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Dynamic and Equilibrium Studies on the sorption of Basic dye (Basic Brown 4) onto Multi-walled Carbon Nanotubes Prepared from Renewable Carbon Precursors

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Abstract

The main objective of this research was to evaluate the adsorption mechanism of Multi-walled carbon nanotubes synthesized from Pine oil, methyl ester of Jatropha curcas oil and methyl ester of Pongamiya pinnata oil in comparison with commercial Activated Carbon for the removal of Basic dye (Basic brown 4). The Multi-walled nanotubes synthesized from respective precursors by spray pyrolysis method were used as adsorbent. The sorbent properties of these materials for the removal of Basic brown 4 dye from aqueous solution was studied. The effect of variables such as temperature, initial concentration, solution pH and the sorbent property of the materials in a batch mode contact time process was investigated. The influences of different factors on the adsorption of Basic brown 4 on these adsorbents were explained in terms of electrostatic fields on the Basic brown 4 dye molecule and on the surface of adsorbents. The specific rate constant measurements confirming the applicability of pseudo second order rate expression for the process. Thermodynamic parameters such as free energy change, enthalpy change and entropy change were calculated. The negative value of free energy change indicates that the Basic Brown dye adsorption process is spontaneous and the positive value of enthalpy change shows the endothermic in nature. The kinetic measurements enabled to propose possible mechanism of adsorption involved in this process.

Keywords: *Activated carbon; Adsorption; Basic Brown 4 dye; Film diffusion; Multi-walled Carbon Nanotubes; Pore diffusion.*

1. INTRODUCTION

Water pollution is mainly due to the discharge of untreated or partially treated waste water into land and water bodies by many industries including leather industries, textile companies and dye manufactures (Kuo *et al.* 2008). Synthetic dye stuffs, mostly based on aromatic molecular structure, are extensively used as coloring agents in the textile, paper, leather, gasoline, pharmaceutical, and food industries. Their discharges into the hydrosphere possess a significant source of

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pollution due to toxic chemicals produced by the anaerobic decomposition and incomplete bacterial degradation of the dyes (Weber *et al.* 1987). The complex aromatic structure and synthetic origin of the dyes make them stable to the heat, oxidizing agents, photo degradation and biodegradation. Due to toxicity of dyes, it is necessary to eliminate dyes from wastewater before its discharge to aqueous bodies (Jambulingam *et al.* 2007; Lata *et al.* 2007; Wang *et al.* 2008). Activated carbon is the most popular and widely used adsorbent for removal of organic dye pollutant because of high adsorption efficiency for the organic compounds (Jambulingam *et al.* 2005; Basar, 2006).

The adsorptive properties of active carbon for removal of pollutants are well documented (Macias-Garsia *et al.* 1993; Karthikeyan *et al.* 2012). One of the major challenges associated with activated carbon as adsorbent is its cost effectiveness and separation inconvenience. Therefore efforts are still needed to carry out investigations for new promising adsorbents. An increased attention is being observed for carbon nanotubes and functionalized nanoparticles(Rao *et al.* 2007; sakthivel *et al.* 2013; Shin *et al.* 2007). These nanomaterials seem to be attractive for prospective environmental applications, because their sorption characteristics are better in comparison to conventional adsorptive materials. The sorption capacity, adsorption kinetics and thermodynamic parameters are the most important parameters of the sorbent characteristics because it determines the favorability of the adsorbent for removing pollutants from solution.

The aim of this work includes comparative kinetic studies of Basic brown 4 dye adsorption onto commercial activated carbon (CAC) and Multi-walled Carbon nanotubes (MWNTs) synthesized from plant based carbon sources viz. Pine oil, methyl ester of *Jatropha curcas* oil and methyl ester of pongamiya pinnata oil. In the present paper the effect of various parameters such as solution pH, initial concentration and temperature on the adsorption process has been presented and discussed.

