
Adsorptive Removal of Congo Red Dye from Aqueous Solutions by Activated Carbon Columns

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ABSTRACT:

Our water stream are getting polluted day by day due to direct discharge of untreated industrial waste. Various industries such as food, paper, textile, cosmetics use dyes for colouring and discharges harmful colored effluents in surface waters. The present paper deals with the dynamic adsorption of congo red dye from aqueous solution using activated carbons (ACG-100 and I-60). The effect of different parameters such as hydraulic loading rate, the bed depth and the feed concentration were studied. The results obtained are S-shaped breakthrough curves shows that the breakthrough time (t_b) increases on increasing the bed depth but decreases on increasing the HLR and feed concentration. The different adsorption zone parameters and column design parameters have been determined using Michaels equations, Bed Depth Service Time (BDST) models, Hutchins equations. The experimental and theoretical values agree reasonably.

KEYWORDS: Adsorption. Fixed bed column, Breakthrough curves, BDST, Hutchins equations.

1 INTRODUCTION

Many industries such as food, paper, textile, cosmetics use dyes for colouring and discharges colored effluents in surface waters which are harmful to human and the aquatic life. Congo red is one such dye which causes skin irritation and allergic reaction when comes into contact with human body [1]. Therefore its removal from water is of considerable importance. Several adsorbents such as red mud [2] and CaCl₂ modified bentonite [3] have been used for the removal of congo red dye from water. The adsorption capacity of these adsorbents is very low. Activated carbon adsorbents because of their high surface area and porosity have been used successfully for the removal of this dye. Namasivayam and Kavitha [4] used an activated carbon prepared from coir pith for an adsorptive removal of congo red dye and found that the adsorption was better under acidic pH. Ahmad and Mondal [5] conducted batch and column adsorption experiments to investigate the removal of dyes such as congo red and malachite green from wastewater by water nut modified carbon (WNMC). Acidic pH was favorable for adsorption of congo red dye and basic pH was favorable for the adsorption for malachite green dye. The column adsorption data was in good agreement with bed depth service time (BDST) model.

Goyal et al [6] reported that the adsorption of methylene blue increased on oxidation of activated carbons due to the formation of acidic carbon-oxygen surface groups and decreased on degassing due to the elimination of these groups. Similar results were observed by Aggarwal and Goyal [7] which showed that the adsorption of cationic dye rhodamine B increased on oxidation but decreased on degassing of the oxidized activated carbons. However in the case of an anionic dye metanil yellow, the adsorption decreased on oxidation of the carbon but it increased when the oxidized samples were degassed. Han et al [8] and Uddin et al [9] checked the applicability of various models such as Thomas, Adams-Bohart, Yoon-Nelson and Clark for the removal of methylene blue using phoenix tree leaf powder and jackfruit leaf powder (JLP) using fixed bed columns to predict the behavior of breakthrough curves and to determine the characteristic parameters of the column that are useful for process design. The present paper describes the column adsorption of congo red dye using activated carbons having different surface area and associated with varying amounts of carbon-oxygen surface groups.

2. MATERIALS AND METHOD

Two samples of activated carbons namely a granulated activated carbon ACG-100 and I-60 were used as adsorbents. The experimental set up consisted of a glass column of 25 mm diameter and 600 mm length. The activated carbon was packed in the glass column supported on perforated plates. Aniline solution of known concentration was prepared and poured into the column. A control valve to regulate the flow and a rotameter to monitor the flow rate were installed in the feed tank. The effluent collected from the column at regular intervals were analyzed with the help of UV-visible Spectrophotometer at a wavelength of 280 nm [10]. The details of the experimental set up are published elsewhere [11,12]. The operating variables in these investigations are the hydraulic loading rate (HLR, 0.97-1.83 m³/hr/m²), bed depth (x, 50-150 mm), the feed concentration (C₀, 50-150 mg/L). Studies have also been carried out on oxidised activated carbon samples. A known amount of activated carbon (5 g) was heated with 50% nitric acid in a beaker using a water bath. The temperature of water bath was maintained at 80 ± 5°C. When all but about 10 ml of the acid was left in the beaker, the heating was stopped. The remaining contents were cooled and washed with hot distilled water until it was free from nitrate ions. The washed carbon sample was dried in an electric oven at 120°C and stored in stoppered glass bottles [6,13,14]. These samples were used to carry column adsorption to study the effect of oxidation on adsorptive removal of congo red dye.

