Film- Pore diffusion Modeling for Sorption of Azo Dye on to One and Three Dimensional Nano Structured Carbon Nano Materials from *Jatropha Curcas*

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Abstract

Multiwalled carbon nanotubes (MWNTs) and Nano porous activated carbon materials were prepared from Jatropha curcas oil and Jatropha curcas stem waste respectively (JCAC and MWNTS). Both carbon materials were utilized as a potential sorbents for toxic textile dye Acid Orange 7 (acid dye) removal. The effects of major variables governing the efficiency of the process such as, temperature, initial dye concentration and pH were investigated. The kinetic measurements helped in determining the specific rate constant confirming the applicability of pseudo second order rate expression. Plausible mechanism of ongoing adsorption process involved was obtained by carrying out kinetic measurements. To compare adsorption of dye on to both adsorbents is particle diffusion or film diffusion, the treatment given by Boyd and Reichenberg was employed. The influence of different factors on the adsorption of Acid Orange 7 on both adsorbents is explained in terms of electrostatic interaction by considering the dye species and the surface characteristics of the adsorbents.

1. INTRODUCTION

Acid Orange 7 present in the effluents produced during the electroplating, paper industries, mining, dyeing, and photographic industries and causes severe environmental and public health problems. Acid Orange 7 has been reported to be toxic to animals and humans and it is known to be carcinogenic. The concentration of Acid Orange 7 in industrial wastewater is in the range 0.06 to 2.68 mg/L (Patterson 1985). The tolerance limit for Acid Orange 7 for discharge into potable water is 0.050

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mg/L in order to comply with this limit, it is essential that industries treat their effluents to reduce the Acid Orange 7 to acceptable level. Many reports have appeared on the development of lowest activated carbon adsorbents developed from cheaper and readily available materials (Babel and Kurniawan 2003). Nanoporous carbon materials with large surface area, micro porous character and chemical nature of their surface have made them potential adsorbents for removal of heavy dyes from industrial wastewater. The adsorptive properties of active carbon for removal of pollutants are well documented (Macias et al. 1993). Adsorption of hazardous soluble chemicals from wastewater in to
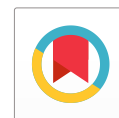
surface of a solid adsorbent has provided a new dimension to wastewater technology (Benfield et al. 1982).

One of the major challenges associated with adsorption by activated carbon is its cost effectiveness. Hence research of recent past mainly focused on utilizing waste materials as alternatives to activated carbon. Rice husks (Youseff et al. 1990; Roy et al. 1993), fruit stones (Namasivayam and Periyasamy 1993; Lopez et al. 1984; Gharaibeh et al. 1998), coconut shells (Alaerts et al. 1989; Manju et al. 1998), peat moss (Allen and McKay 2001; Chen et al. 2001), ferronia shell (Karthikeyan *et al.* 2008) and ipomoea carnia stem waste (Karthikeyan et al. 2007) are some of the waste materials which have been fruitfully tried for this purpose. In the present work, we have prepared multi-walled carbon Nanotubes (MWNTS) and Nanoporous active carbon from Jatropha curcas oil and Jatropha curcas stem wastes respectively, which are used as an adsorbents for Acid Orange7 (AO7) removals and the adsorption capacity of chosen adsorptions were regulated by many influencing factors, such as temperature, pH variations and initial dye concentrations.

2. EXPERIMENTAL

2.1 Adsorbent

The study of *Jatropha curcas* based material is used as adsorbent is expected to be economical, environmentally safe and it has practical importance. The textile dye, AO7, was purchased from sigma- Aldrich (Germany) and all the chemicals used were obtained as research grade chemicals and were used without purification.