2. EXPERIMENT

2.1 Preparation of adsorbent s

The plant based carbon sources viz. pine oil, methyl ester of *Jatropha curcas* oil and methyl ester of *pongamiya pinnata* oil were used as a precursors for the synthesis of MWNTs by CVD process (Maheswari *et al.* 2012; Karthikeyan *et al.* 2010a, 2010b). Final

Table. 1: Physico-chemical characteristics of chosen adsorbents

Parameters	PMWNTs	JCMWNTS	PPMWNTS	CAC
Bulk density, (g mL^{-1})	0.28	0.26	0.52	0.43
Ash content, (%)	2.53	2.13	24.7	2.12
pH	6.7	6.6	6.1	6.3
Moisture content, (%)	1.7	0.8	1.2	3.2
Surface area, ($m^2 g^{-1}$)	138	143	118	648
Diameter	20-40nm	20-40nm	20-40nm	180-250 μm
Purity, (%)	>95	>94	>95	>98
I_G/I_D ratio	1.84	2.14	0.78	-
Point of zero charge (P^H_{pzc})	6.7	6.8	5.4	6.2

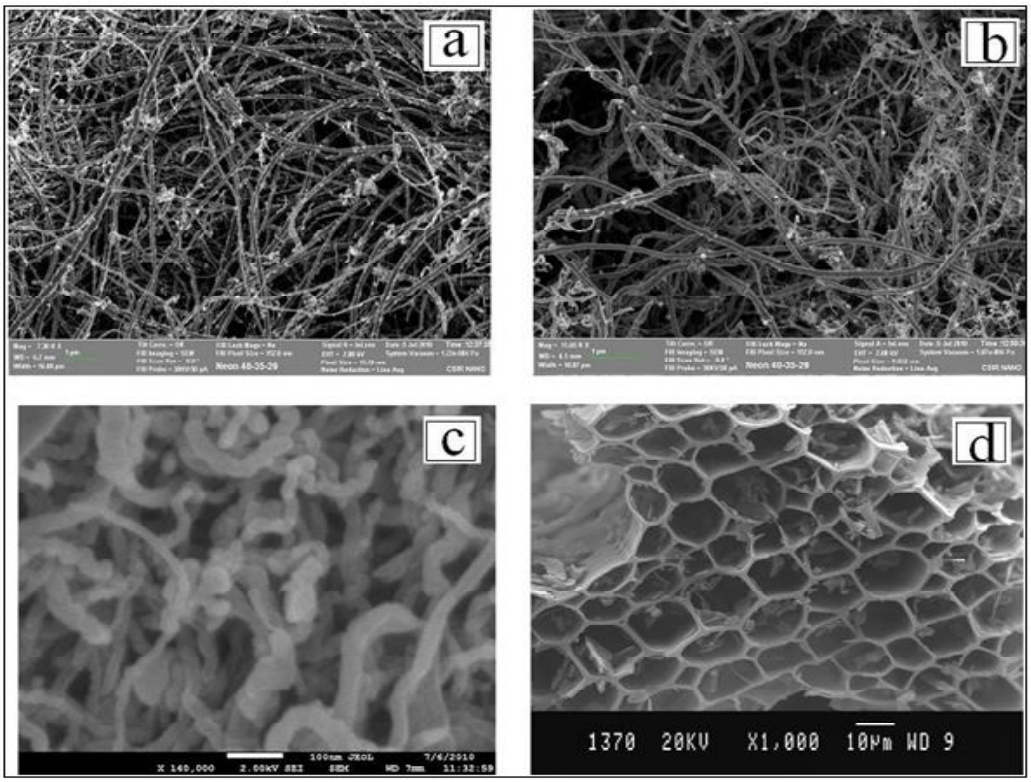

Fig. 1 : (a) The SEM image of PMWNTs; (b) JCMWNTS (b); (c) PPMWNTs and (d)CAC

products obtained in each case were purified by chemical method using HNO_3 (Mahalingam *et al.* 2012) and stored separately in a vacuum desicator until used. The resulting MWNTs from pine oil, methyl ester of *Jatropha curcas* oil and methyl ester of pongamiya pinnata oil were named as PMWNTs, JCMWNTs and PPMWNTs respectively. Activated carbon powder were obtained from M/s Raj Carbon, Tuticorin, India and used as such. The properties of chosen adsorbents are given in Table 1. and the Scanning Electron Microscopic images of the adsorbents are shown in Fig. 1.