3. RESULTS AND DISCUSSIONS

The breakthrough curves for congo red dye showing effluent concentration at different time intervals for two activated carbons i.e. ACG-100 and I-60 at HLR=1.22 m³/hr/m² and feed concentration of 50 mg/L with a bed depth of 80 mm are shown in Fig.1. The breakthrough curves are S-shaped and show that the breakthrough time 't_b' is longer for ACG-100 than I-60. At 10% breakthrough t_b is 144 min for ACG-100 and 88 min for I-60 (cf Fig.1).

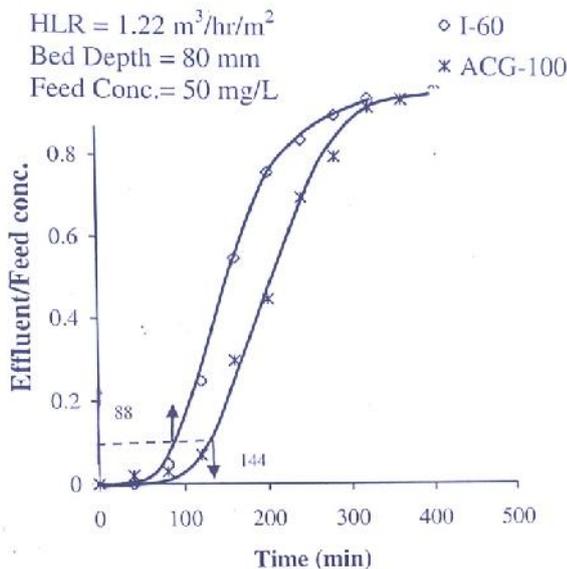


Fig. 1: Breakthrough curves for congo red on different activated carbons

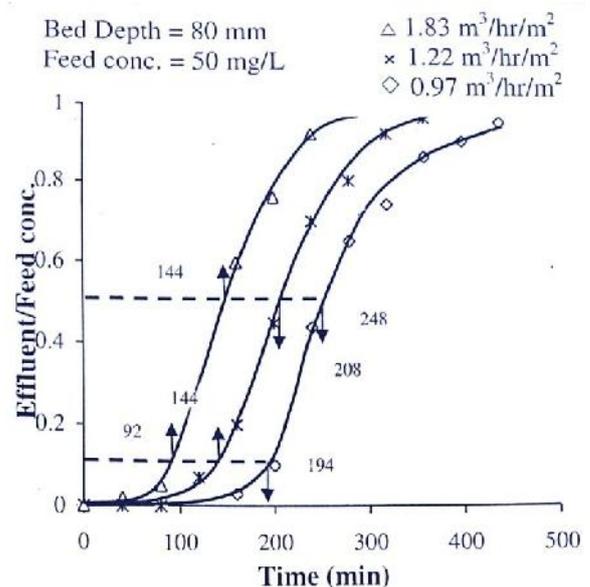


Fig.2: Effect of hydraulic loading rate on breakthrough curves on ACG-100

3.1 Effect of variable parameters on the breakthrough curves

Fig. 2 shows the effect of HLR on the breakthrough curves by using a bed depth of 80 mm and a feed concentration of 50 mg/L. It is seen that an increase in HLR at constant bed depth and feed concentration decreases the breakthrough time (t_b). At 10% effluent concentration t_b decreases from 194 min to 92 min for ACG-100 (cf Fig.2) and 120 min to 52 min for I-60 (Figs not given). This is due to the fact that at low HLR, the bed is in contact with the feed solution for a longer period of time and results in larger adsorption. The

effect of bed depth on the breakthrough curve at a constant HLR and feed concentration for the ACG-100 is shown in Fig. 3 (Fig. not given for I-60). The breakthrough curve of the longer beds tends to be more gradual meaning that the column takes more time to get exhausted. At 10% breakthrough concentration, the breakthrough time increases from 88 min to 328 min in case of ACG-100 (cf Fig.3) and from 48 min to 168 min in case of I-60 (Fig. not given for I-60 on increasing the bed depth from 50 mm to 150 mm).

