

# Acid Orange 10 adsorption on novel mesoporous activated Carbon obtained from cotton boll pod(rind) – an agricultural waste



## Chemistry

**KEYWORDS :** Activated carbon; cotton boll pod (rind); Adsorption; Porosity; Isotherms; Kinetics

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## ABSTRACT

The adsorption of acid dye (Acid Orange 10), on a highly mesoporous activated carbon obtained from cotton boll pod by steam activation method was investigated in terms of size of dye molecule, pore size and surface charge of the activated carbon. The results were compared with that on a micro porous commercial activated carbon (CAC). The sterically small sized acid dye adsorption capacities of cotton boll pod (rind) carbon (ACBPC) and commercial activated carbon (CAC) were found to be 182.48 mg and 197.63 mg per g of the adsorbent respectively. The amounts of acid dye, which is large in one or two dimensions of molecular structures, adsorbed on the mesoporous ACBPC was much more comparable than that on micro-porous CAC. The adsorbed amounts of acid dye decreased with increasing pH (in alkaline pH) in which the  $pH > pH_{zpc}$  of ACBPC. The results, suggest that the adsorption of acid dye on activated carbon varies greatly by changing pore size and surface charge of activated carbon. The results indicate that ACBPC could be employed as low-cost alternative to commercial activated carbon in wastewater treatment for the removal of acid dyes.

## 1. Introduction

The economical decolourisation of textile processing effluents by removal of dyes remains as an important problem although a number of techniques have been developed<sup>[1]</sup>. Activated carbon has been successfully used as an adsorbent for the removal of dyes from waste water. Activated carbon can be produced from a number of precursor materials including wood, agricultural wastes, coal, etc. the adsorptive properties of activated carbons are derived from their extensive internal pore structure, which are not only present with a high surface area but also with a desired pore size distribution for the adsorption of molecular species.

With increasing ecological and economical significance of environmental protection, the use of waste biomass as feedstock material for the production of activated carbon is attractive. In the present study, the feedstock materials, namely cotton boll pod (rind) residues which are produced by cotton cultivation<sup>[2]</sup> in large quantities. The prepared high surface area porous carbons are expected to be excellent adsorbents for the removal and recovery of high molecular compounds. From this point of view, in this work, attempt was made to study the adsorption effect on the molecular size of the dyes at different parameters. The results were discussed in terms of pore size, surface area and kinetic potential of activated carbon.

## 2. Experimental

### 2.1. Preparation of activated carbon

The raw material, cotton boll pod, waste product from the processing of cotton was collected from a local agricultural field, pulverized and washed with water. The activation was performed by heating the sample in a muffle furnace using a purpose made stainless steel reactor at a rate of 5°C/hr to 850°C for 2 hours under nitrogen gas atmosphere. When the activation temperature was reached, the  $N_2$  gas flow was switched to steam (100%  $H_2O$ , 0.1g/min) and the sample was held at the specified temperature for predetermined activation time (40 minutes). After activation the sample was allowed to cool in a nitrogen flow<sup>[3]</sup>. The samples were grounded, sieved to 0.100mm mesh size and dried at 100.5°C overnight before the determination of their chemical properties. Finally, the product was stored in a vacuum desiccator until required.

### 2.2 Adsorbent Characterization

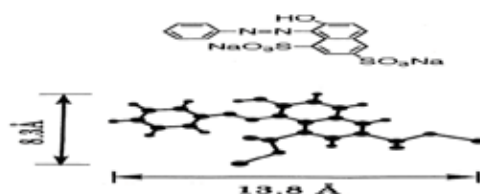
The BET surface area of the activated carbon ( $S_{BET}$  ACBPC) was obtained from  $N_2$  adsorption isotherm at 77K with sorpitometer [Smartsorb-91(India)]. Based on these data, the manufacturer's software provides the Pore characteristics viz., the total pore volume ( $V_{pore}$ ) by the BJH theory<sup>[4]</sup> micro and meso pore size by both t – plot method and BJH method respectively<sup>[5,6]</sup>.

