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ADSORPTION OF AN ACID TEXTILE DYE IN FIXED BED COLUMN SYSTEM BY ACTIVATED CARBON PRODUCED FROM TREE BARKS

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ABSTRACT

In the present study, a low cost activated carbon which produced from *Eucalyptus camaldulensis* barks (ECAC) was used for the removal of Acid red 360 (360) with fixed bed column adsorption systems. The data from the column experiences were fitted to the Thomas and BDST models to predict the dynamic behavior, breakthrough performance, and adsorption capacity of the column. The BDST model described (R^2=0.997) the fix bed adsorption process well with correlation coefficients range between from 0.975 to 0.999. Also BDST model showed that the breakthrough time has a linear relationship with the bed depth. The Thomas model predicted 259.41 mg/gr maximum adsorption capacity of the EBMC for AR360 with a 0.997 correlation coefficient under certain conditions. The experiments showed that the breakthrough time significantly increased by increasing column bed depth and decreased by increasing initial AR360 concentration.

Keywords: Activated carbon, *Eucalyptus,* Adsorption

INTRODUCTION

Influent wastewaters of treatment plants coming from industrial plants may contain various chemicals such as dyes that are difficult to remove from wastewaters. The dye producing capacity of industries is very large. These wastewaters contain about 10000 different dyes, and their weight is approximately 0.7 million tons. During the dyeing processes, a large amount of these dyes are discharged by effluents to the receiving environment (1). The amount of dye loss varies from 2% to 50% depending on the type of dye during the dyeing process (2).

Dyes are stable and resistant to being biodegradable, and they can cause aesthetic problems even in low concentrations in an aquatic environment (3, 4). Colored wastewaters may cause serious ecological problems. Their carcinogenic and toxic effect to certain forms of aquatic life is well known (1). When dyes reach to the aquatic environment, they cover the water surface and prevent light transmission and photosynthesis (5).

Adsorption systems have gained prominence as treatment processes which ensure good quality effluents that are low in the concentrations of dissolved organic compounds, such as dyes (6). Activated carbon is one of the most popular and widely-used adsorbents. In most industries, activated carbon is used for the treatment of toxic, non-biodegradable process effluents and as a tertiary treatment following biological oxidation (7). On the other hand, application of commercially activated carbons remains limited due the high cost resulting from the production of activated carbon from expensive materials, such as coal (8).

The aim of this study is to investigate the use of an activated carbon produced from *Eucalyptus camaldulensis* bark as a novel low-cost adsorbent for the removal of Acid Red 360 from aqueous solution with fixed bed column systems. The *E. camaldulensis* barks were selected as a low-cost adsorbent due to their renewable characteristics, and their wide availability and accessibility.

MATERIAL AND METHODS

Synthesis of ECAC.

Eucalyptus camalduensis barks were collected from the campus of Cukurova. The barks were washed with water to remove impurities and dried at 60°C for 48 hours. The barks were crushed and sieved to 2-4 mm particle size. Then the material was carbonized at 400°C for three hours with 15°C/min heating rate. NaOH was used for the chemical activation of carbonized barks. 4 N NaOH (500 mL) was used for impregnation of 20 g carbonized barks at 80°C until the liquid phase evaporated. Chemically activated material was washed with distilled water and thermally reactivated at 600°C for two hours. ECAC was cooled at room temperature, crushed and sieved to desired particle sizes.

Dye

The AR360 concentrations in the solutions were determined by using a UV–visible recording spectrophotometer (Chebios Opitimum-one). To calculate the concentration of the dyes in the aqueous solution, calibration between the dye concentration (C) and absorbency (A) was employed. The dye concentrations were analyzed at a 531 nm wavelength.

Column Experiments.

Column experiments were achieved according to the rapid small scale column test (RSSCT) procedure. RSSCT was applied to reduce the experience time and the cost (7).Data obtained from RSSCT can be used for predicting the performance of full scale carbon columns. Mathematical models (eq(1)-(2)) were used to define the relations between parameters for small and large columns**.**

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \frac{t_{SC}}{t_{LC}} \quad (1)$$

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \frac{d^2{}_{SC}}{d^2{}_{LC}} \quad (2)$$

$EBCT_{SC}$ = Empty bed contact time for small column, min
$EBCT_{LC}$ = Empty bed contact time for large column, min
t_{SC}= Service time for small column, min
t_{LC}= Service time for large column, min
d_{SC}= Particle diameter in short column, mm
d_{LC}= Particle diameter in large column, mm (9).