Jatropha curcas stem waste material was soaked well with 10% of $ZnCl_2$ solution for a period of 24 hours. At the end of 24 hrs the excess of $ZnCl_2$ solution were decanted off and air-dried. Then the materials were placed in the muffle furnace carbonized at 400°C. The dried materials were powdered and activated in a muffle furnace kept at 800°C for a period of 60 minutes. After activation, the carbon of obtained were washed sufficiently with 4N HCl to remove cations. Then the obtained material was washed with plenty of water to remove excess of acid, dried then to desired particle size tight lid container.

Jatropha curcas oil was used as a precursor for the synthesis of MWNTs by CVD process described in our previous work (Karthikeyan et al., 2010). Final products obtained in each case were stored separately in a vacuum desicator until used. The resulting nanoporous carbons named as JCAC and MWNTS.

The N_2 adsorption-desorption isotherms of activated carbons were measured at 77K using a gas sorption analyzer (NOVA 1000, Quanta Chrome corporation) in order to determine the surface areas and the total pore volumes. The surface areas were calculated using the BET equation.

2.2 Batch adsorption studies

All reagents used were of AR grade (E merk). 50ml of Acid Orange 7 solution of known concentration (C_0) and initial pH was taken in a 100ml screw-cap conical flask with a required amount of adsorbent and was agitated at a speed of 200 rpm in a thermostatic shaker bath at 27° C for a specified period of time. Then the solution was filtered through a 0.45 μm membrane filter.

2.3 Determination of Acid Orange 7

Acid Orange 7 was estimated spectrophotometrically. The amount of Acid Orange 7 adsorbed in mg/L at time, t was computed by using the following equation.

$$q_t = \frac{C_0 - C_t}{m_s} \times V \qquad (1)$$

where, C_0 and C_t are the Acid Orange 7 concentration in mg/L initially and a given time t, respectively,

V is the volume of the Acid Orange 7 solutions in ml and m_s is the weight of the activated nanoporous carbon. The percentage of removed Acid Orange 7 ions (R %) in solution was calculated using eqn. (2)

$$\% \, Removal = \frac{C_0 - C_t}{C_0} \times 100 \qquad (2)$$

The initial concentration of Acid Orange 7, pH and temperature was investigated by varying any one parameters and keeping the other parameters constant.

2.4 Adsorption dynamics

The study of adsorption dynamics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface.   The kinetics of Acid Orange 7 adsorption on the activated nanoporous carbons were analyzed using pseudo first order (Lagergren 1898), pseudo second order (Ho et al. 2000) kinetic models and Elovich equation (Chien and Clayton 1980). The conformity between experimental data and the model predicted values was expressed by the correlation coefficients. A relatively high r^2 value indicates that the model successfully describes the kinetics of Acid Orange 7 adsorption.

2.5 The pseudo first – order equation

The pseudo first - order equation (Lagergren 1898) is generally expressed as follows.

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (3)$$

where, q_e and q_t are the adsorption capacity at equilibrium and at time t, respectively (mg g⁻¹), k_1 is the rate constant of pseudo first –order adsorption (l min⁻¹).

After integration and applying boundary conditions t =0 to t = t and q_t= 0 to $q_t = q_t$, the integration form of equation (3) becomes.

$$\log(q_e - q_t) = \frac{\log(q_e) - k_1}{2.303} \times t \qquad (4)$$

The value of log (q_e – q_t) were linearly correlated with t. The plot of log (q_e – q_t) Vs t should give a linear relation ship from which k_1 and q_e can be determined from the slope and intercept of the plot, respectively.

2.6 The pseudo second – order equation.

The pseudo second – order adsorption kinetic rate equation is expressed as (Ho et al. 2000)

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (5)$$

where, k_2 is the rate constant of pseudo second order adsorption (g. mg⁻¹. min⁻¹). For the boundary conditions t = 0 to t = t and q_t = 0 to q_t = q_t, the integrated form of equation (5) becomes.

