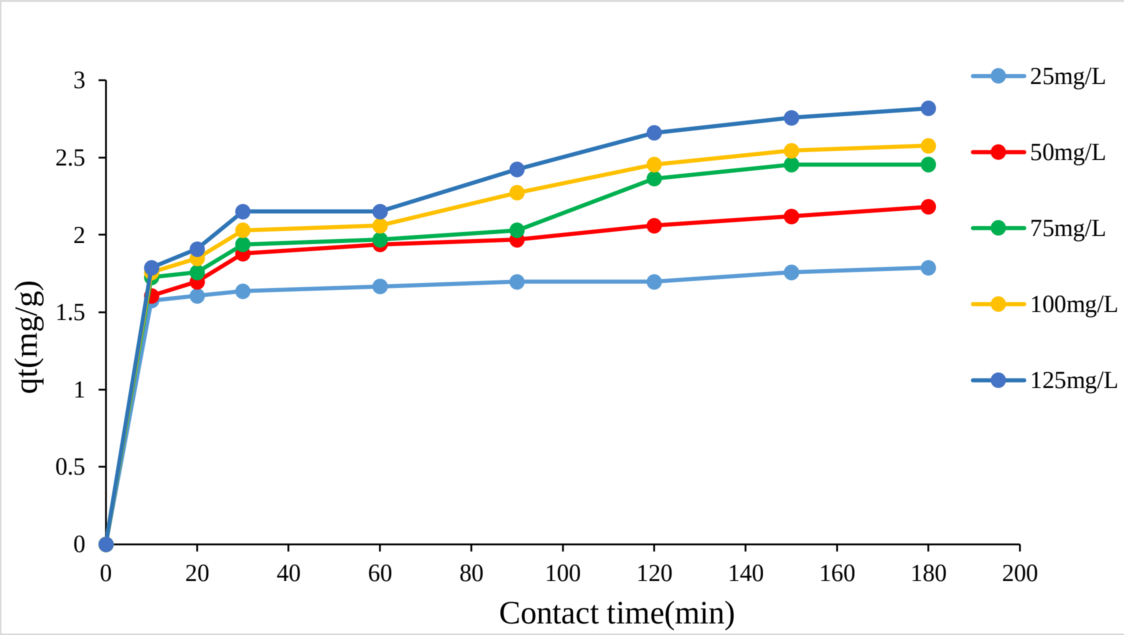

Figure 3. Effect of initial concentration on the adsorption of Red 3BS on LLS at 30°C.

According to Banerjee and Chattopadhyaya, 2017, the adsorption capacity increased when the initial concentration increased. Therefore, based on the experimental data, the highest uptake of 25mg/L of initial dye concentration was 1.788 mg/g while for the highest uptake 25 mg/L of initial dye concentration was 2.818 mg/g. Similar trend was observed by Ahmad and Alrozi, 2011, the higher initial dye concentration gives a strong driving force to overcome the mass resistance between the solid phase and aqueous phase. Therefore, it has been proved the initial concentration of Red 3BS influenced the operating condition of adsorption system onto activated LLS adsorbent. According to Hasan *et al.*, 2008, the increase in initial dye concentration contribute to the increase in adsorption capacity onto the cross-linked chitosan- oil palm ash adsorbent onto Reactive Blue 19.

3.3 Effect of Solution pH

Figure 4 illustrate the graph on the effect of pH on adsorption of Red 3BS dye onto activated LLS adsorbent. The experiment tested on 75mg/L initial concentration of Red 3BS with 100mL of constant volume by adding 1.0g of adsorbent and agitated under 150rpm for 2 hours. The initial pH value of reactive Red 3BS without adjustment was recorded as 4.6. Later the pH condition was adjusted to the range from 2 to 12 with the addition of 0.5 M sodium hydroxide (NaOH) or 0.5 M sulphuric acid (HCL).