2.2 Preparation of dye solution

All chemicals were purchased in analytical (Merck, India) and were used without further purification. Basic brown 4 dye stock solution of 1000 mg L^{-1} was prepared. The experimental solutions were obtained by diluting teh dye stock wolution with distilled water when ever necessary pH of the solution was adjusted with 0.01N HNO_3 or NaOH solutions. The properties of the Basic Brown 4 dye are given in Table 2 and its molecular structure is shown in Fig 2.

2.3 Adsorption experiment

For adsorption studies, the batch mode contact time technique was used because of its simplicity. The adsorption experiments were carried out by agitating chosen quantity (50 mg) of adsorbent in 100 mL dye solution of appropriate concentration (25, 50, 75 mg L^{-1}) at a speed of 200rpm in a thermostatic shaker bath at 30 °C for specified period of time. The Basic

brown 4 dye concentration in tghe solution was measured at 459 nm wavelength using UV-vis spectrometer (Elico make Bio-UV Spectrophotometer model BL-192).

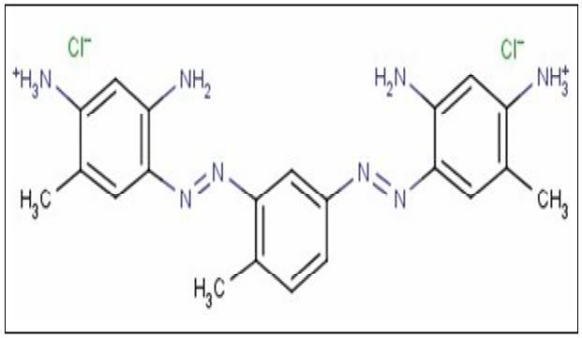

Fig. 2 : Chemical structure of Basic Brown 4 dye molecule

Table 2. Details of Basic Brown 4 dye

Parameter	Value
Suggested Name	Basic Brown 4
C.I Number	45170
C.I. Name	Basic violet
Class	Rhodamine
Ionization	Basic
Empirical formula	C21 H26 Cl2N8
Formula weight	479

2.4 The effect of solution pH on adsorption of dye

The pH of the solution influences the distributio of the ionized due species and overall charge on the surface of adsorbent. As the interaction between the dye molecule and the adsorbent is basically a combined result of charges on the dye molecule and the surface of the adsorbent, the adsorption behavior of the dye on each adsorbents were studied over a pH range of 2-10 and the results are depicted in Fig.3a. The Fig.3a shows that solution pH significantly affects the extent of adsorption of dye on each adsorbent. The maximum uptake of Basic brown 4 dye is observed at solution pH above 6 for chosen adsorbents. An increased dye adsorption above the point of zero charge (P^{H}pzc) of adsorbents may be attributed to the increase in electrostatic attraction between adsorbents and dye. A large decrease in adsorption capacity at solution pH below 4 may be due to the electrostatic repulsion between positively charged adsorbents and the Basic Brown 4 dye molecule

2.5 Effect of agitation time

Agitation time is one of the crucial parameters in the adsorption process, as it influences extend of adsorption in a solution. The effect of agitation time on the adsorption of Basic Brown dye onto the chosen adsorbents at 30 °C was studied for solution pH 6.5. The results were shown in Fig 3b. The adsorption curves for the uptake of Basic Brown 4 dye by the chosen adsorbents are single, smooth and continuous till the saturation of dye on the adsorbent. It is observed that the maximum amount of Basic Brown dye adsorption occurs within the contact time of 30 minutes and it reaches equilibrium at 180 min.

2.6 Effect of temperature on kinetic rate constant and rate parameters

Among the factors that affect adsorption process, solution temperature best revels suitability of the adsorbent. To study the effect of temperature on adsorption property of these adsorbents for the removal of Basic Brown 4 dye, experiments were conducted at three different temperatures (30, 45 and 60 °C) with solution pH 6.5 and initial dye concentration 20 mg/L for 300 min as process time. It was observed that increased the solution temperature significantly affected the adsorption of Basic brown 4 dye on the chosen adsorbents.

