ADSORPTION OF REMAZOL DYE ONTO GRANULAR ACTIVATED CARBON IN FIXED BED: A CASE STUDY OF RED 3BS

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ABSTRACT

A remazol reactive dye, namely Red 3BS, was used in the adsorption study using granular activated carbon (GAC). In batch test, dye solution was shook with the activated carbon for 5 days for equilibrium to achieve. The Langmuir adsorption isotherm was found to fit the experimental data from batch test better than the Freundlich adsorption isotherm. This was due to the relatively high ambient temperature that allowed only monolayer adsorption to occur. The van der Waals force that forms multilayer adsorption was overcome by the adsorbate due to the high ambient temperature. In fixed bed column modeling, adsorption of Red 3BS dye at three different flow rates was investigated. Empty bed contact times (EBCT) determined at varying the flow rates ranged between 3.85 – 47.51 minutes. The bed depth service time graph (BDST) was found to be linear for Red 3BS dye, as expected. The correlation coefficients (R^2) obtained for the BDST graph for the dye was greater than 0.98. In this study, the Adam-Bohart model was found to fit the experimental data better for higher EBCTs as compared to lower EBCTs.

Key words: *Dye, Activated Carbon, Breakthrough Curve, Bed Depth Service Time, Empty Bed Contact Time*

INTRODUCTION

One of the major concerns of textile wastewater is coloured effluent and the disposal of these wastes into receiving waters. Coloured effluents have been produced, most certainly, since the dyeing technique was invented. Though not particularly toxic, dyes have an adverse aesthetic effect because they are visible pollutants. The presence of colour will affect photosynthetic activity in aquatic life due to reduced light penetration.

The main pollution source of textile wastewater as in batik industry comes from the dyeing processes. Remazol reactive dyes are, commercially a very important class of textiles dyes, whose losses through processing are partcularly significant and difficult to treat. Many physical and chemical treatment methods including adsorption, coagulation, precipitation, filtration, electrodialysis, membrane separation and oxidation have been used for the treatment of dye containing effluents. The adsorption process is one of the most efficient methods of removing pollutants from wastewater. Further, the adsorption process provides an attractive alternative treatment, especially if the adsorbent is inexpensive and readily available [1].

Activated carbon is the most widely used adsorbent for the removal of colour from textile effluents because it has a high capacity for organic matter. Activated carbon is produced from organic based materials such as in this case, coconut shells. The raw material is carbonized to obtain the char or carbonaceous material, which is activated to yield the highly porous final product. The activated carbon particle has two types of pores existing in it by which adsorption take place, i.e. macropores ($>10^{-1}\mu m$) and the micropores (10^{-3}-$10^{-1}\mu m$). The macropores provide a passageway to the particle's interior and to the micropores but do not contribute substantially to the particle surface area. The micropores, on the other hand, are responsible for the large surface area of activated carbon particles and are created during the activation process. It is in the micro pores that adsorption largely takes place [2].

The purpose of this study was to predict the breakthroughs in an activated carbon column. The bed depth service time (BDST) model proposed by Adam and Bohart as offering the simplest approach and most rapid prediction of adsorber performance [3]. In this study, the batch test was conducted to investigate the adsorption capacity of remazol reactive dye, red 3BS, onto the granular activated carbon.

Theory

The original work on BDST was carried out by Adam and Bohart, who proposed a relationship between bed depth (H) and the time taken for breakthrough to occur [4]. The focus of this relationship is that the rate of adsorption is controlled by the surface reaction between the adsorbate and the unused capacity of the adsorbent (solid). The service time (t) was related to the process conditions and operating parameters:,

$$\ln\left(\frac{C_O}{C}-1\right)=\ln\left(e^{KN_O H/V}-1\right)-KC_o t \quad (1)$$

where t is the time required for the effluent to reach specified breakthrough concentration, K is a rate constant, and V is the superficial liquid velocity and N_O is the initial value of adsorptive capacity. The values of the function $e^{KNoH/V}$ is usually much larger than unity, the unity term within the bracket is often neglected, leaving t,

$$t=\frac{N_O}{C_O V}H-\frac{1}{KC_O}\ln\left(\frac{C_O}{C}-1\right) \quad (2)$$

Assuming C_O and V are constants, a plot of t versus H should yield a straight line where this graph is called the bed depth service time or BDST graph. Both parameters N_O and K can be obtained from the slope and the intercepts respectively.

