Removal of Basic Blue 3 from Aqueous Solution by Adsorption Onto *Durio ziberthinus Murray* Husk

Siew-Teng Ong,* Siew-Ling Lee, Suat-Yen Tan, Pei-Sing Keng and Yung-Tse Hung

Abstract—Durian husk (DH), a fruit waste, was studied for its ability to remove Basic blue 3 (BB3) from aqueous solutions. Batch kinetic studies were carried out to study the sorption characteristics under various experimental conditions. The optimum pH for the dye removal occurred in the pH range of 3-10. Sorption was found to be concentration and agitation dependent. The kinetics of dye sorption fitted a pseudo-second order rate expression. Both Langmuir and Freundlich models appeared to provide reasonable fittings for the sorption data of BB3 on durian husk. Maximum sorption capacity calculated from the Langmuir model is 49.50 mg g^{-1}.

Keywords—Durian husk, Batch study, Sorption, Basic Blue 3

I. INTRODUCTION

THE extensive usage of dyes in many industries to color their products resulted in a huge amount of colored waste and this is worrying for both toxicology and aesthetical reasons [1]. Therefore, the removal of dyes from wastewater has become environmentally important not only for their high chemical and biological oxygen demand and suspended solids but also for their perturbing effect in photosynthetic activity in aquatic life due to reduced light penetration.

Some researchers have also determined that some dyes, dye precursors and their biotransformation products are toxic, mutagenic and carcinogenic in nature [2]. For example, basic dyes, which are predominantly used in colouring acrylic fibre, are generally more toxic than other classes of dyes [3]. Thus, the removal of basic dyes (such as BB3 in this study) from the environmental is worthwhile noting.

The range of conventional methods for dye removal includes advanced oxidation process, membrane separation, ion-exchange, photodegradation and carbon sorption. However, treating coloured wastewater by conventional treatment methods posted several difficulties and therefore,

researches have been focused on seeking a better and economical alternative. Amongst all, liquid phase adsorption is one of the most popular investigated methods for the removal of dyes. Sorption techniques have become increasingly popular not only because of its relatively low initial treatment cost, ease of operation, flexibility and simplicity of design, but also insensitivity to toxic pollutants and the availability of wide range of sorbents.

The commercially available activated carbon is considered to be an efficient sorbent for the removal of various dyes but the usage of activated carbon has been limited by its high cost due [4]. However, this sorption process still remains as an attractive alternative for the treatment of dye wastewaters if the sorbent is inexpensive and does not require an additional pre-treatment step before its application.

The amount of durian shell generated is approximately 350,000 tonnes, and direct discharge of this solid waste will cause the environmental problems [5]. Exploring the possibility usage of this locally abundant waste material not only will reduce the environment burden but could also be beneficial to the economy. However, a very limited study in the literature, has, hitherto reported on the potential of durian husk as the sorbent for dyes removal. Therefore, in this study efforts are attempted to evaluate the feasibility of using this solid waste as a sorbent for basic dye removal.

II. MATERIALS AND METHODS

A. Sorbent

Durian husk (DH) was collected and washed thoroughly to ensure the removal of dirt and other impurities. DH was then sun dried to remove the moisture content and the dried DH was ground to pass through a 1 mm-sieve.

B. Sorbate

Synthetic dye solution of Basic Blue, BB3 (C.I. = 51004, FW = 359.89, λ_{max} = 654 nm, Aldrich 25% purity) was used as sorbate in this study. This commercial dye was used without any further purification. Standard dye solution of 1000 mg L^{-1} of BB3 was prepared as stock solution and subsequently diluted when necessary.

C. Surface Characterization

Field emission scanning electron microscopy (FESEM) analysis was carried out to study the surface morphology of durian husk. The micrograph was taken using FESEM JSM 6701F (JEOL) operated at emission current of 2.00 kV with working distance of 6.0 mm.