2.6.1 Kinetics of adsorption

Adsorption kinetics is used to investigate the mechanism and the rate controlling steps of adsorption. The kinetic date obtained is then applied to different

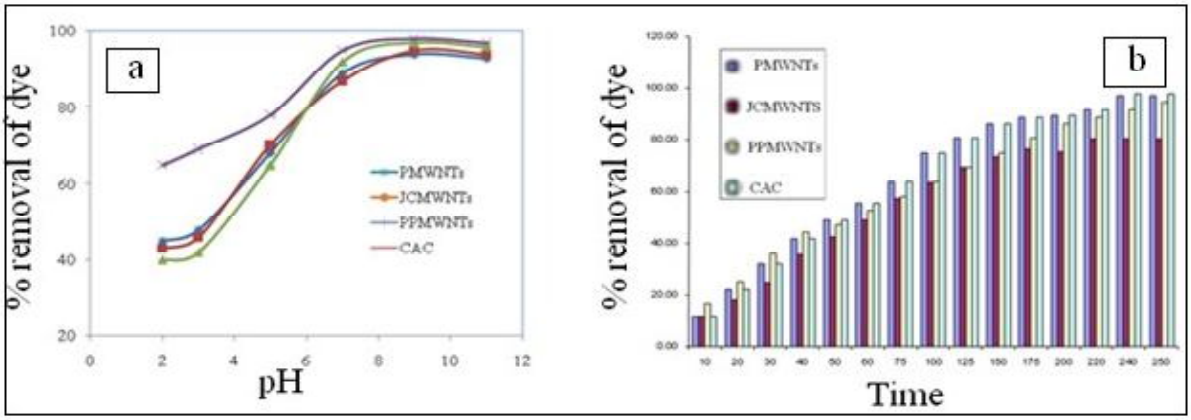

Fig . 3a. Influence of pH on adsorption of Basic Brown 4 dye; 3b. Influence of agitation time on adsorption of Basic Brown 4 dye