MATERIALS AND METHODS

Adsorbate and adsorbent

Granular activated carbon (GAC) used as an adsorbent made from coconut shell was supplied by Kekwa Indah Sdn Bhd in Nilai, Negeri Sembilan. Red 3BS, a remazol reactive dye is used as adsobate in this study.

Preparation of adsorbent

The GAC was crushed using a stainless steel blender to reduce the size. The crushed GAC was sieve using 2 sieves with the size of 250µm and 850µm respectively, where the those retained between these two sieve were used in the study. This was to reduce the time needed to achieve equilibrium. The GAC was washed thoroughly with deionised water to remove any impurities [4]. Washed GAC was then heated in an oven at 110°C for 24 hours [5]. After the GAC had been dried in the oven, it was then stored in a desiccator for use as required.

The apparatus used in the study were washed with deionised water to remove impurities which may cause some adsorbate in the liquid phase to adsorb onto the impurities surface instead and may affect the accuracy of the experimental result.

Experimental Procedure

In the fixed bed column modeling, the column that was used had an inside diameter of 0.025 m and 1.5 m high. Preliminary studies had shown that the GAC used had low adsorption capacity for Red 3BS dye. Therefore, the height of GAC packed was 0.6 m. The tank containing the Red 3BS dye sample was placed at a higher elevation so that the dye solution could be introduced into the column by gravitational flow. Three flow rates were used for the dye which was in the range of 5 – 40 ml/min. The initial concentration of the dye solution was predetermined and was in the range between 70 and 80 mg/L. At various time interval, the absorbance of the effluent sample was determined using UV spectrophotometer, model Cary 50 Series and the concentration obtained from the calibration curve.

RESULTS AND DISCUSSION

Adsorption Isotherms

The equilibrium isotherms were determined previously and were found to conform to a Langmuir better than the Freundlich adsorption isotherm [6]. The correlation coefficient, (R^2) obtained for the Langmuir equation was 0.9191 while the correlation coefficient obtained for the Freundlich equation was 0.8726. The Freundlich and Langmuir adsorption isotherm constant for Red 3BS dye is shown in Table 1.

Table 1. Langmuir and Freundlich constants for the adsorption of 3BS dye [6].

Adsorption Equation	*Equation*	*Constant*	*R^2*
Freundlich	$q_e = 1.72\, C_e^{0.2147}$	$k_f = 1.72$ $1/n = 0.2147$	0.8726
Langmuir	$q_e = \dfrac{0.812C_e}{1+0.189C_e}$	$a = 4.30$ mg/g $b = 0.189$ L/mg	0.9191

Column Studies

The calibration curves obtained for Red 3BS dye is shown in Fig. 1. The correlation coefficient (R^2) obtained is greater than 0.99. Therefore, within this range of concentration, absorbance varies linearly with concentration, which follows the Lambert – Beer law [5].