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_t \qquad (6)$$

Which is the integrated rate law for pseudo second – order reaction. Equation (6) can be rearranged to obtain equation (7), which has a linear form.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}(t) \qquad (7)$$

If the initial adsorption rate h (mg g⁻¹ min⁻¹) is

$$h = k_2 q_e^2 \qquad (8)$$

Then Equations. (7) And (8) become:

$$\left(\frac{t}{q_t}\right) = \frac{1}{h} + \frac{1}{q_e}(t) \qquad (9)$$

The plot of (t/q_t) and t of equation (7) should give a linear relationship from which q_e and k_2 can be determined form the slope and intercept of the plot, respectively.

2.7 The Elovich equation

The Elovich model equation is generally expressed (Chien and Clayton 1980) as

$$\frac{dq_t}{d_t} = \alpha \exp(-\beta q_1) \qquad (10)$$

where, is the initial adsorption rate (mg.g^{-1} min^{-1}), b is the adsorption constant (g. mg^{-1}) during any one experiment.

To simplify the Elovich equation, assumed ab$_t$ >> t and by applying the boundary conditions q$_t$ = 0 at t = 0 and q$_t$=q$_t$ at t = t Eq (10) becomes;

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \qquad (11)$$

If Acid Orange 7 adsorption fits the Elovich model a plot of qt vs ln t should yield a linear relation ship with slope of (1/b) and an intercept of (1/b) In (a b)

3. RESULT AND DISCUSSION

3.1 Characterization of adsorbent

`Physico-chemical characterizations of the adsorbents were presented in Table 1.

Table 1 . Characteristics of the Nano structured Carbon materials

Parameter	JCAS	MWNTs
Bulk density (g/ml)	0.42	0.43
Ash content (%)	2.15	2.23
pH	6.2	6.9
Moisture content (%)	3.57	4.41
Surface area (m^2/g)	698	459
Iodine number(mg/g)	622	413
pH $_{zpc}$	6.2	7.9
Carbonyl (mmol/g)	0.02	0.03
Lactonic (mmol/g)	0.048	0.042
Phenolic (mmol/g)	0.015	0.015
Acidic (mmol/g)	0.029	0.031
Basic (mmol/g)	0.442	0.363

3.2 Optimum pH

The pH value of the solution being an important controlling parameter in adsorption is mainly influenced by the two factors: (i) Distribution of the dye ionized species in the solution phase and (ii) Overall charge of the adsorbent. Therefore the interaction between dye molecule and the adsorbent is basically a combined result of charges on the dye molecules and the surface of the adsorbent. The adsorption behavior of the dye on both the adsorbents was studied over a wide pH range of 2 -10. Fig.1 depicts that the pH significantly affects the extent of adsorption of dye over both adsorbents and a reduction the amount adsorbed with increasing pH was observed in both cases. Fig.1 also specifies that maximum uptake of the Acid Orange 7 is observed at pH 7.0 as well as a large decrease in adsorption capacity was observed as the pH is increased above 8 in both case. When the solution pH is above the pKa of dye (pKa for AO7 is 8.86), the adsorption decreases due to the electrostatic repulsion between dissociated adsorbate and adsorbent surface. Below the isoelectric point of both adsorbent(pH$_{pzc}$ of JCAC is 6.2 MWNTs is 7.9), the surface of adsorbent may
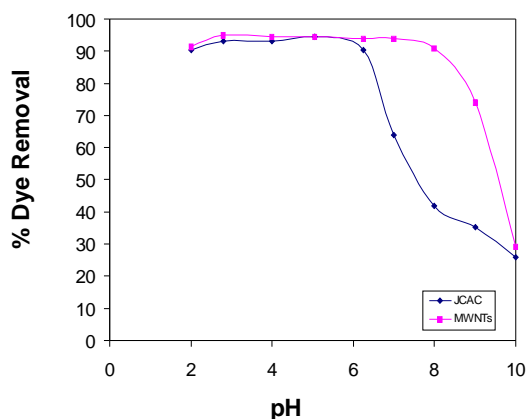