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D. Batch Studies

All the batch sorption experiments were performed in duplicate by agitating 0.10 g of sorbent in 20 mL of 100 mg L⁻¹ dye solution at their natural pH (except the effect of pH parameter) in a centrifuge tube at 150 rpm on an orbital shaker for 4 h at room temperature (25 ± 2 °C) unless otherwise stated. The results presented are the means value. At the end of the sorption process, the mixtures were centrifuged at 3000 rpm phase separation. The BB3 dye concentrations were analysed using Perkin Elmer Lamda 35 double-beam UV/visible spectrophotometer at the wavelength corresponding to maximum absorption, $\lambda_{max} = 654$ nm. Dilutions were carried out when the measurement exceeded the linearity of the calibration curve.

The percentage uptake of BB3 was calculated by the following equation:

$$\text{Percentage removal} = \frac{C_o - C_e}{C_o} \times 100\% \qquad (1)$$

where C_o and C_e (mg L⁻¹) are the initial and equilibrium liquid phase concentration of BB3, respectively.

To study the effect of pH in the removal of BB3, a series of solution with concentration of 100 mg L⁻¹ was prepared. The initial pH of the dye solutions was adjusted to the range of 2-10 by adding dilute HCl or NaOH. Contact time experiments were performed with concentrations ranging from 50 to 200 mg L⁻¹. The samples were withdrawn and analyzed for their dye concentrations at predetermined intervals. Sorption isotherms were obtained by varying BB3 concentrations from 25 to 200 mg L⁻¹. Linear regression analyses were also carried out for isotherm studies to identify the best fit model for the sorption studies. The effect of agitation rate was studied by varying the agitation rates from 50 to 250 rpm.

III. RESULTS AND DISCUSSION

A. Characterization of Durian Husk

Fig. 1a and 1b depict the FESEM images of pristine durian husk. An unsmooth surface with structure of irregular in shape was found in the sample prepared. As shown in the FESEM image of higher magnification (Fig. 1b), the durian husk has a non porous configuration, in well agreement with previous report [6].

B. Effect of pH

The pH at point of zero charge (pH_{pzc}) of DH was determined by the mass titration method and found to be 5.0 [7]. As the surface charge of the sorbent and the degree of ionization of the sorbate will be affected by the pH of the solution, therefore the influence of initial pH was the first parameter to be investigated in this study. Fig. 2 shows the results of the percentage uptake of BB3 from pH 2 to 10. It is suggested that at lower pH, the sorbent's surface may get positively charged which is not favorable for the sorption of dye cations due to electrostatic repulsion. With increasing pH, the number of negatively charged sites increased, resulting in sorption sites that were made available for binding with BB3, and thus facilitate a higher percentage uptake. A noticeable and abrupt decrease in the percentage uptake was observed as the initial pH was increased from 10 to 11. The decrease is considered to be closely related to the precipitation that occurred. Similar observation was reported in the removal of Basic Green 4 by modified rice straw [8].
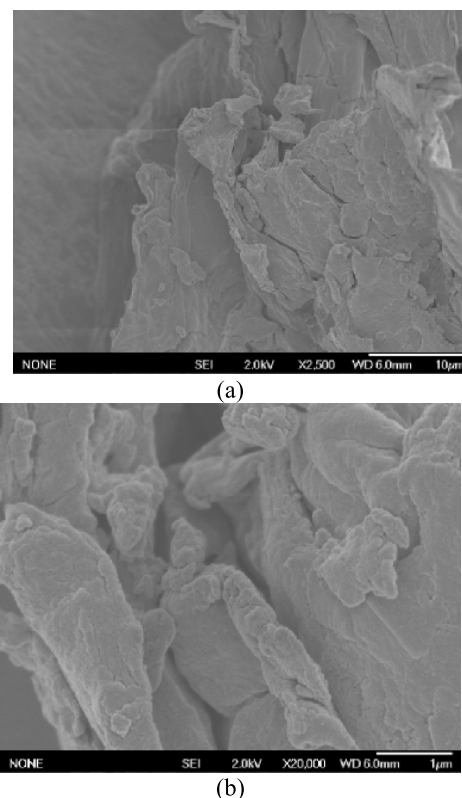

(a)

(b)