In this study, the bed depth for Red 3BS dye was held constant except for the flow rates. Therefore, the Adam-Bohart equation has to be modified. Changing of the flow rate will affect the superficial liquid velocity *V*. Empty bed contact time or *EBCT* is the contact time between the activated carbon and the liquid phase. Therefore,

$$t = \left(\frac{N_O}{C_O}\right) EBCT - \frac{1}{C_O K}\ln\left(\frac{C_O}{C} - 1\right) \tag{3}$$

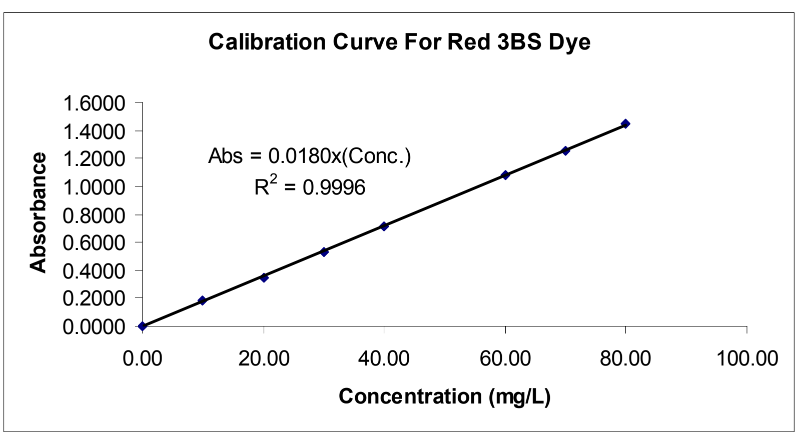

Fig. 1. Calibration curve for Red 3BS dye.

The BDST graph can be obtained by plotting *t* versus *EBCT*. BDST graph was plotted for breakthrough points at 0.3, 0.5, and 0.6 for Red 3BS dye. BDST graphs obtained Red 3BS dye is shown in Fig. 2.

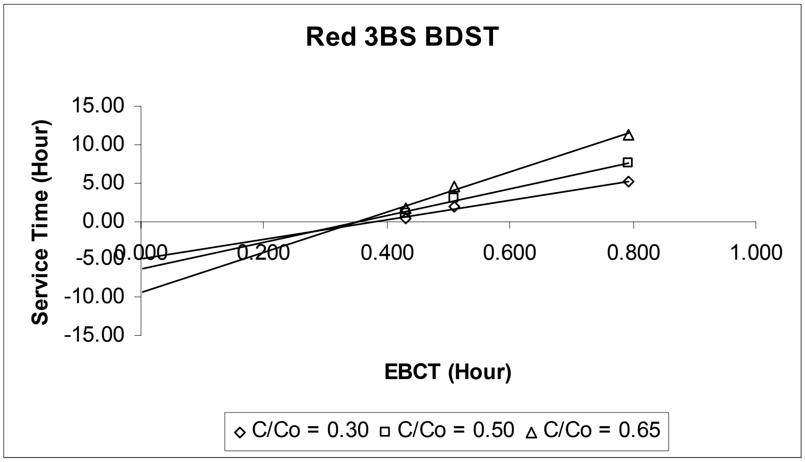

Fig. 2. Bed depth service time graph for Red 3BS dye.

The BDST graph shows a linear relationship for the selected breakthrough points with different EBCT for Red 3BS dye. The correlation coefficients obtained from the graph was greater than 0.98, which means that equation (3) can be used to predict various breakthrough points for different EBCT. Table 2 shows the correlation coefficient obtained for the selected breakthrough points for Red 3BS dye.

From the BDST graph, the adsorptive capacity N_O, can be determined from the slope. The slope from the BDST graph represents N_O/C_O. The rate constant, *K* can be determined from the interception of the linear line on the y-axis, as

$$K = -\frac{1}{C_O b}\ln\left(\frac{C_O}{C}-1\right) \quad (4)$$

To predict the breakthrough curve, the breakthrough point at 0.3 will be used for Red 3BS dye. Table 3 shows the constant N_O and *K* obtained at breakthrough point 0.3. In Fig. 3, the experimental data was fitted with the Adam-Bohart equation with three different EBCT.

Table 2. Calculated correlation coefficient for BDST graph on Red 3BS dye.