Fig. 1. Effect of of pH on percentage of removal of Acid Orange 7 by JCAC and MWNTS
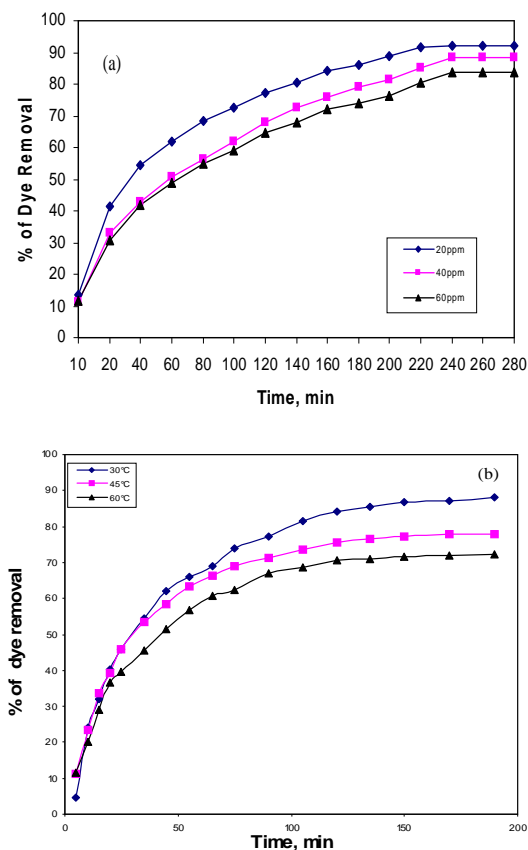
Fig 2. Effect of concentration on adsorption of Acid Orange 7 over (a) JCAC (b) MWNTS at different temperatures

acquire positive charge leading to an increased anionic dye adsorption due to electrostatic attraction. Apparently, the lower solution pH value, the more positive charges on carbon surface, the more attractive to negative charged dye on the nanoporous carbon surface.

3.3 Effect of concentration

The batch adsorption experiments were carried out by using three different concentrations of dye ion viz. 20mg/L, 40mg/L and 60mg/L at pH 6.5 at the reaction temperature of 30 °C were selected for each adsorbent.

Figures 2a and 2b clearly reveals the extend of adsorption of dye ion on both adsorbents increases linearly with increase in concentration of the adsorbent and than remains constant.

3.4 Effect of Temperature on kinetic rate constant and rate parameters

For both adsorption process, adsorption experiments were now carried out with fixed initial dye ion concentration (20mg/L) at pH 6.5 and at different temperature viz. 30 °C. 45 °C and 60 °C. The analysis of the data in (Table 2) reveals that the influence of temperature of the lead has very little influence on the pseudo first order and Elovich rate constants. The table 2 also reveals that the influence of the temperature of dye on pseudo second order rate constant is appreciable.

It is obvious that the adsorption of dye on both adsorbent is best described by pseudo second order rate equation with regression coefficient value is grater than 0.98.

Thermodynamic Parameter

The thermodynamic parameters obtained for the adsorption systems were calculated using the following equation (Inbaraj and Sulochana 2002).

$$K_c = \frac{C_{Ae}}{C_e} \qquad (12)$$

$$\Delta G = - RT \ln K_c \qquad (13)$$

$$\log K_c = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303\,RT} \qquad (14)$$

K_C is equilibrium constant, C_{Ae} is the solid phase concentration at equilibrium, C_e is residual concentration at equilibrium, R is gas constant (J/mole) and T is the temperature in Kelvin.