### 2.3 Determination of zero point charge ( $pH_{zpc}$ )

The adsorbent (100mg) suspension (particle size, 0.100mm) was prepared in 50ml solution of  $NaNO_3$  electrolyte of concentration, approximately  $10^{-3}$  M. Aliquots of suspension were adjusted to various  $pH$  values with dilute NaOH and  $HNO_3$  solutions. After one-hour equilibration, the initial  $pH$  values were measured. Then 1.0 g of  $NaNO_3$  was added to each aliquot to bring final electrolyte concentration to about 0.45M. After an additional hour's agitation, final  $pH$  was measured. The results were plotted with  $\Delta pH$  {final pH – initial pH} against final pH. The pH at which  $\Delta pH = 0$  yielded  $pH_{zpc}$ <sup>[7]</sup>.

### 2.4 Dye Characteristics

Acid Orange 10 (C.I. 13065) was obtained from Fluka, USA, in 70% purity. The molecular structure and size of dye was calculated with molecular modeling system CAChe<sup>[8]</sup>. The estimated molecular structure and size in three dimensions of this dye are 13.8Å, 8.3 Å and 4.1 Å as shown in figure 1. All other chemicals were of AR grade and purchased from E. Merck (India). Double distilled water was used for solution preparation. The solution pH was adjusted by adding a small amount of 0.1M HCl or NaOH. A Systronics UV-VIS spectrophotometer (160 A) was employed for absorbance measurements using cells of path length 1cm.



**Figure 1. Molecular structure of Acid Orange 10**

### 2.5 Analysis

Adsorption experiments were carried out by shaking adsorbents with 50 ml dye solution of required concentration and pH at 30°C in a thermostated bacteriological incubator shaker operated at 200rpm. The samples were withdrawn from the shaker and the dye solution was separated from the adsorbent by centrifugation. Dye concentration in the supernatant solution was estimated by measuring absorbance at maximum wavelength ( $\lambda_{max} = 414$  nm) and computing concentration from the calibration curve. Kinetics of adsorption was determined by analyzing adsorptive uptake of the dye colour from aqueous solution at different time intervals. Isothermal studies were conducted by adding various doses of adsorbent and shaking the reaction mixture for the equilibrium time. Influence of the pH was studied by adjusting the reaction mixture to different initial pH value and analyzing the residual colour for equilibrium contact time. The amount of dye adsorbed onto the carbons,  $Q_e$  (mg/g), was calculated by mass balance relationship

$$Q_e = V (C_0 - C_e) / W$$

Where  $C_0$  and  $C_e$  are the initial and equilibrium liquid-phase concentrations of dye (mg/l), respectively,  $V$  the volume of the solution (l), and  $W$  the weight of the carbon used (g).

### 3. Results and discussion

#### 3.1. Characteristics of the Cotton boll pod activated carbon

Figure 2 shows the nitrogen adsorption-desorption isotherms of Cotton boll pod carbon (ACBPC). From the figure it is evident that quantifiable adsorption of nitrogen occurs within the relative pressure 0.3. Moreover there is a significant difference in the adsorption-desorption loop indicating the presence of good quantity of mesopores.

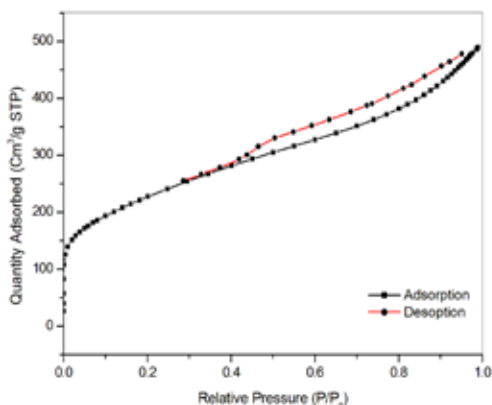


Figure 2.  $N_2$  adsorption-desorption isotherms of ACBPC

From the isotherm shape, it is evident that ACBPC exhibits Type I adsorption isotherm according to IUPAC classification<sup>[5]</sup>. The isotherms with an almost horizontal plateau with increasing slope indicate highly porous material with a narrow pore size distribution.