Fig. 1 FESEM images of DH with magnifications of (a) 2 500 ×; (b) 20 000 ×

C. Effect of Initial Dye Concentration and Contact Time

The influence of initial BB3 dye concentrations on the dye uptake by DH as a function of time is shown in Fig. 3. The percentage of uptake decreased with increasing solution concentration while the amount of dye adsorbed increased. The rate of sorption was very rapid and equilibrium was achieved within 120 minutes. As depicted from the same figure, the time taken to achieve equilibrium was independent of the initial dye concentration. The rapid uptake at the initial stage indicates that there were many available sites for sorption and attributes to the rapid attachment of the dye molecules to the surface of the sorbent.
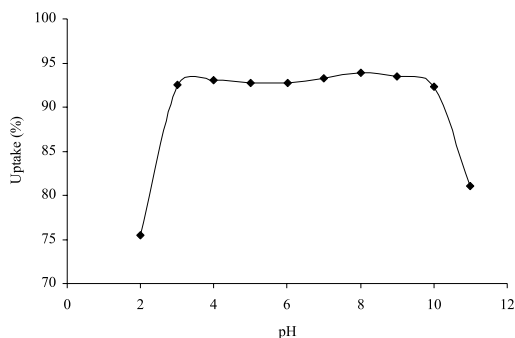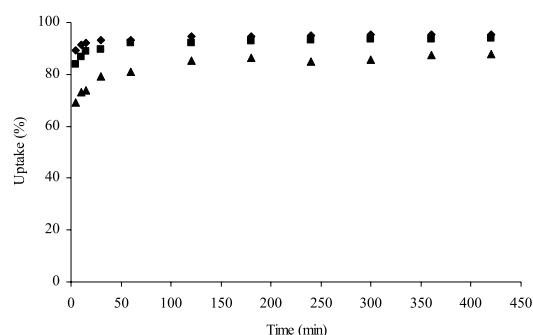
Fig. 2 Effect of pH on the adsorption of BB3 by DH

Fig. 3 Effect of initial dye concentrations and contact time on adsorption of BB3 by DH. $\blacklozenge$, $\blacksquare$, $\blacktriangle$ – 50, 100 and 200 mg L^{-1} of BB3

It is generally accepted that in a dynamic well stirred solid-liquid system, the sorption process can be separated into three stages [9-11]. At the first stage, BB3 dye molecules had to diffuse through the solution to the external surface of the DH, also known as film mass transfer. The second stage involved the diffusion within the pores of DH internal structure which required a longer time before it reached equilibrium and the third stage is the sorption of BB3 on the active sites on the internal surface of the pores. In addition, it was observed that the time profile of the removal was a smooth and continuous curve leading to saturation, indicating the possibility of the formation of monolayer coverage of dye on the surface of durian husk [12].

D.Kinetic Studies

In order to explore the kinetics involved in BB3 sorption, the experimental data was studied with respect to two different kinetic models, namely pseudo-first order model [13] and pseudo-second order model [14]. The linearized equations are expressed as follows:

pseudo-first order equation:

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{2}$$

and

pseudo-second order equation:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \tag{3}$$

where q_e = the amount of BB3 adsorbed at equilibrium (mg g^{-1}), q_t = the amount of BB3 adsorbed at time t (mg g^{-1}), k_1 = the rate constant of pseudo-first order kinetics (min^{-1}), h ($k_2 q_e^2$) = the initial sorption rate (mg g^{-1} min^{-1}) and k_2 = the rate constant of pseudo-second order kinetics (g mg^{-1} min^{-1}).

Values of k_1 for the pseudo-first order kinetic model were obtained from the slopes of the linear plots of log (q_e - q_t) versus t for the studied concentrations. It was found that the pseudo first order kinetic model did not fit well for the whole range of concentrations studied as the equilibrium sorption capacities calculated from this kinetic model gave unreasonable values compared to those determined experimentally (Tables 1 & 2). The application of pseudo second order kinetic model appeared to provide a better correlation of the experimental data than the pseudo first order model for the dye system. In addition the correlation coefficients for the pseudo first order kinetic model obtained at various concentrations are in general lower than those of the pseudo second order model (Tables 1 & 2). It thus appears that the system under study is more appropriately described by the pseudo-second order model which was based on the assumption that the rate limiting step may be chemical sorption or chemisorption involving valency forces through sharing or exchange of electron between sorbent and sorbate [15]. A number of authors have also reported on the applicability of pseudo-second order kinetics for the sorption process [16-20]. The values of q_e, k_2 and h against C_o in the corresponding linear plots of the pseudo-second order equation were regressed to obtain expressions for these values in terms of the initial dye concentration. Each of these parameters can be expressed as a function of C_o for BB3 as reported by [15]:

$$q_e = \frac{C_o}{A_q C_o + B_q} \tag{4}$$

$$k_2 = \frac{C_o}{A_k C_o + B_k} \tag{5}$$

$$h = \frac{C_o}{A_h C_o + B_h} \tag{6}$$

where A_q, B_q, A_k, B_k, A_h and B_h are constants related to the respective equations. The constant values can then be determined from the slopes and intercepts of the linear plots.