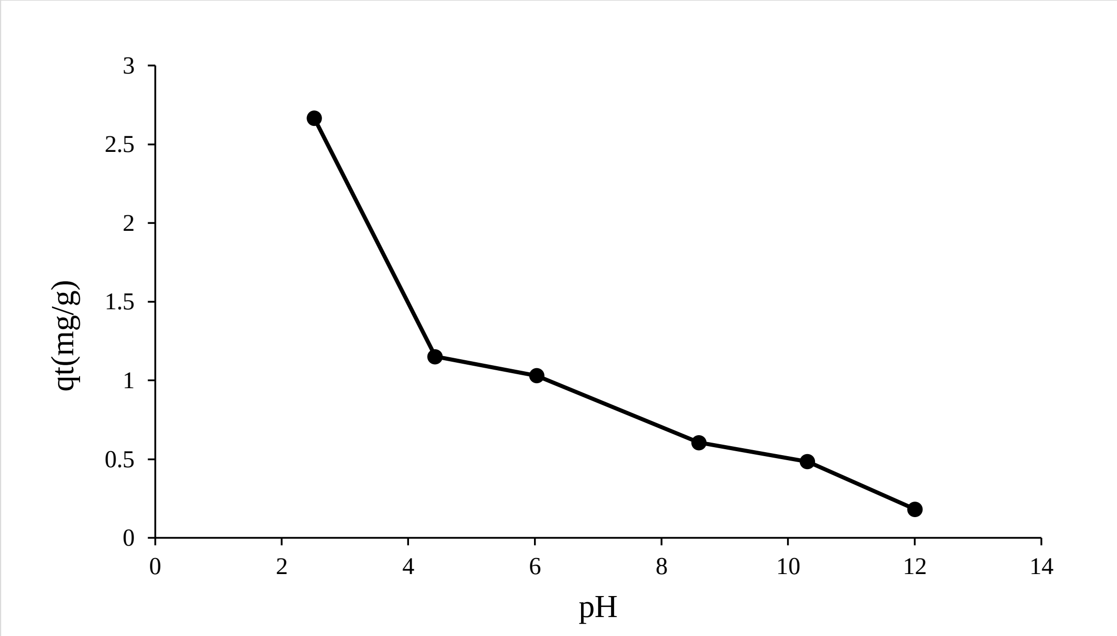

Figure 4. Effect of pH on the Red 3BS adsorption (C_0 = 75 mg/L, T = 30 ^{o}C).

In the adsorption behaviour study, pH parameter is one of the important factor that measure absorbability between the adsorbent and the dye solution. The pH factor influences the ionization degree of Red 3BS dye solution and the adsorbent surface properties. As depicted as in Figure 4., the adsorption capacity increased from 0.007mg/g to 2.667mg/g as the pH of solution decreased from 12 to 2. Which the favourable optimum result of the dye uptake was at pH 2. The favourable condition of adsorption mechanism at lower can be depended to electrostatic mutual action between sulfonate groups of the dye and protonated amino groups of the adsorbent functional that may present higher positive charge (Asouhidou *et al.*, 2009). Similarly investigated from previous study on the adsorption of RO16 onto STAC, as the solution has low pH value, more H+ ions adsorbed on the surface due the electrostatic attraction (Venkateswaran, 2017). To conclude, the lower the pH value, the higher the adsorption capacity, hence, it indicates that dye uptakes is much higher in acidic solution compare to in neutral and alkali solution.

3.4 Adsorption Isotherm

Adsorption isotherm modelling had been evaluated to study the adsorption system mechanism involves the adsorption of Red 3BS dye onto LLS activated carbon. The result obtained from experimental was investigated based on the data distribution adsorption at equilibrium between solid-liquid phases for each particular initial concentration of Red 3BS dye (25 mg/L -125 mg/L) with constant temperature of 30°C. Hence, two type of isotherm modelling were evaluated such as Langmuir isotherm model and Freundlich isotherm model to examine best fitted in establishing the suitable model for the design determination (Pathania, *et al.*, 2017). The distribution of adsorption at equilibrium between the two phases was evaluated by using Langmuir modelling as shown in Figure 5 and Freundlich modelling as shown in Figure 6. In this research study, from the straight line plotted, both Langmuir and Freundlich fitted well on the isotherm model evaluation. Based on the correlation coefficient R^2 shown in Table 2, the adsorption isotherm with LLS adsorbent can be well described by Langmuir isotherm for Red 3BS dye. The linear form of Langmuir isotherm is expressed as

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \qquad (3.0)$$

where qe is the amount of dye adsorbed per unit weight of adsorbent (mg/g) and Ce is the equilibrium concentration of dye in solution (mg/L). The constant Q_0 signifies the adsorption capacity (mg/g) and b is related with the energy of the adsoprtion (L/mg). A plot of Ce/qe versus Ce (Figure 4) yields a straight line with slope $1/Q_0$ and intercept $1/Q_0b$. Further, Table 2 lists that the computed maximum adsorption capacity, Q_0 of Red 3BS onto the LLS adsorbent.