Table 1: Texture characteristics of activated carbons as determined from  $N_2$  adsorption at 77K

Source	$S_{BET}$ ( $m^2/g$ )	$S_{mic}$ ( $m^2/g$ )	$S_{meso}$ ( $m^2/g$ )	$V_{total}$ ( $cm^3/g$ )	$V_{mic}$ ( $cm^3/g$ )	$V_{meso}$ ( $cm^3/g$ )	Average pore dia (nm)	pH <sub>ZPC</sub>
CAC	1026	630	396	0.598	0.361 (60%)	0.237 (40%)	1.8	-
ACBPC	781.42	269.22	512.2	0.758	0.0314 (4.2%)	0.7265 (95.8%)	2.598	5.8

The slightly increasing slope value is the characteristic indication of the development of mesopores at high pressure. The presence of hysteresis loops in desorption isotherms reveal the development of mesoporosity<sup>[5]</sup>. The porous properties of the activated carbon resulting from steam activation of cotton boll pod calculated from the above isotherms are given in Table 1. It is clear that ACBPC has an obviously larger  $V_{meso}$  value than, and nearly the same  $V_{micro}$  and  $S_{BET}$  values as CAC. From table 1, the values of  $D_p$  indicate a characteristic of meso porous structure (ie., pore diameter (2 nm < d < 50 nm) for ACBPC.

Table 2: Adsorption rate constants for adsorption of Acid Orange 10

	Adsorption rate constants for adsorption of Acid Orange 10											
	Pseudo- first order kinetics				Pseudo- Second order kinetics					Intra particle diffusion rate constant		
	$K_1 \times 10^{-2}$ (1/min)	$q_{exp}$ (mg/g)	$q_{cal}$ (mg/g)	$r^2$	$K_2 \times 10^{-3}$ (mg/g min)	$q_{exp}$ (mg/g)	$q_{cal}$ (mg/g)	$h$	$r^2$	$K_3 \times 10^{-3}$ (mg/g min)	$q_{exp}$ (mg/g)	$r^2$
CAC	3.194	18.1200	14.3851	0.9812	3.2311	18.1200	19.8203	1.2693	0.9988	3.356	14.0446	0.9880
ACBPC	2.8264	17.9800	13.3503	0.9836	2.9601	17.9800	19.7678	1.1567	0.9987	2.939	15.3679	0.9941

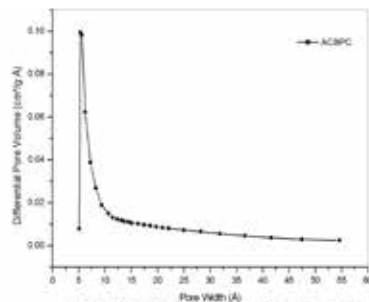


Figure 3. Horvath-Kawazoe Pore size distributions of ACBPC

Figure 3 illustrates the pore size distribution of ACBPC based on the differential pore volume. The results show that the large surface area and total pore volume of ACBPC is comparable with that of commercial activated carbons in the liquid phase adsorption. It is noted that total pore volume is usually used as an indication for the adsorption capacity, because its measurement is based on converting the amount of adsorbate (i.e., nitrogen) adsorbed at a relative pressure 0.975 to the volume of liquid nitrogen.

#### 3.2 Kinetic studies

Successful application of the adsorption demands innovation of cheap, nontoxic, easily available adsorbents of known kinetic parameters and sorption characteristics. Foreknowledge of the optimal conditions would herald a better design and modeling of the process. Thus, the effect of contact time on the uptake of acid orange 10 on CAC and ACBPC were investigated from kinetic point of view. Preliminary investigations on the rate of uptake of acid orange 10 on CAC and ACBPC indicated that the processes are quite rapid and typically 50–60% of the ultimate adsorption occurs within the first hour of contact (Figure 4). This adsorption subsequently gives way to a very slow approach to equilibrium and the equilibrium is achieved in 2–3 hours in the case of ACBPC.

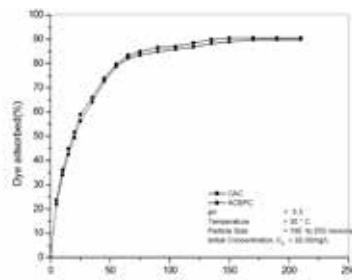


Figure 4. Effect of contact time for the adsorption of Acid Orange 10 on CAC and ACBPC

This may be due to the fact that the activated carbon is composed of macro and micro pores. In the process of dye colour adsorption, initially dye molecule has to first encounter the boundary layer effect and then it has to diffuse from boundary layer film onto adsorbent surface and finally it has to diffuse into the porous structure of the adsorbent<sup>[9]</sup>. It is suggested that the high adsorption of acid dye on ACBPC than CAC depends on the pore size and high meso pore volume of ACBPC in addition to specific surface area. That is, if acid dye has one large dimension in its molecular structure, the adsorption should change by the relation between one large dimension of dye molecule and pore size of activated carbon. From the figure 4 it is found that the time profile of dye uptake by both CAC and ACBPC is a single, smooth, and continuous curve leading to saturation, suggesting the possible monolayer coverage of dye on the surface of the adsorbent<sup>[10]</sup>.