In column adsorption experiments, three initial concentrations of AR360 were prepared at 100 mg/L, 200 mg/L and 400 mg/L. A plexiglass column, 20 cm length and 0.9 cm internal diameter, was used for column experiments. Feeding of dye solution to the column was carried out under upflow conditions by a peristaltic pump. Effluent dye concentrations (C_t, mg/L) was periodically collected and analyzed by spectrophotometer. The breakthrough concentration was determined (C_b) at 10% initial concentration and 90% of initial concentration was determined exhaust point. Three different bed depths (5 cm, 10 cm, 15 cm) and a constant flow rate, 20 ml/min were used in the study. The sorbent was closed by glass wool for good inlet solution distribution and escape of sorbent particles from column was prevented.

Table 1. Column parameters

Parameters	Bed Depth		
	15 cm	**10 cm**	**5 cm**
ECAC amount, g	5	3.3	1.65
EBCT, min	0.477	0.318	0.159
Vcolumn, cm^3	9.54	6.36	3.18
Carbon particle size, mm	0.15	0.15	0.15
Flow rate, mL/min	20	20	20

RESULTS AND DISCUSSION

Breakthrough curves

The breakthrough curves of the different AR360 concentrations at different bed depths are given in Figure 1. It was found that the initial AR360 concentration and ECAC bed depth had significant effect on breakthrough time. The breakthrough curves show that increasing bed depth of sorbent caused to an increase in breakthrough time due to an increase of the surface area of sorbent. The increasing in the retention time allows the dye molecules to diffuse deeper into EBMC (10). Therefore, high dye removal efficiencies were obtained at high bed depths. Increasing of feeding dye concentration leads to reach breakthrough time earlier due to more sorbate contact with adsorption sites. The parameters of breakthrough curves are given in Table 2.