Table 2. Effect of Temperature on kinetic parameters for the chosen Adsorbents - Adsorbate systems

Adsor-bent	Initial Temper-ature	Pseudo first order		Pseudo Second order			Elorich Model		
		k_1 l min^{-1}	r^2	k_2 g mg^{-1} min^{-1}	H mg g^{-1} min^{-1}	r^2	β g min^{-1}	α mg g^{-1} min^{-1}	r^2
JCAC	30^0	0.217	0.978	0.0171	12.550	0.991	32.701	0.137	0.977
	45^0	0.106	0.977	6.107	5.207	0.995	15.704	0.143	0.975
	60^0	9.061	0.871	1.417	1.526	0.989	2.372	0.231	0.977
MWNTS	30^0	0.131	0.974	0.120	22.615	0.988	203.709	0.211	0.977
	45^0	0.135	0.980	0.011	15.210	0.992	74.150	0.139	0.967
	60^0	0.168	0.971	0.128	11.229	0.988	121.554	0.358	0.977

DH and DS was obtained from the slope and intercept of Vant Hoff plot (1/t Vs ln K_c). Table 3 gives the value of DG, DS and DH for the adsorption of JCAC and MWNTS. The negative values of free energy change (DG) indicate the feasibility and spontaneous nature of adsorption of JCAC & MWNTs. The positive value of DS is due to the increased randomness during the adsorption of adsorbents.

Mechanism

The high correlation coefficients obtained using pseudo first order and pseudo second order Models, it was impossible to concludes which adsorption mechanism actually occurred and was responsible for the ability of adsorbent to review other sources of information in an attempt to identify the specific adsorption mechanism.

In adsorption process of dye ion on the solid surface, the dye species migrate towards the surface of the adsorbent. This type of migration proceeds till the concentration of the adsorbate species, adsorbed, on to the surface of the adsorbent. Once equilibrium is attained, the migration of the solute species from the solution stops. Under this situation, it is possible to measure the magnitude of the distribution of the solute species between the liquid and solid phases. The magnitude of this kind of distribution is a measure of the efficiency of the chosen adsorbent in the adsorbate species.

When a powdered solid adsorbent material is made in contact with a solution containing dye, the dyes first migrate from the bulk solution to the surface of the liquid film. This surface exerts a diffusion barrier. This barrier may be very significant or less significant. The involvement of a significant quantum of diffusion barrier indicates the dominant role taken up by the film diffusion in the adsorption process. Furthermore, the rate of an adsorption process is controlled either by external diffusion, internal diffusion or by both types of diffusions.

The external diffusion controls the migration of the solute species from the solution to the boundary layer of the liquid phase. However, the internal diffusion controls the transfer of the solute species from the external surface of the adsorbent to the internal surface of the pores of the adsorbent material (Gupta et al. 2005).

Table 3 . Thermodyanamic parameters for Acid Orange 7, JCAC and MWNTS adsorption.

Adsorbent	$\Delta G \times 10^4$ (KJ mol^{-1})			ΔH	ΔS
	30^{0}C	45^{0}C	60^{0}C	(KJ mol^{-1})	(KJ mol^{-1})
JCAC	-20.96	-31.26	-33.62	59.53	130.34
MWNTs	-11.79	-10.74	-10.20	13.12	431.85

It is now well established, that during the adsorption of dye ion over a porous adsorbent, the following three consecutive steps are taken place (Gupta et al. 2003). (i) transport of the ingoing adsorbate ions to external surface of the adsorbent (film diffusion).

(ii) transport of the adsorbate ions within the pores of the adsorbent except for a small amount of adsorption, which occurs on the external surface (particle diffusion).

(iii) adsorption of the ingoing adsorbate ions on the interior surface of the adsorbent.

Out of these three processes, the third process is considered to be very fast and is not the rate limiting step in the uptake of organic compounds (Weber Jr. et al. 1963). The remaining two steps impart the following three possibilities:

Case 1: External transport > internal transport, where rate is governed by particle diffusion.
Case 2: External transport < internal transport, where the rate is governed by film diffusion.
Case 3: External transport H" internal transport, which accounts for the transport of the adsorbate ions to the boundary and may not be possible within a significant rate, which later on gives rise to the formation of a liquid film surrounded by the adsorbent particles with a proper concentration gradient.