### 3.3 Dynamic rate constant modeling

Kinetics of sorption is one of the important characteristics in defining the efficiency of sorption. Various kinetic models have been proposed by different workers where the adsorption has been treated as first-order, pseudo-first-order<sup>[11]</sup>, and pseudo-second-order processes<sup>[11]</sup>. Different systems conform to different models. The Lagergren rate equation is the one most widely used for the sorption of a solute from a liquid solution<sup>[13,14]</sup>.

$$\log (q_e - q_t) = \log C_{\max} - (K_{ad} / 2.303) \cdot t$$

where  $q_e$  and  $q_t$  are the amounts of the dye adsorbed at equilibrium and at time  $t$ , in  $\text{mg g}^{-1}$ , and  $K_{ad}$  the first-order rate constant, was applied to the present studies of dye adsorption. As such, the values of  $\log(q_e - q_t)$  were calculated from the kinetic data of Figure 4 and plotted against time in Figure 5. The plots are found to be linear, indicating that Lagergren's equation is applicable to the dye adsorption on carbonaceous adsorbent. The pseudo first-order rate constants calculated from the slope of the plots (Figure 5) are found to be  $0.0465 \text{ min}^{-1}$  for CAC and  $0.0424 \text{ min}^{-1}$  for ACBPC at  $30^\circ\text{C}$ .

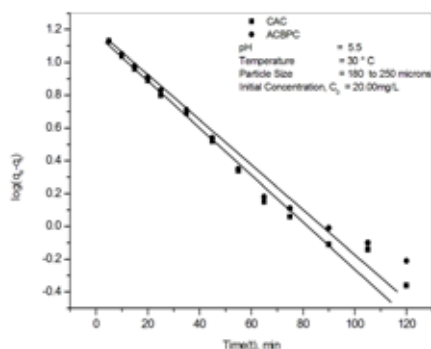


Figure 5. Lagergren plots corresponding to the adsorption of Acid Orange 10 on CAC and ACBPC

In the present case, the pseudo first-order Lagergren equation is found to be applicable over the initial 20–30 min of the sorption process and not applied satisfactorily throughout the complete range of contact time. It is evident from the figure 5, after a short initial contact time there was a considerable deviation in the plots of  $\log(q_e - q_t)$  versus “time” from the theoretical data. The  $q_e$  values calculated from the plots are lower than the experimental one in Table 2. Therefore, it may be concluded that pseudo first-order rate equation is unable to explain the present adsorbent systems satisfactorily.

The linearised form of rate of adsorption for pseudo second order model<sup>14</sup> is

$$t/q_t = 1/k_2 q_e^2 + t/q_e$$

where  $q_e$  is amount of dye adsorbed at equilibrium ( $\text{mg/g}$ ),  $q_t$  is amount of dye adsorbed at time  $t$  ( $\text{mg/g}$ ),  $k_2$  is rate constant for second order adsorption ( $\text{g/mg min}^{-1}$ ). A plot of  $t/q_t$  versus  $t$  should give a linear relationship, from which  $q_e$  and  $k_2$  can be determined from the slope and intercept of the plot respectively.

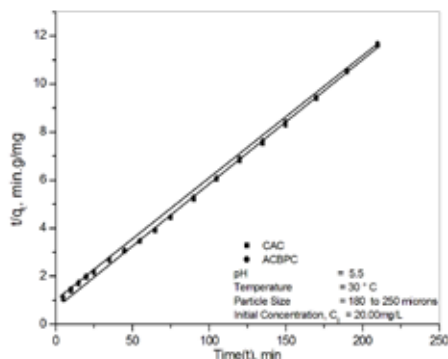


Figure 6. Pseudo Second order plots corresponding to the adsorption of Acid Orange 10 on CAC and ACBPC

From Table 2 the correlation coefficient  $R^2$  for this linear plots are superior (in all cases  $> 0.9950$ ), and its calculated equilibrium adsorption capacity  $q_{e,cal}$  is consistent with the experimental data. These suggest that the pseudo second-order adsorption mechanism is more operative than pseudo first-order rate equation and that the overall rate of the dye adsorption process appears to be predominantly controlled by the chemisorption process in association with physisorption.