Dye	*Breakthrough point (C/C_O)*	*Slope*	*Interception at y-axis*	R^2
	0.3	12.90	-5.035	0.9942
Red 3BS	0.5	17.68	-6.350	0.9947
	0.65	26.08	-9.250	0.9810

In order to determine whether the Adam-Bohart model fitted with the experimental data, a statistical measure the root mean square error or RMSE was used. This statistical measure was also used by Summers and Robert [7] to simulate the breakthrough of DOC by activated carbon beds. The root mean square error was calculated using equation (5) and the calculated RMSE for Red 3BS dye are shown in Table 4.

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$$RMSE = \left[\frac{\sum_{j=1}^{m} (X_j^P - X_j)^2}{n_r} \right]^{1/2} \tag{5}$$

where, X_j^P = predicted fractional concentration

X_j = measured fractional concentration

n_r = number of data

Table 3. Calculated adsorptive capacity and rate constant at breakthrough point 0.3.

Dye	*C_O (mg/L)*	*N_O (mg/L)*	*K (L/mg.h)*
Red 3BS	75.37	972.3	0.002233

Table 4. Calculated root mean square error for Red 3BS dye.

Dye	*EBCT (min)*	*RMSE*
	11.37	0.1283
Red 3BS	30.52	0.1636
	47.51	0.1303

Generally, the RMSE value increased when the EBCT decreased. This means that lower EBCT or faster flow rate used in the column test will result in greater deviation from the Adam-Bohart equation. The reason is that, when flow rate is slower the equilibrium corresponding to the batch experiment could be reached. The shape of the breakthrough curves that were produced from slower flow rates approximates closely to the ideal breakthrough curve [5]. Therefore for faster flow rates, the breakthrough curves deviate further from the ideal breakthrough curves which result in larger RMSE values. The experimental data obtained for the breakthrough curve from the experiment deviated from the Adam-Bohart equation by about 8 to 16 percentage.

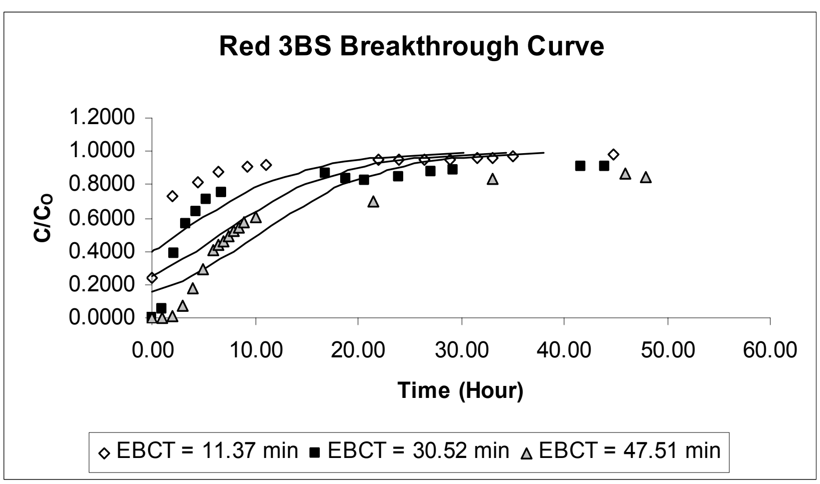

Fig. 3. Simulation of Adam-Bohart equation for Red 3BS dye.

CONCLUSION

The BDST model is a useful tool for determining the performance of bed operating under different process variables such as flow rates. The relationships proposed to predict the effect of these parameters gave a reasonable approximations to experimental results. The deviations for the *EBCT* that were studied ranged between 8 – 16 %. The experiment also found that the activated carbon that was used had low adsorptive capacity for Red 3BS dye. The RMSE that were calculated showed that the experimental data obtained for higher EBCT was closer to the prediction by the Adam-Bohart equation. The reason to this is that a high contact time with the activated carbon will produce an ideal breakthrough curve, as predicted by the Adam-Bohart equation.

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