In the batch-mode contact time adsorption experiments, rapid stirring is maintained. This Acid Orange 7 to the transport of the adsorbed species from the solution to the pores of the adsorbent material and this step may control the rate of the adsorption process.

According to Michelson et al., (1975) for film diffusion to be rate-determining step, the value of the film diffusion coefficient, D_f should be in the range $10^{-6} – 10^{-8}$ cm^2/ sec. If pore diffusion were to the rate limiting, the pore diffusion coefficient, D_p, should be in the range 10^{-11}- 10^{-13} cm^2/ sec. In order to find out the nature of the process responsible for adsorption on to chosen adsorbent, attempts were made to calculate the diffusion co-efficient of the process.

Assuming spherical geometry of the sorbents (Bhattacharya et al. 1984), the overall rate constant of the process can be correlated to the pore diffusion coefficient in accordance with the expression,

$$t_{1/2} = 0.03 \frac{r_0^2}{D_p} \qquad (15)$$

or to the film diffusion coefficient in accordance with

$$t_{1/2} = 0.23 \frac{r_o^\partial}{D_f} \times \frac{\overline{C}}{C} \qquad (16)$$

where r_o is radius of the sorbent (cm), D_p and D_f are pore diffusion coefficient (cm^2/sec) and film diffusion coefficient (cm^2/sec) respectively, is equilibrium loading of the adsorbent , " is the film

thickness (cm) and $t_{1/2}$ is the time for half change (sec) .

Since the Nano porous carbon materials used were of the size of 75microns, and the film diffusion coefficients and pore diffusion coefficients were calculated.

The adsorption of dye on MWNTs is remarkably different from JCAC in severalFirst , due to their one dimentional nano structure, the external surface available for adsorption is considerably larger than the surface area arising from inner cavities. The predominance of outer cavity surface area to inner cavity surface area determines the adsorption characteristics of dye on MWNTs than JCAC. Another noteworthy difference should be ascribed to the interstitial space between individual nanotubes. Then considering the pseudo first order rate constant k_L, for the adsorption of Acid Orange 7. The values of D_p and D_f were calculated under the given set of operating conditions, and are presented in the Table 4.

The present study indicates the D_p values in the order of 10^{-11} to 10^{-10} cm/sec and the D_f values in the order of 10^{-10} to 10^{-9} for the respective Lagergren plots for Acid Orange 7 and hence, the investigator concludes that the mechanism of the removal of Acid Orange 7 in the present study by both adsorbents is complex.

Since both external Mass transfer and intraparticle diffusion constants varied with initial Acid Orange 7 concentration indicating the occurrence of both film diffusion and intra particle diffusion, the sorption data were further analyzed by the kinetic expression given by Boyd et al. (1947) as

$$F = 1 - \frac{6}{\pi^2} \sum_{N-1}^{\alpha} \frac{1}{n^2} \exp\left[\frac{-Dit\pi^2 n^2}{r^2} \right] \qquad (17)$$

$$F = 1 - \frac{6}{\pi^2} \sum_{N-1}^{\alpha} \frac{1}{n^2} \exp\left[-n^2 \beta_t \right] \qquad (18)$$

Where F is the fractional attainment of equilibrium at time t and is obtained by using following equation and n. is the integer value.

$$F = \frac{q_t}{q_e} \qquad (19)$$

Where q_t and qe are the amounts adsorbed at time t and at equilibrium respectively.

On the basis of F values, corresponding values of B_t were obtained from equation 19 (Reichenberg, 1953). The B_t vs time plots for the sorption of Acid Orange 7 over JCAC and MWNTS (Figure 3a and 3b) are found to be linear in beginning. Thus the process is seems to be particle diffusion controlled in this region, while during the later deviation from linearity occurs and they also did not pass through the origin through out concentration range at 30, 45 and 60°C Thus the overall process can be interpreted as film diffusion.