The adsorption capacities  $q_t$  of AO10 at 120 min for CAC and ACBPC reached over 85% of the calculated equilibrium adsorption capacities  $q_{e,cal}$  in Table 2. This is evident that the carbon in our experiments had very high equilibrium adsorption capacity  $q_e$ , the adsorption rates became very fast and the equilibrium times were short, indicating a high degree of affinity between the dyes and the carbon<sup>15</sup>.

The data of solid-phase dye concentrations against time at an initial dye concentration of  $50 \text{ mg/L}$  were further processed for testing the role of diffusion (as the rate-controlling step) in the adsorption process. Adsorption process incorporates the transport of adsorbate from bulk solution to the interior surface of the pores<sup>[5]</sup>. There is a possibility that the transport of dye from the solution into the pores of the adsorbent is the rate controlling step in batch experiments with rapid stirring.

The rate parameters for intraparticle diffusion ( $k_p$ ) for different dyes are determined using the following equation<sup>[15]</sup>.

$$q_t = k_p t^{1/2}$$

where  $k_p$  is the intraparticle diffusion rate constant. Due to mass transfer effects, the shape of  $q_t$  versus  $t^{1/2}$  plot is curved at a small time limit [5].

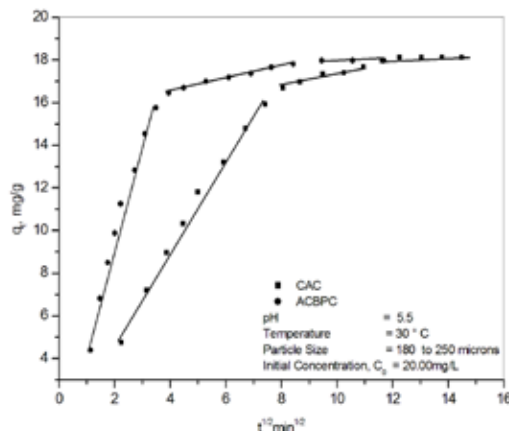


Figure 7. Intraparticle diffusion plot for the adsorption of Acid Orange 10 on CAC and ACBPC

From figure 7, it is evident that the plots have the same general features, initial curved portion followed by linear portion and a plateau. The initial curved portion is attributed to the bulk diffusion and the linear portion to the intra-particle diffusion. These phenomena have been reported for the adsorption of dye on activated carbon [9]. At a certain time limit (about 25 min), the curves reveal a linear characteristic that the intraparticle diffusion controls the adsorption process (Figure 7). The extrapolation of the linear straight lines to the time axis gives intercepts  $C$ . If  $C$  is equal to zero, the only controlling step is intraparticle diffusion. However, in the present study,  $C \neq 0$ , indicates that the adsorption process is rather complex and involves more than one diffusive resistance. The values of  $k_{id}$  and the quantity adsorbed by intra particle diffusion are obtained from the slope and intercept of the straight lines, and are presented in table.2. From the  $q_{id}$  values, it is evident that intra particle diffusion is more for ACBPC ( $15.36792 \text{ mg/g}$ ) than CAC ( $14.04457 \text{ mg/g}$ ) which is again characteristic of mesoporous material.

### 3.4 Adsorption isotherm studies

Once the equilibrium time was known, adsorption isotherm studies for CAC and ACBPC were performed. The respective ad-

sorption isotherms for AO10 at 30°C are shown in Figure 8. The isotherms have been classified according to Giles' classification [16]. Giles has classified adsorption isotherms into four main groups: L, S, H and C. According to the above classification both carbons show L-type isotherm (Figure 8).