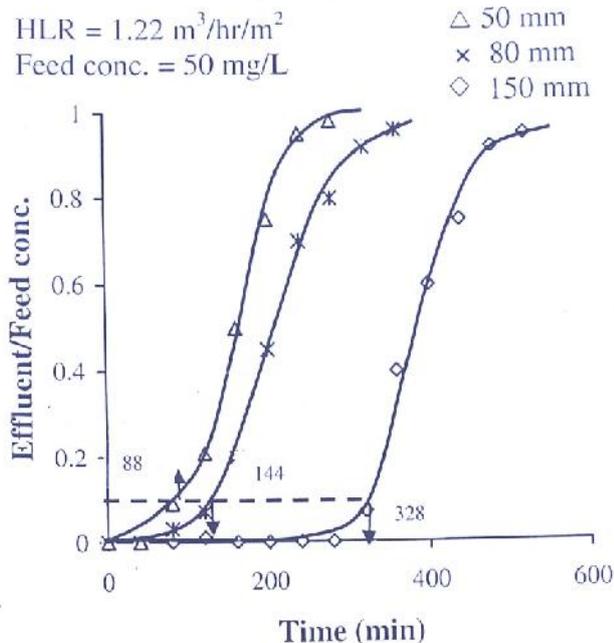


Fig.3: Effect of bed depth on breakthrough curves for congo red on ACG-100

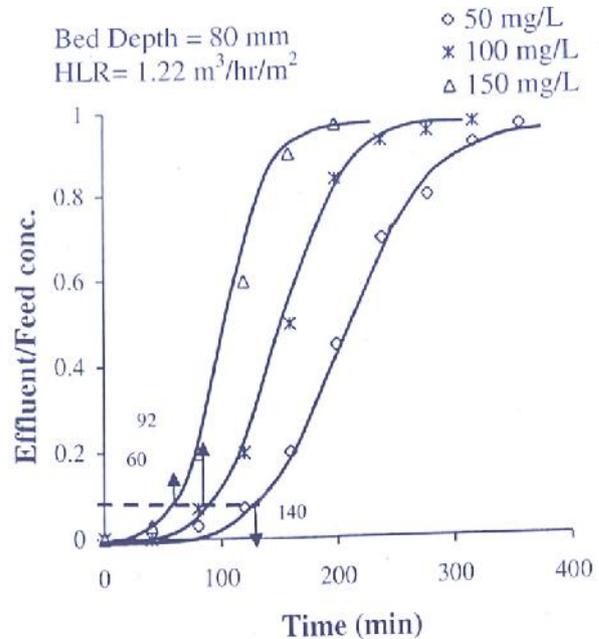


Fig.4: Effect of feed concentration on breakthrough curves for congo red on ACG-100

Fig.4 shows the effect of feed concentration on the breakthrough curves at constant bed depth of 80 mm and HLR of 1.22 m³/hr/m². In this case the breakthrough time for any effluent concentration decreases with increase in the influent concentration. At 10% breakthrough concentration, the breakthrough time decreases from 140 min to 60 min for ACG-100 (cf Fig.4) and from 88 min to 28 min for I-60 (Fig. not given for I-60).

3.2 Adsorption capacity variation with varying HLR

The amount of congo red dye adsorbed by a carbon at different values of HLR has been calculated from the breakthrough time t_b at 50% breakthrough concentration using the relationship

$$\text{Effective Adsorption Capacity (mg/g)} = \frac{t_b \cdot Q \cdot (C_o - C_e)}{m} \quad \text{----- (1)}$$

where Q is the liquid flow rate in L/hr, C_o and C_e are the influent (feed) and effluent concentrations in mg/L and m is the mass of the carbon (g) in the bed. The effective adsorption capacity in this case may be understood as the amount of dye adsorbed in a given period of time. The amount adsorbed has been plotted against the hydraulic loading rate in Fig. 5. The adsorption increases with increase in HLR but the rate of increase become slower at higher loading rates and tends to attain a maximum value around HLR = 1.83 m³/hr/m². The maximum adsorption capacity for I-60 is about 3.24 mg/g corresponding to HLR of 1.83 m³/hr/m² while that for the ACG-100 it is around 6.75 mg/g.