Thus, the generalized predictive models for BB3 adsorbed at any contact time and initial concentration within the given range with relationship of q_t, C_o and t can be represented as follows by substituting the various values in the equations mentioned earlier into Equation (3).

TABLE I
PSEUDO-FIRST ORDER KINETIC MODEL PARAMETERS FOR DIFFERENT INITIAL BB3 CONCENTRATIONS

Initial BB3 conc. (mg L^{-1})	$q_{e, exp}$ (mg g^{-1})	Pseudo-first order kinetic model		
		$q_{e, cal}$ (mg g^{-1})	k_1 (min^{-1})	R^2
50	8.435	0.152	-4.201×10^{-3}	0.235
100	18.377	0.5925	-2.011×10^{-4}	0.002
200	30.860	2.805	3.502×10^{-3}	0.579

TABLE II
PSEUDO -SECOND ORDER KINETIC MODEL PARAMETERS FOR DIFFERENT INITIAL BB3 CONCENTRATIONS

Initial BB3 conc. (mg L^{-1})	$q_{e, exp}$ (mg g^{-1})	Pseudo-second order kinetic model			
		$q_{e, cal}$ (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	h (mg mg^{-1} min^{-1})	R^2
50	8.435	8.482	1.396×10^{-1}	10.040	1.000
100	18.377	18.519	4.091×10^{-2}	14.025	1.000
200	30.860	32.154	8.501×10^{-3}	8.787	0.999

The theoretical model for BB3-DH system can therefore be represented as:

$$q_t = \frac{C_o t}{0.0973 C_o - 0.1913 + (0.0026 C_o + 5.1126)t} \quad (7)$$

Equation 7 was employed to represent the generalized predictive model for BB3 adsorbed at any contact time and initial dye concentration within a given range. Fig. 4 shows a typical plot of comparison between the experimental and theoretically pseudo-second order modelled time profile for BB3 sorption by DH. It is evident that the pseudo-second order rate law provided a good prediction for the amounts of BB3 adsorbed over the studied range.

E. Sorption Isotherms

The sorption properties and equilibrium data, commonly known as sorption isotherms can provide the basic and fundamental information on the sorbate-sorbent interactions. As the information gathered from this parameter are important for evaluating the applicability of the sorption process as a unit operation therefore the equilibrium sorption data of BB3 on DH are fitted into two well-known isotherms, namely Langmuir and Freundlich equations.

The linear form of Langmuir isotherm model is given by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{Q_o K_L} + \frac{C_e}{Q_o} \quad (8)$$

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

$$\log q_e = \frac{\log C_e}{n} + \log K_f \quad (9)$$

where C_e = the equilibrium liquid phase dye concentration (mg L^{-1}), q_e = the amount of dye adsorbed at equilibrium (mg g^{-1}), Q_o = the maximum sorption capacity (mg g^{-1}), K_L = the sorption equilibrium constant (L mg^{-1}), n = Freundlich constant for intensity and K_f = Freundlich constant for sorption capacity. The slope of $1/n$ ranging between 0 and 1 is a measure of sorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero [21] A value for $1/n$ below one indicates a normal Langmuir isotherm while $1/n$ above one is indicative of cooperative sorption [22].
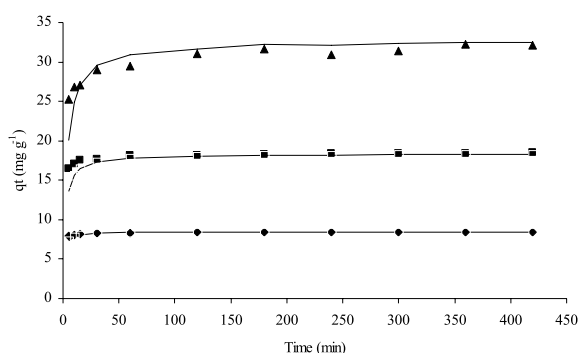