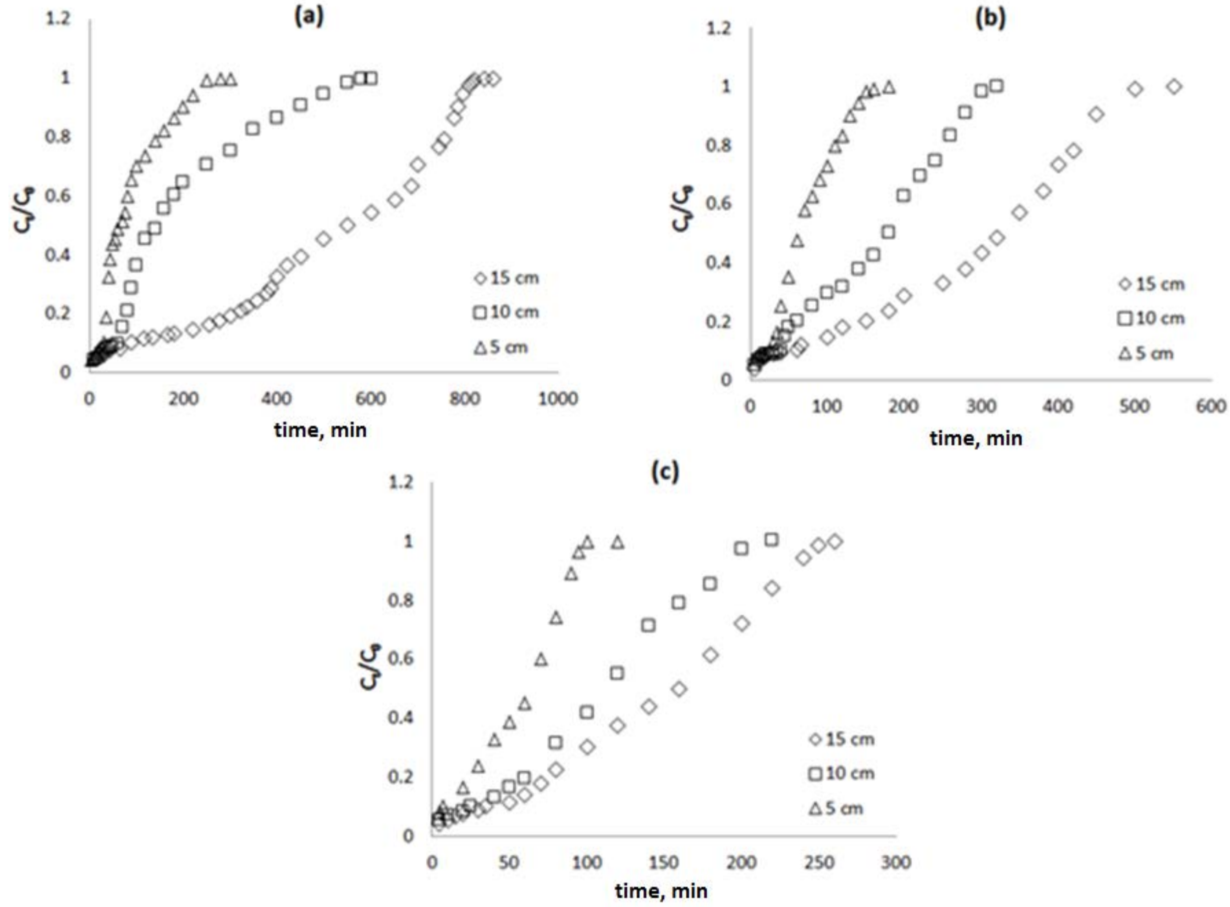

Figure 1. The breakthrough curves of different AR360 concentrations for different bed depths (pH=7, T=20 °C, Q= 20 mL/min)

Table 2. Parameters of breakthrough curves

C_0 (mg/L)	Bed depth (cm)	%10 t_b (min	%90 t_{exh} (min)
100	5	34	280
	10	60	600
	15	88	840
200	5	23	180
	10	40	320
	15	63	550
400	5	7	100
	10	25	210
	15	35	270

Data obtained from RSSCT was used for the prediction of large column performance. The small scale and large scale column performances were given Table 3. It can be seen from Table 3, while t_b was found to be 88 min (100 mg/L AR360 and 15 cm bed depth) for small scale column, the t_b was calculated 36 hours (100 mg/L AR360 and 15 cm bed depth) for large scale column. Table 3 showed that ECAC possesses a potential low-cost adsorbent for the removal of AR360.

Table 3. Performance of small and large column

Parameters		AR360 Concentration, mg/L								
		100			200			400		
		5 cm	10 cm	15 cm	5 cm	10 cm	15 cm	5 cm	10 cm	15 cm
t_b	Small Column (min)	34	60	88	23	40	63	7	25	35
	Large Column (h)	14.2	25	36	8.5	16.6	26.19	2.91	10.5	14.5
EBCT	Small Column (min)	0.159	0.318	0.477	0.159	0.318	0.477	0.159	0.318	0.477
	Large Column (min)	3.97	7.95	11.9	3.97	7.95	11.9	3.97	7.95	11.9
V, m/h	Small Column	18.86								
	Small Column	3.77								

Fixed Bed Column Isotherms

The data from the column experiences were fitted to the Thomas and BDST models to predict the dynamic behavior, breakthrough performance, and adsorption capacity of the column.

Thomas Model. The Thomas model is one of the most widely used models in fixed bed columns adsorption systems. This model uses the Langmuir isotherm and second order reversible reaction kinetics. Thomas assumes a constant separation factor which is feasible for favorable and unfavorable sorption conditions. According to the Thomas model, chemical reaction kinetics do not limit the phenomenon of the adsorption. Generally, the sorption is controlled by an interphase mass transfer. This model is usually convenient for the adsorption processes in which external and internal diffusion limitations are not present. The Thomas adsorption model derived the mathematical expression (eq(3)) for the fixed bed columns with a typical breakthrough curve. C_0 is the initial dye concentration (mg/L), C_t is the concentration (mg/L) at time (min), k_T is the Thomas constant (L/min/mg), Q is the volumetric flow rate (mL/min), q_m is the maximum adsorption capacity in column (mg/g), m is the mass of adsorbent in the column (g), and V is the throughput treated volume (L). The linear equation of the Thomas model was given in eq (1). The k_T and q_m were obtained from the slope and intercept of the linear plot of ln [(C_0/C_t) - 1] versus (V) (11). The constants of the Thomas model for the different experimental conditions are given in Table 2.

$$\ln\left(\frac{C_0}{C_t}-1\right)=\frac{k_T q_m m}{Q}-\frac{k_T C_0}{Q}V \qquad (3)$$

Table 4.Thomas model constants

C_o (mg/L)	Bed depth (cm)	q_m(mg/g)	k_T (L/min.mg)	R^2
100	5	204.96	0.0583	0.953
	10	124.09	0.125	0.939
	15	132.3	0.268	0.905
200	5	244.77	0.0469	0.965
	10	188.61	0.0909	0.951
	15	167.87	0.219	0.971
400	5	234.05	0.0525	0.978
	10	259.41	0.0658	0.997
	15	257.01	0.133	0.937

The regression coefficients obtained from the Thomas model range from 0.905 to 0.997 According to the R^2 values, the Thomas model yielded a moderate fit to the experimental data. The Thomas model predicted 259.41 mg/g q_m for 400mg/L AR360 and 10 cm bed depth. Generally the predicted adsorption capacity was increased with increasing initial dye concentration and decreasing ECAC bed depth.