At low values of HLR, the adsorbate solution gets more time to pass through the adsorbent which leads to higher mass transfer and results in higher adsorption. On the other hand when HLR is increased the adsorbate passes very quickly through the adsorbent bed and gets less time for mass transfer and hence results

in less adsorption. The optimum HLR from the present studies has been found to be $1.83 \text{ m}^3/\text{hr}/\text{m}^2$. The difference in breakthrough curves of the two carbons (cf Fig.1) also shows that ACG-100 is a better adsorbent than I-60 for congo red dye adsorption. This can be attributed to the larger surface area of ACG-100 ($1600 \text{ m}^2/\text{g}$) than the I-60 carbon ($705 \text{ m}^2/\text{g}$) [12].

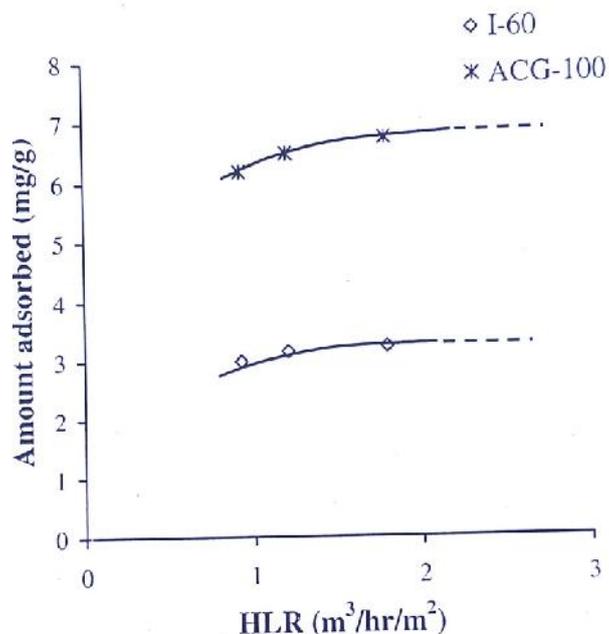
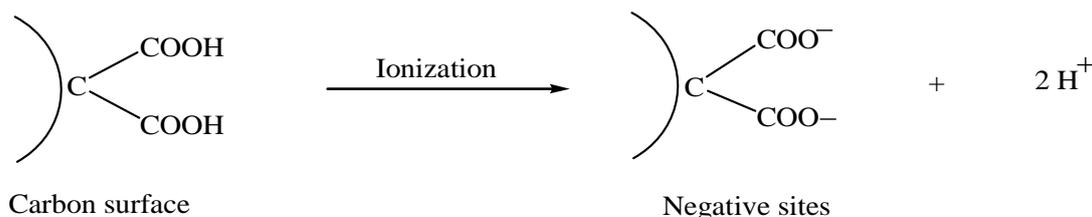


Fig. 5: Effect of hydraulic loading rate on adsorption capacity of activated carbon

3.3 Mechanism of adsorption:

The acidic surface groups which are mainly present as carboxylic groups ionise in water leaving negatively charged COO^- sites on the carbon surface.



In the aqueous solution, the sulfonate groups of the dye are dissociated and converted to anionic dye ions



This results in electrostatic repulsive interactions between the negatively charged carbon surface sites and the negatively charged dye anions. On oxidation the concentration of the negative sites on the carbon surface increases which results in a decrease in the amount adsorbed whereas on degassing the amount adsorbed increases due to the elimination of these acidic surface groups.