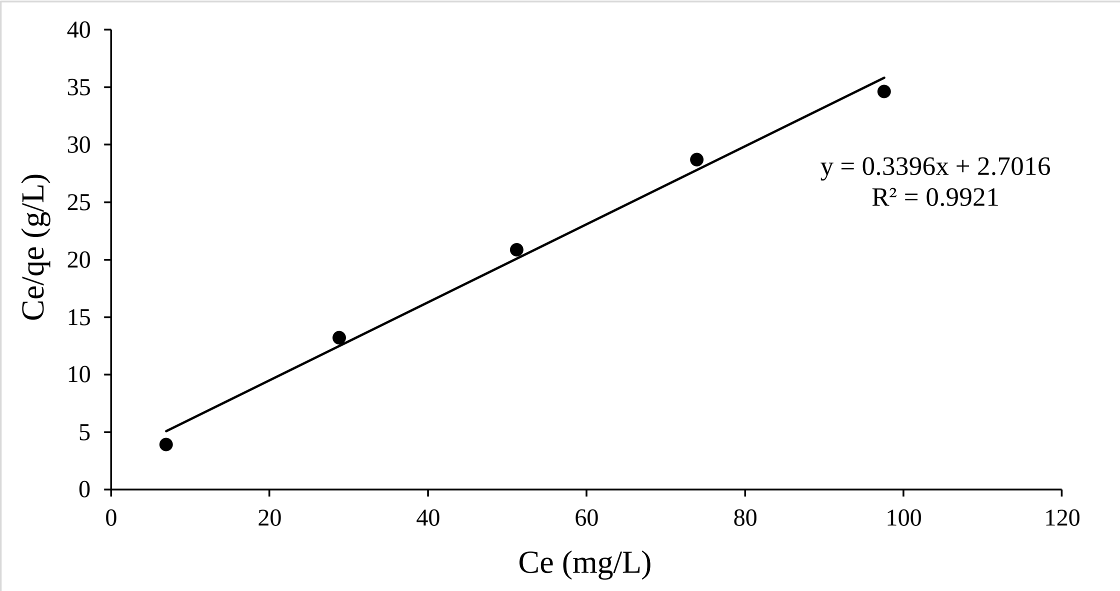

Figure 5. Langmuir adsorption isotherm of Red 3BS on LLS activated carbon at 30^{0}C.