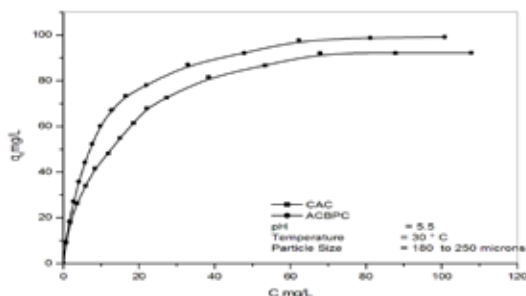


Figure 8. Adsorption isotherms for Acid Orange 10 on CAC and ACBPC

The data show that the affinity of AO10 to ACBPC is higher. This is due to it having higher effective surface area (meso porosity). The lack of correlation between the adsorptive capacity and the physical properties of an activated carbon has been reported in the literature for a variety of solutes and activated carbon types. With regard to the adsorption of dyes, Walker and Weatherly<sup>[17]</sup> reported that only 14% of the  $S_{BET}$  of a commercial activated carbon (Chemviron F400, Calgon Carbon, UK) was available for the adsorption of three acid dyes with ionic weights of around 460 g/mol. It may be concluded that surface associated with the micro pore structure was found to be redundant in the adsorption of large molecular weight compounds such as dyes<sup>[7]</sup>. Regarding the relation between pore size and molecular sizes of adsorbates, Tamai et al<sup>[8]</sup> reported that pore size rather than  $S_{BET}$  plays an important role in the adsorption of dyes with at least one dimension larger than the size of micropores. Acid orange 10 with a molecular dimension greater than the limiting diameter attributed to micropores may be excluded from the microporous network and hence ACBPC, which has a more opened porous structure, performed the best.

### 3.5 Quantification of the adsorption isotherm data

The isothermal equilibrium data were processed employing Langmuir and Freundlich isotherm equations. The equilibrium concentrations in the adsorption experiments were treated by the classical linearised Langmuir equation [18]

$$Q_e = Q_m \cdot b \cdot C_e / (1 + b \cdot C_e)$$

onlinearisation, the above equation becomes

$$C_e / Q_e = 1 / Q_m + \{ 1 / Q_m \cdot b \} \cdot C_e$$

where  $Q_m$  (mg/g) and  $b$  (l/mg) are isotherm constants obtained by linear plots of  $C_e$  versus  $C_e / Q_e$  (Figure 9) for a particular solute-adsorbent combination and are shown in Table 2. The Langmuir isotherm equation was chosen because it has been commonly used to model data in wastewater adsorption treatment systems<sup>[19]</sup> and especially for dyes<sup>[20]</sup>.

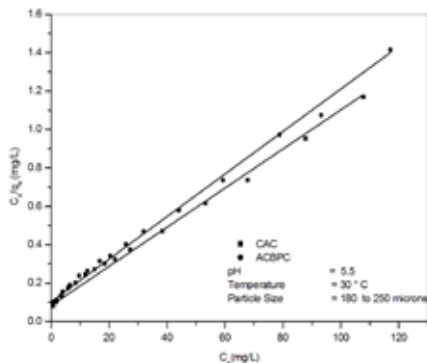


Figure 9. Langmuir plot for the adsorption of Acid Orange 10 on CAC and ACBPC

The Langmuir model (Table 2) gave satisfactory correlation coefficients ( $r^2 \geq 0.979$ ) for the dye-activated carbon systems evaluated. A basic assumption of the Langmuir theory is that sorption takes place at specific homogeneous sites within the adsorbent. It is then assumed that once a dye molecule occupies a site, no further adsorption can take place at that site and a saturation value, i.e.  $Q_m$ , is reached which corresponds to the completion of a monolayer. At a low initial dye concentration  $1 \gg bC_e$  and hence  $Q = Q_m b C_e$ , which is analogous to Henry's law.

Table 3. Adsorption isotherm constants for adsorption of Acid Orange 10

	Adsorption Isotherms constants for adsorption of Acid Orange 10					
	Langmuir isotherm				Freundlich Isotherm	
	$Q_e$ (mg g <sup>-1</sup> )	$K_f \times 10^{-3}$ (L mg <sup>-1</sup> )	$R_L$	$r^2$	$K_f$ (mg g <sup>-1</sup> ) (L mg <sup>-1</sup> ) <sup>1/n</sup>	$n$
CAC	109.84	7.4824	0.1628	0.9914	12.6808	1.9862
ACBPC	98.12	8.5973	0.186	0.9944	12.4902	2.0436