3.4 Critical bed depth of the adsorption column

The design parameters such as the adsorption capacity N_0 (mg/cm^3), the adsorption rate constant, k ($\text{Lmg}^{-1}\text{hr}^{-1}$) have been calculated from the slopes and intercepts of the linear plots using the Bohart-Adams equation. Bed Depth Service Time Model (BDST) proposed by Bohart and Adams [15,16] is based on the surface rate reaction theory which defines a relationship between the bed depth x and the breakthrough time t_b

(also called as service time, t) for a given concentration of the effluent. According to Bohart and Adams, the service time t of a column is related to the process conditions and operating parameters as

$$\ln\left(\frac{C_o}{C_e} - 1\right) = \ln\left(\text{Exp} \frac{kN_o x}{V} - 1\right) - kC_o t \quad \text{--- (2)}$$

Since the exponential term is usually much larger than unity, the unity term in the parentheses on the right hand side is often neglected so that a rearrangement gives a linear relationship between t and x .

$$t = \frac{N_o}{C_o V} x - \frac{1}{C_o k} \ln\left(\frac{C_o}{C_e} - 1\right) \quad \text{----- (3)}$$

Where C_o is the feed concentration (mg/L), C_e is the desired breakthrough concentration of the effluent (mg/L), x is the bed depth (cm), k is the adsorption rate constant ($\text{Lmg}^{-1}\text{hr}^{-1}$), N_o is the adsorption capacity (mg/cm^3), V is the linear flow velocity of the feed to the bed (cm/hr) and t is the service time (hr) of the column under these conditions. This equation can be used to determine the service time t of an adsorption column of bed depth x knowing the values of N_o , C_o and k which must be determined from column experiments operated over a range of linear velocity values V . However, this relationship requires data from at least nine different columns experiments to calculate its parameters.

Hutchins suggested modification of Bohart-Adam equation which requires three fixed bed column experiments to collect the necessary data [17]. In this technique called the bed depth service time (BDST) approach, the Bohart-Adam equation can be expressed in the linear form as

$$t = ax + b \quad \text{----- (4)}$$

$$\text{where Slope} = a = \frac{N_o}{C_o V} \quad \text{and} \quad \text{Intercept} = b = \frac{1}{kC_o} \ln\left(\frac{C_o}{C_e} - 1\right)$$

To develop the BDST correlation, the breakthrough data for each bed depth can be used to make a BDST plot for service time t which is the operating time to obtain certain removal of the adsorbate at each bed depth. From the slopes and the intercepts of linear plots between bed depth and service time, the values of N_o and k can be calculated. At time $t = 0$, the Eq. (3) can be solved for bed depth x_o as

$$x_o = \frac{V}{kN_o} \ln\left(\frac{C_o}{C_e} - 1\right) \quad \text{----- (5)}$$

where x_o is the minimum bed depth of the adsorbent sufficient to produce an effluent concentration C_e . The quantity is also called the critical bed depth. The critical bed depth x_o can also be obtained from the BDST linear plots as the intercept on the abscissa where $t = 0$. These graphic values of x_o obtained by extrapolating the linear plots in Fig.6 have been compared with x_o values obtained from equation (5). These calculated and graphical values of x_o are compared in Table 1 for the two carbons. It is apparent that the two values agree reasonably. This indicates that the Bohart-Adams equation and BDST approach are applicable to the column adsorption of congo red dye and. Hutchins [17] suggested that the design parameters obtained from one column experiment could be used to obtain design parameters for other flow rates and influent concentrations. According to this BDST approach if a value of slope parameter ' a ' is determined experimentally for one flow rate, the value ' a_2 ' at any other flow rate can be calculated by the relationship

$$a_2 = a_1 \frac{Q_1}{Q_2} \quad \text{----- (6)}$$

where Q_1/Q_2 is the ratio of the two flow rates. It was assumed that the value of the intercept parameter ' b ' does not change significantly by change in flow rates.