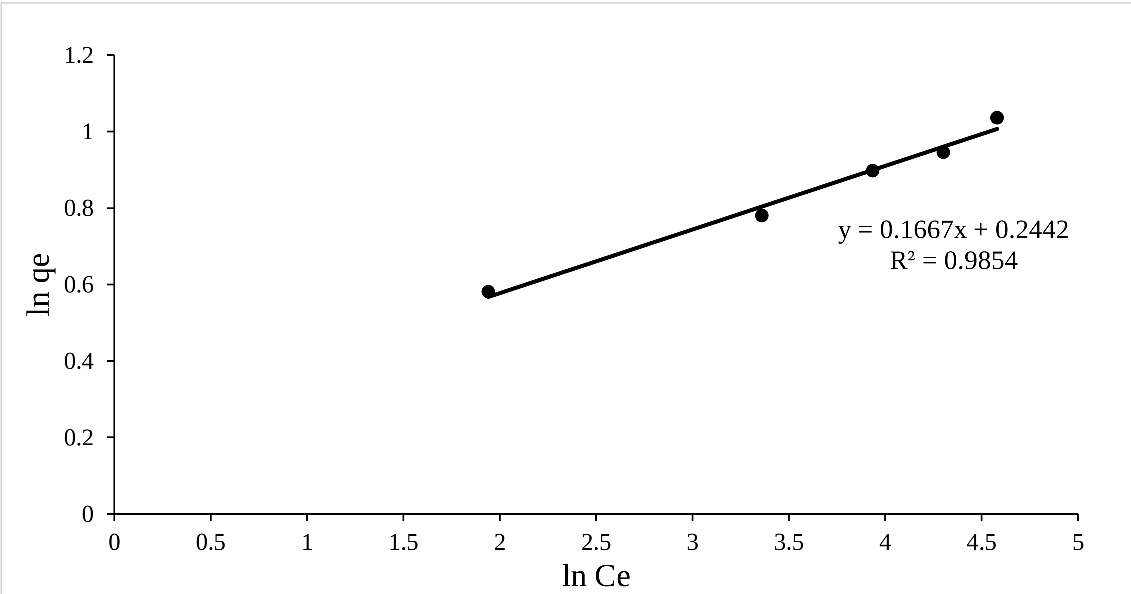

Figure 6. Freundlich adsorption isotherm of Red 3BS on LLS activated carbon at 30^{0}C.

Table 2 Adsorption constant of Red 3BS on LLS activated. Carbon using Langmuir and Freundlich isotherm model

	B (*L/mg*)	*Q_{max}* (*mg/*)	*R^2*		*K_F*	*1/n*	*R^2*
Langmuir isotherm	0.126	2.945	0.992	Freundlich isotherm	1.277	0.167	0.985

3.5 Adsorption Kinetics

In order to investigate the mechanism of adsorption on Red 3BS dye onto LLS activated carbon, the pseudo-first-order model and pseudo-second-order model were used to test the experimental data of initial concentration. The slope and intercept of plot of log (q_e-q_t) versus t were used to determine the pseudo-first-order rate constant k_1 (h^{-1}), while the plot t/qt versus t shows a linear relationship. There is no need to know any parameter beforehand and *qe* and k_2 can be determined from the slope and intercept of the plot. The kinetics modelling was evaluated based on the experimental data plotted for adsorption capacity obtained of initial concentration of Red 3BS dye (25 mg/L -125 mg/L) for each particular contact time with constant temperature of 30°C. Based on the results correlation coefficients of the pseudo-second-order kinetic model for the linear plots of Red 3BS dye are more than 0.99. While pseudo-first-order are more than 0.77. Thus suggesting that adsorption can be described by the pseudo-second-kinetic model as can be seen in Table 3. Further, Tan et al, 2008 also presented that the methylene blue onto activated carbon prepared from coconut husk fits well the pseudo-second-order kinetic model.

Table 3 Kinetic parameters of Red 3BS adsorbed onto LLS activated carbon at different initial concentrations

C_0 (mg/L)	Pseudo-first -order kinetic model			Pseudo-seconds-order kinetic model		
	$q_{e,\,cal}$ (mg/g)	k_1 (h^{-1})	R^2	$q_{e,\,cal}$ (mg/g)	k_2 (h^{-1})	R^2
25	0.238	0.005	0.877	1.769	0.176	0.9989
50	0.986	0.0062	0.953	2.214	0.068	0.9989
75	0.973	0.0068	0.770	2.569	0.087	0.9900
100	1.252	0.0092	0.906	2.687	0.035	0.9951
125	1.444	0.0082	0.926	2.958	0.026	0.9927

4. CONCLUSION

The adsorption of reactive Red 3BS dye onto activated LLS adsorbent were carried out at various parameter which the adsorbent dosage ranges 0.2 g - 1.0 g, initial concentration is in the range 25 mg/L-125 mg/L and contact time range from 10 - 180 minutes, and initial pH range 2 - 12. The amount of dye adsorbed increases as the adsorbent dosage increases due to the increased the surface site availability of adsorbent. The maximum adsorption observed at pH 2 for LLS activated carbon. A decrease in the pH of solutions leads to a significant increase in the adsorption capacity of dye Red 3BS on the adsorbent. The experimental data shows that the adsorption of Red 3BS onto activated LLS adsorbent was best described by Langmuir isotherm model with adsorption capacity 2.945 (mg/g). It was found that the pseudo-second-order model was better in describing the adsorption kinetics of Red 3BS on LLS activated carbon.

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