Freundlich equation, which was also applied for the adsorption of dye<sup>[21,22]</sup>, is given as

$$Q_e = K_f C_e^{1/n}$$

where  $K_f$  is roughly an indicator of the adsorption capacity and  $1/n$  the adsorption intensity. In general, as the  $K_f$  value increases the adsorption capacity of the adsorbent for a given dye increases. The magnitude of the exponent  $1/n$  gives an indication of the favorability of adsorption values  $n > 1$  represent favourable adsorption condition<sup>[10]</sup>. Hence the above equation can be rearranged to linear form

$$\log Q_e = \log K_f + 1/n \log C_e$$

In the present study, Linear plots of  $\log Q_e$  vs.  $\log C_e$  (Figure 10) (correlation coefficient  $> 0.9$ ) shows that the adsorption of Acid orange 10 onto ACBPC and CAC also follow the Freundlich isotherm.

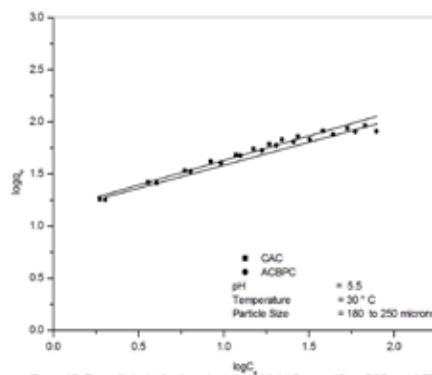


Figure 10. Freundlich plot for the adsorption of Acid Orange 10 on CAC and ACBPC

Isotherms having a step increase in adsorption capacity and a well-defined plateau on completion of a monolayer of dye on CAC or ACBPC are associated with very high adsorption affinity and relatively strong adsorbent-adsorbate interactions<sup>[23]</sup>. The molecular dimensions of the acid dye are 13.8 Å, 8.3 Å and 4.1 Å as shown in figure 1. This suggests the observed effect of the pore size on adsorption by both CAC and ACBPC is due to steric hindrance associated with the size of the acid dye molecules which limits its penetration into the pore structure of the carbon. The adsorption result by both micro and meso porous carbon also suggests the dye preferentially penetrates the surface of the carbon with the narrower side of the dye molecule. High  $1/n$  values for the adsorption of CAC and ACBPC carbon are indicative of co-operative adsorption<sup>[24]</sup> which is consistent with limitations to dye adsorption imposed by steric hindrance of narrower sized pores observed in this study. Lower  $1/n$  values for the adsorption of ACBPC carbon are indicative of stronger adsorption<sup>[1]</sup> which, as suggested by this study oc-

curs with carbon having wider and more accessible pore areas. The adsorption isotherms results indicate that ACBPC, having a preponderant mesoporous character and the largest mean pore diameter (Table 3), is equivalent to or superior to the commercial product in the adsorption of the anionic dye.

One of the essential characteristics of the Langmuir isotherm could be expressed by dimensionless constant called equilibrium parameter,  $R_L$  [25]

$$R_L = 1/(1+bC_0)$$

where  $C_0$  is the initial solute concentration (mg/l). The values of  $R_L$  indicates the type of isotherm to be irreversible ( $R_L=0$ ), favourable ( $0<R_L<1$ ), linear ( $R_L=1$ ) or unfavourable ( $R_L>1$ ). It has been seen that the adsorption of acid orange 10 on CAC and ACBPC are favourable (Table 4) [26, 27, 28].

**Table 4. Longmuir Adsorption isotherm's dimensionless constants ( $R_L$ ) for adsorption of Acid Orange 10**

Concentration mg/L	CAC	ACBPC
10	0.5720	0.5377
20	0.4006	0.3677
30	0.3082	0.2794
40	0.2504	0.2253
50	0.2109	0.1887
60	0.1822	0.1624
70	0.1603	0.1425
80	0.1431	0.1269
90	0.1293	0.1144
100	0.1179	0.1042
120	0.1002	0.0884
140	0.0871	0.0767
160	0.0771	0.0678
180	0.0691	0.0607
200	0.0626	0.0550

### 3.6 Effect of pH

Activated carbons are materials with amphoteric character; thus, depending on the pH of the solution, their surfaces might be positively or negatively charged. At  $pH > pH_{zpc}$  the carbon surface becomes negatively charged favouring the adsorption of cationic species. On the other hand, adsorption of anionic species will be favoured at  $pH < pH_{zpc}$  [29]. Although pore size distribution and the relative size of the adsorbate molecules have a significant effect on adsorption capacity, the chemical nature of the adsorbent also plays a major role. To investigate the role of surface chemistry on the adsorption capacity of dyes, the effect of equilibrium pH was studied. The experiments were carried out by varying the initial pH, under a constant initial dye concentration of 20 mg/l and a carbon dosage of 50mg/l. The dependence of the equilibrium adsorption capacity of activated carbons for dyes on equilibrium pH is illustrated in Figure 11.