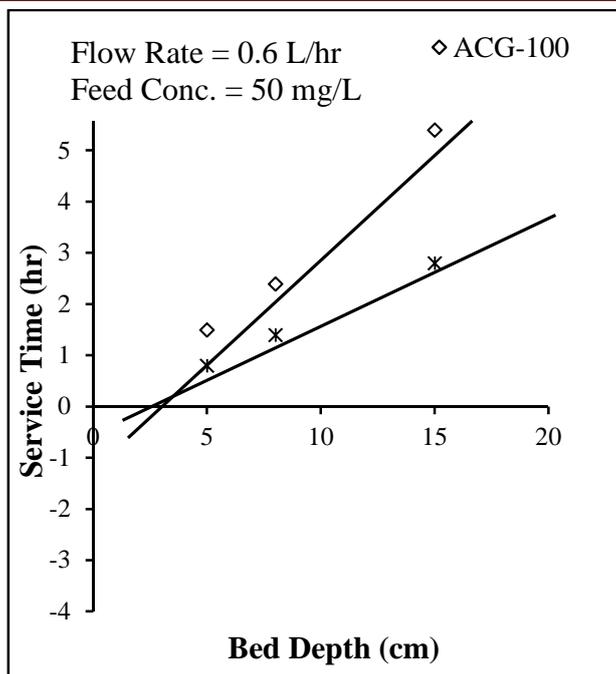


Fig. 6: BDST plots for both activated carbons for 10% breakthrough concentration

Table 1: Parameters of the Bohart-Adams equation using BDST plots at different flow rates for Feed concentration = 50 mg/L

Carbon Sample	Flow Rate (L/hr)	Slope (hr/cm)	Intercept (hr)	K (L mg ⁻¹ hr ⁻¹)	N ₀ (mg/cm ³)	Critical Bed Depth, x ₀ (cm)	
						Using Eqn.5	From graph (Fig.6)
ACG-100	0.60	0.40	-0.70	0.06	1.92	1.77	1.71
I-60	0.60	0.22	-0.34	0.13	1.07	0.90	1.30

Similarly the data collected at any influent concentration can be adjusted to design systems for other influent concentrations. If a column experiment is carried out at one influent concentration C₁, the BDST equation (4) can be expressed as

$$t_1 = a_1 x + b_1$$

It is then possible to predict the equation for influent concentration C₂ as

$$a_2 = a_1 \frac{C_1}{C_2} \quad \text{-----(7)}$$

$$b_2 = b_1 \left(\frac{C_1}{C_2} \right) \frac{\ln \left(\frac{C_2}{C_F} - 1 \right)}{\ln \left(\frac{C_1}{C_B} - 1 \right)} \text{-----(8)}$$

where a_1 and a_2 are slopes, b_1 and b_2 are the intercepts and C_B and C_F are the effluent concentrations at influent concentrations of C_1 and C_2 . Thus equation (4) for t_2 can be written as

$$t_2 = a_2 x + b_2$$

$$t_2 = a_1 \frac{C_1}{C_2} + b_1 \left(\frac{C_1}{C_2} \right) \frac{\ln \left(\frac{C_2}{C_F} - 1 \right)}{\ln \left(\frac{C_1}{C_B} - 1 \right)} \text{-----(9)}$$

In order to examine the applicability of the BDST approach to the adsorption column data obtained in these investigations, the values of a_2 and b_2 were calculated for influent concentration of 100 mg/L and 150 mg/L at a flow rate of 0.6 L/hr with bed depth of 80 mm from the a_1 and b_1 values obtained from experimental run at 50 mg/L influent concentration under similar conditions of flow rate and bed depth. The breakthrough time or service time (t_2) corresponding to an effluent concentration of 10 % were calculated using equation (9) both for the ACG-100 and the I-60 and are given in Table 2. The values obtained from experimental runs at these two influent concentrations are also included in Table 2. It is seen that the calculated and experimental values generally agree. Similar values of breakthrough times (service time) were calculated at flow rates of 0.9 L/hr and 0.48 L/hr using the experimental value at flow rate of 0.6 L/hr. The calculated and the experimental values of breakthrough time for the two carbons are recorded in Table 3. The two values agree very closely. This indicates that the BDST approach is generally applicable to the column adsorption data for congo red.