Table 4. D_p and D_f values for the chosen adsorbent - adsorbate system

Temper-ature, °C	$t_{1/2}$, s	JCAC		MWNTS	
		D_p x 10^{-10}, cm^2	D_f, x 10^{-9}, cm^2	D_p x 10^{-10}, cm^2	D_f, x 10^{-9}, cm^2
30	354552	1.1410	6.419	1.574	7.225
45	4633.39	0.6892	4.478	0. 965	5.737
60	4755.37	0.6561	4.132	0. 672	4.393
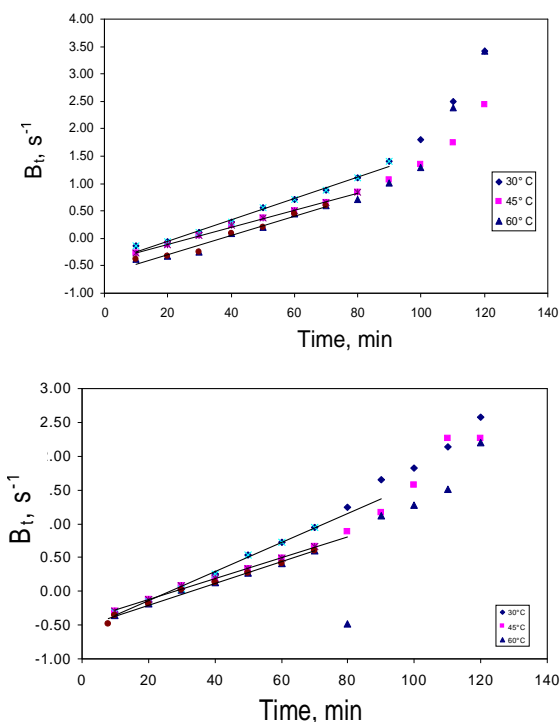
Fig. 3 : Time vs B$_t$ plots different temperature of (a) Acid Orange 7- JCAC adsorption and (b) Acid Orange 7-MWNTS adsorption

From the slop of the straight line obtained from time versus B$_t$ graph, the B value (time constant) was calculated. The values of effective diffusion coefficient (D$_i$) were calculated at different temperatures using the following Equation.

B = ð²D$_i$ / r², here 'r' is the radius of the absorbent particle. The Di values are given in the Table 5. The plot of 1/T versus log D$_i$ was found linear (not given) with negative slope indicating thereby the increase in the mobility of ions. This is due to the fact that with the rise in temperature the mobility of ions increases, which consequently decreases the retarding force acting on the diffusing ions.

The Values of energy of activation E$_a$, entropy of activation "S$^\#$ and pre-exponential

constant D$_o$ were calculated using following Equations.

$$D_i = D_o \ \exp [\ \text{-}E_a \ / \ RT]$$

$$D_o = (\ 2.72 \ d^2kT/h) \ . \ \exp \ [ÄS^\# \ / \ R]$$

Where d is the average distance between the successive exchange sites and is taken as 5 A°. R, h and k are the Gas, Planck, and Boltzmann constants, respectively. The values of E$_a$, D$_i$, Do, "S$^\#$ and other parameters are given in Table 4.

4. CONCLUSIONS

Removal of Acid Orange 7 from aqueous solution was possible using several abundantly available low cost adsorbents. The adsorption of Acid Orange 7 was found to be dependent on pH, temperature and concentration for both adsorbents. Thermodynamic parameters obtained for both the adsorbents accounts for feasibility of the process at each concentration. Further the kinetic studies apparently reveal that the removal takes through a film diffusion process at all the concentrations and temperature for JCAC as well as MWNTS from *Jatropha Curcas*. The percentage saturation was found to be almost 93 and 94% for the JCAC and MWNTS respectively. The kinetics of Acid Orange 7 adsorption on different adsorbents was found to follow a pseudo second -order rate equation.

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