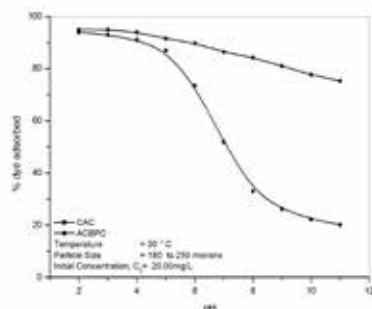


Figure 11. Effect of pH for the adsorption of Acid Orange 10 on CAC and ACBPC

For CAC, it was found that the surface nature ( $pH_{zpc}$ ) is only significantly modified at extreme pH values, i.e. for  $pH < 5.0$  and  $pH > 10$ . This means that within the range of pH 6–9, the surface of CAC is almost neutral, which in turn makes the adsorption capacity remain almost constant within this pH range, with no change in the electrostatic interaction between the solutes and the adsorbent surface. Adsorption capacity for the anionic dyes increases only at acidic pH levels ( $pH < 5$ ) because of electrostatic interaction with the positively charged surface. For ACBPC, the amount of adsorption decreases when the pH increased. This may be explained as the carbon surfaces acquire a basic character on high temperature ( $>800^\circ\text{C}$ ) heat treatment [30]. Galiatsatou et al. [16, 31] reported that the steam activation at  $800^\circ\text{C}$  increases the basic surface groups of activated carbon with increasing activation time. It has been reported that the basic surface properties arise from two types of interactions: (i) electron-donor acceptor (EDA) complex formation that predominates in carbon of low oxygen content and (ii) pyrone-type groups contribution, which prevails in carbons of high oxygen content [9, 30]. Two possible mechanisms of adsorption of AO10 on ACBPC and CAC may be considered: (a) electrostatic interaction between the protonated groups of carbon and acidic dye and (b) the chemical reaction between the adsorbate and the adsorbent. At low pH (4 and below), a significantly high electrostatic attraction exists between the positively charged surface of the adsorbent and anionic dye. As the pH of the system increases, the number of negatively charged sites increase and the number of positively charged sites decrease [31]. A negatively charged surface site on the adsorbent does not favour the adsorption of dye anions due to the electrostatic repulsion. Also, lower adsorption of AO10 at alkaline pH is due to the presence of excess -OH ions competing with the dye anions for the adsorption sites. However, with respect to the electrostatic interaction between dye molecules and the surface of ACBPC and CAC, the influence of electrostatic repulsion on the adsorption appears to be moderated, because the dyes still adsorb in spite of the opposite charge on the carbon surface as a function of solution pH. This is accordingly, and in agreement with the results reported by Dai [32] that there may be a participation of non-specific dispersion interactions between activated carbon and the ionic dyes.

### 4. Conclusion

It is reasonable to conclude from the present investigations on the adsorption of anionic dyes on adsorbent prepared from largely available agricultural waste cotton boll rind, carbonaceous adsorbent possessing organic nature and consequently having higher surface area with high porosity is efficient for the removal of dyes. The ACBPC is mainly meso porous in nature and acidic in character, while a commercial AC used as reference was found to be more micro-porous. The fitted Freundlich and Langmuir model suggests co-operative adsorption occurs in these narrow sized pores. Generally accessible micro pore areas showed significant adsorption which proved to be better in comparison to adsorption of commercially available micro porous activated carbon. The acidity of the carbon and the total surface area played complementary roles in promoting the adsorption of acid orange 10. The adsorption of dyes on carbonaceous adsorbent is pseudo second order and pore-diffusion-controlled; and the carbonaceous adsorbent is about 80–90% as efficient as commercial activated carbon and thus can be used in its place for the removal of dyes from effluents in view of its cheaper cost.



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