3.5 Effect of oxidation of activated carbons on column studies of congo red

A few column studies have been carried out to examine the effect of oxidation of the activated carbon on congo red dye adsorption. It is seen from the Fig.7 that the breakthrough time is lower in the case of oxidized carbon samples than the as-received carbons. The 10% breakthrough time for as-received activated carbon ACG-100 at HLR= 0.97 m³/hr/m², bed depth of 80 mm and feed concentration of 50 mg/L is 192 min which decreases to 104 mins (cf Fig. 7) for nitric acid oxidised ACG-100 sample. This is due to the presence of carbon-oxygen surface groups which increases on oxidation. Due to the anionic nature of the dye, there are repulsive interactions between the dye molecules and the negatively charged carbon surface sites. This results in a decrease in the adsorption. This indicates that unoxidised carbons are better adsorbents for congo red dye.

Table 2: Comparison of breakthrough times for different concentrations obtained from breakthrough curves and from calculation
Bed Depth = 80 mm Flow Rate = 0.6 L/hr

Carbon Sample	Feed Conc. = 100 mg/L		Feed Conc. = 150 mg/L	
	t_b (exptl.) (hr)	t_b (calcul.) (hr)	t_b (exptl.) (hr)	t_b (calcul.) (hr)
ACG-100	1.53	1.25	1.01	0.81
I-60	0.80	0.73	0.47	0.48

Table 3: Comparison of breakthrough times for different flow rates obtained from breakthrough curves and from calculations

Bed Depth = 80 mm Feed Conc. = 50 mg/L

Carbon Sample	Flow rate = 0.48 L/hr		Flow rate = 0.9 L/hr	
	t_b (exptl.) (hr)	t_b (calcul.) (hr)	t_b (exptl.) (hr)	t_b (calcul.) (hr)
ACG-100	3.2	3.3	1.53	1.46
I-60	2.0	1.9	0.87	0.86

Bed Depth = 80 mm × As-Received carbon
 HLR = $0.97 \text{ m}^3/\text{hr}/\text{m}^2$ ◇ Oxidized carbon
 Feed conc. = 50 mg/L

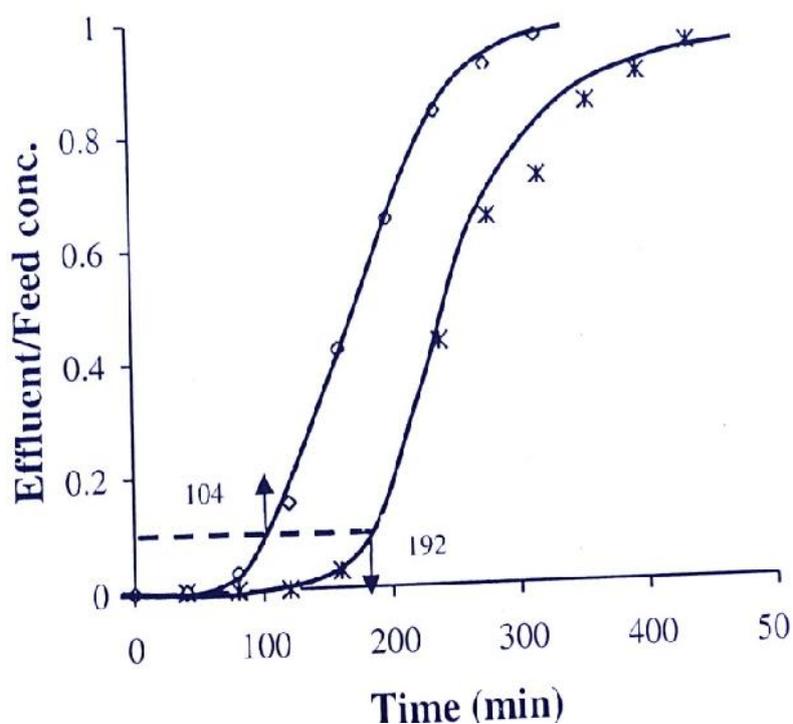


Fig.7. Comparison of adsorption of congo red dye on as-received and oxidised ACG-100.

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