Fig. 4 Comparison between the measured and pseudo-second order modelled time profiles for BB3 adsorption by DH. ♦, ■, ▲ – 50, 100 and 200 mg L^{-1} of BB3. Symbol- experimental; Line – theoretical

The parameters determined from each isotherm model are listed in Table 3. Although based on different assumptions: Langmuir model implies monolayer coverage and constant sorption energy while the Freundlich model deals with physicochemical sorption on heterogeneous surfaces, the experimental data appeared to fit in well in both isotherm models. Applicability of both isotherms to sorption of dyes by agricultural wastes and activated carbons prepared from wastes have been reported previously [16,23,24]. Notwithstanding this, Langmuir model allows the calculation of maximum sorption capacities (Table 3) that could be useful for the comparison of the sorption efficiency of material studied.

F. Effect of Agitation Rate

The experimental results obtained from a series of contact time studies for the sorption of BB3 onto DH in which the degree of agitation was varied from 50 rpm to 250 rpm are presented in Fig. 5. It was noted that the uptake of BB3 increased with increasing agitation rate from 50 to 150 rpm, thereafter, the effect was minimal. Agitation rate is a classic parameter in sorption process. The speed of agitation has an influential role in the distribution of the BB3 dye molecules in

the bulk solution and the formation of the external boundary layer.

TABLE III
LANGMUIR AND FREUNDLICH ISOTHERM MODEL CONSTANTS AND CORRELATION COEFFICIENTS FOR SORPTION OF BB3 BY DH

Langmuir Isotherm	Q_o (mg g^{-1})	K_L (L mg^{-1})	R^2	R_L
	49.50	0.092	0.995	0.056
Freundlich Isotherm	K_F	$1/n$	R^2	
	4.854	0.666	0.984	
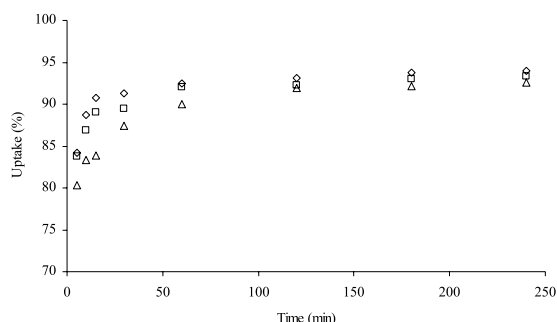
Fig. 5 Effect of agitation rate on sorption of BB3 by DH. △, □, ◇, – 50, 150 and 250 rpm

Increasing the degree of agitation would reduce the resistance of the boundary film and increase the system mobility and hence increase the rate of sorption. Similar observations have been reported in the removal of Reactive Orange 16 and Methylene Blue by modified rice husk [16,25]. From the study of beech sawdust, the effect of stirring speed on the sorption rate constant was affected by the agitation speed of 0 to 200 rpm [26]. However, the small effect of agitation in the range of 200 to 600 rpm showed that external mass transfer was not the rate limiting step, and implied that intraparticle diffusion resistance need to be included in the analysis of the overall sorption.

IV. CONCLUSION

This study has shown the effectiveness of durian husk as a potential low cost sorbent for the removal of BB3 in aqueous solutions. In the batch studies, the results indicated that sorption capacity of durian husk was considerably affected by initial BB3 concentrations, contact time, pH, agitation rate and temperature. The optimal pH for the removal of BB3 was in the range of 3-10. Equilibrium sorption data conform to both Langmuir and Freundlich isotherms and maximum sorption capacity was 49.50 mg g^{-1}. Analysis of the kinetics data implied that pseudo-second order kinetics model provided a better correlation of the experimental results than pseudo-first order kinetic. The sorption profiles derived based on the pseudo-second order kinetic model showed good agreement with the experimental curves. Besides, the percentage of BB3 uptake increased with elevating agitation rate and temperature.

The thermodynamics data showed that the sorption was an endothermic process.

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