BDST Model

The BDST is a simple model for predicting the relationship between the bed depth and the service time in terms of the inlet concentrations and adsorption conditions. This model is based on physically measuring the capacity of the bed at different breakthrough values. According to the BDST model, the bed depth and the breakthrough time show a linear relationship. It ignores the intra-particle mass transfer resistance and external film resistance such that the adsorbate is adsorbed onto the adsorbent surface directly. It states that the bed height, Z and service time, t of a column bears a linear relationship (12). t_b is the service time (min), N_o is the volumetric adsorption capacity (g/L), C_0 is the initial concentration (mg/L), C_b is breakthrough concentration (mg/L), Z is the depth of bed (dm), Q linear volumetric flow rate (L/min), and K_a is the BDST rate constant (L/g.min). The linear equation of BDST is given in eq (4).

$$t_b = \left(\frac{N_0}{C_0}\right)Z - \frac{1}{K_a C_0}\ln\left(\frac{C_0}{C_b} - 1\right) \tag{4}$$

The K_a and N_0 were calculated from the intercept and slope of the linear plot of ln (C_0/C_b-1) against t_b. The parameters and plots of the BDST model are given in both Table 5 and Figure 4.

The regression coefficients obtained from the BDST model range from 0.975 to 0.999. R^2 values demonstrate that the breakthrough time (t_b) has a highly linear relationship with the bed depth (13). The N_0 was used to predict adsorption capacity of ECAC for AR360 under a continuous flow condition. The N_0 was found to be 224.45 g/L for 400 mg/L AR360. The value of N_0 indicates that the ECAC is an effective adsorbent for the removal of AR360.

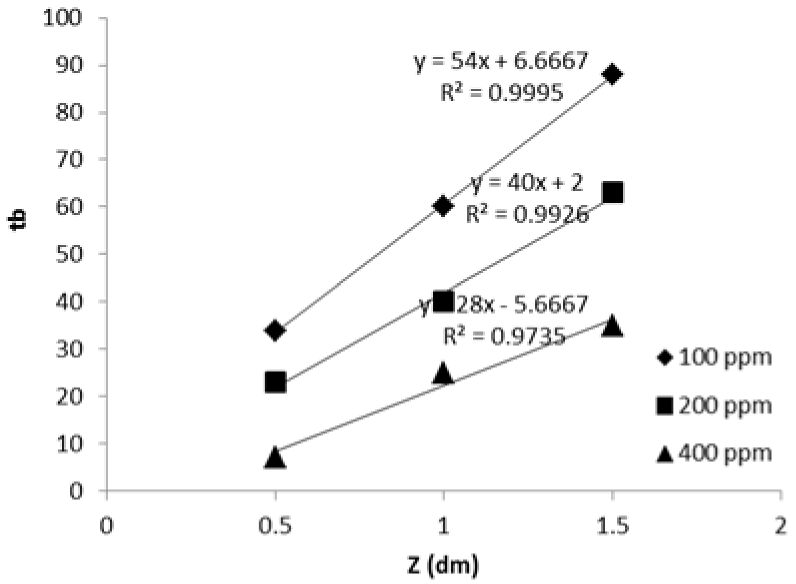

Figure 4. Plots of BDST model

Tablo 5. BDST Parameters

Parameter	AR360 Conc. (mg/L)		
	100	200	400
N (g/L)	10.8	16.25	224.45
K_a (L/g/min.)	-0.00329	-0.00549	-0.000962
R^2	0.999	0.992	0.975

CONCLUSIONS

The result from the present study show that the ECAC can be used as an alternative low cost adsorbent for the effective removal of AR360 from aqueous solution with a fixed bed column adsorption system. It was found that the initial dye concentration and ECAC bed depth had a considerable effect on the breakthrough time. The experiments showed that the breakthrough time significantly increased by increasing the bed depth. On the other hand the breakthrough time decreased by increasing dye concentration. While t_b was found to be 88 min (100 mg/L AR360 and 15 cm bed depth) for small scale column, it was calculated 36 hours (100 mg/L AR360 and 15 cm bed depth) for large scale column. The data was fitted to the continuous systems adsorption isotherms. The Thomas model predicted 259.41 mg/gr maximum adsorption capacity of the ECAC for AR360 with a 0.997 correlation coefficient under certain conditions. The BDST model showed that the breakthrough time has a linear relationship with the bed depth.

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