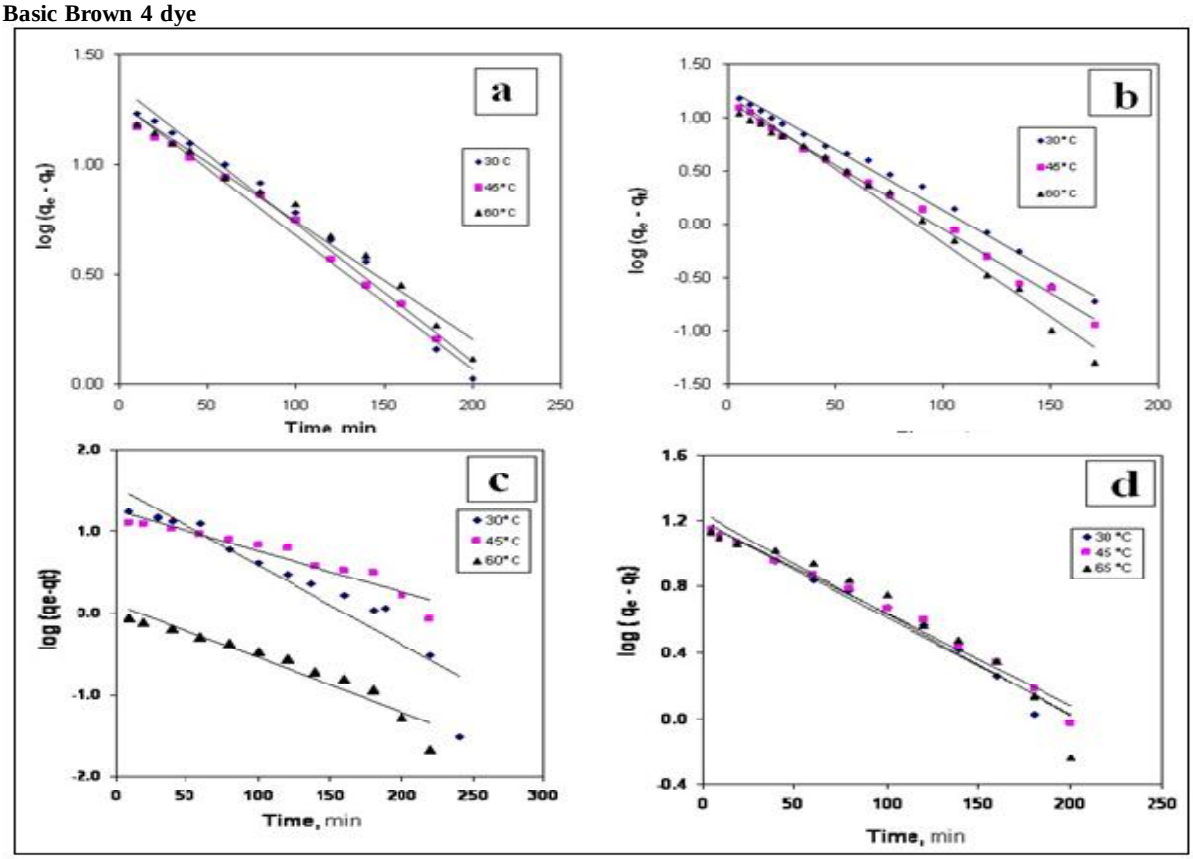

Fig 4 : Pseudo-first order plots for adsorption of Basic Brown dye onto PMWNTs, JCMWNTs, PPMWNTs and CAC at 30°C First order

models to describe the interaction between the Basic brown 4 dye molecule and the chosen adsorbents. The pseudo-first order, pseudo-second order and Elovich kinetic models were used to understand the complex dynamics of the adsorption process. To determine the equation that best described the adsorption of dye, a standard error of estimate was calculated for each kinetic equation viz. pseudo first order kinetic, pseudo-second order and Elovich equation. A relatively high value of the regression coefficient (R^2) and low standard error of estimate (SE) were used as criteria for the best fit (Chien et al. 1980). The R^2 and SE were calculated using the following equations.

$$R^2 = [Sq^2 - Sq - q')^2] / Sq^2 \quad (1)$$

$$SE = [\Sigma q - q')^2 / [N-2]0.5 \quad (2)$$

where q and q' are the measured and calculated amount of dye adsorbed on adsorbent respectively at time t and N is the number of measurements (Steel et al., 1960).

2.6.1.1 Pseudo-first order kinetic model

The pseudo-first order equation (Lagergren, 1898) is generally expressed as first order rate expression as shown below.

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

Where q_a and q_t are the adsorption capacity (mg g^{-1}) at equilibrium and at time t respectively, k1 is the rate constant of pseudo-first order adsorption (min^{-1}). Integrating the equation with boundary condition at initial time (t=0), qt=0 and at any time (t>0), the amount of dye adsorbed is q_t and then rearranging the rate law for a pseudo-first order reaction becomes

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

The plot of $\log(q_e - q_t)$ versus t should give a straight line. The pseudo-first order plot order for the adsorption of basic Brown 4 dye on the chosen adsorbents is given in Fig. 4. k_1 and q_e values were determined from the slope and intercept of the plot respectively. The calculated values are summarized in Table 3.

2.6.1.2 Pseudo-second order kinetic model

The pseudo-second order equation (Ho *et al.* 2000) has been considered for describing the adsorption of Basic Brown 4 dye on chosen adsorbates. The linearized form of the pseudo-second order rate equation is given as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{1}{q_e}(t) \quad (5)$$

Where k_2 is the rate constant of pseudo second order adsorption (g mg^{-1} min^{-1}), q_e and q_t are the values of the amount of dye adsorbed per unit mass of adsorbate at equilibrium and at any time t, respectively. If the initial adsorption rate h (mg g^{-1} min^{-1}) is expressed as

$$h = k_2 q_e^2 \quad (6)$$

then the equation (3) becomes

$$\left(\frac{t}{q_t}\right) = \frac{1}{h} + \frac{1}{q_e}(t) \quad (7)$$

The plot of t/q_t versus t should give a linear relationship from which k_2 and q_e can be determined respectively from the intercept and slope of the plot Fig. 5. The calculated values are summarized in Table 3.

2.6.1.3 Elovich model

The Elovich equation is another kinetic model used to describe the adsorption of Basic Brown 4 dye on chosen solid adsorbents. The equation (Chien *et al.*1980) is generally expressed as

$$\frac{dq_t}{d_t} = \alpha \exp(-\beta q_1) \quad (8)$$

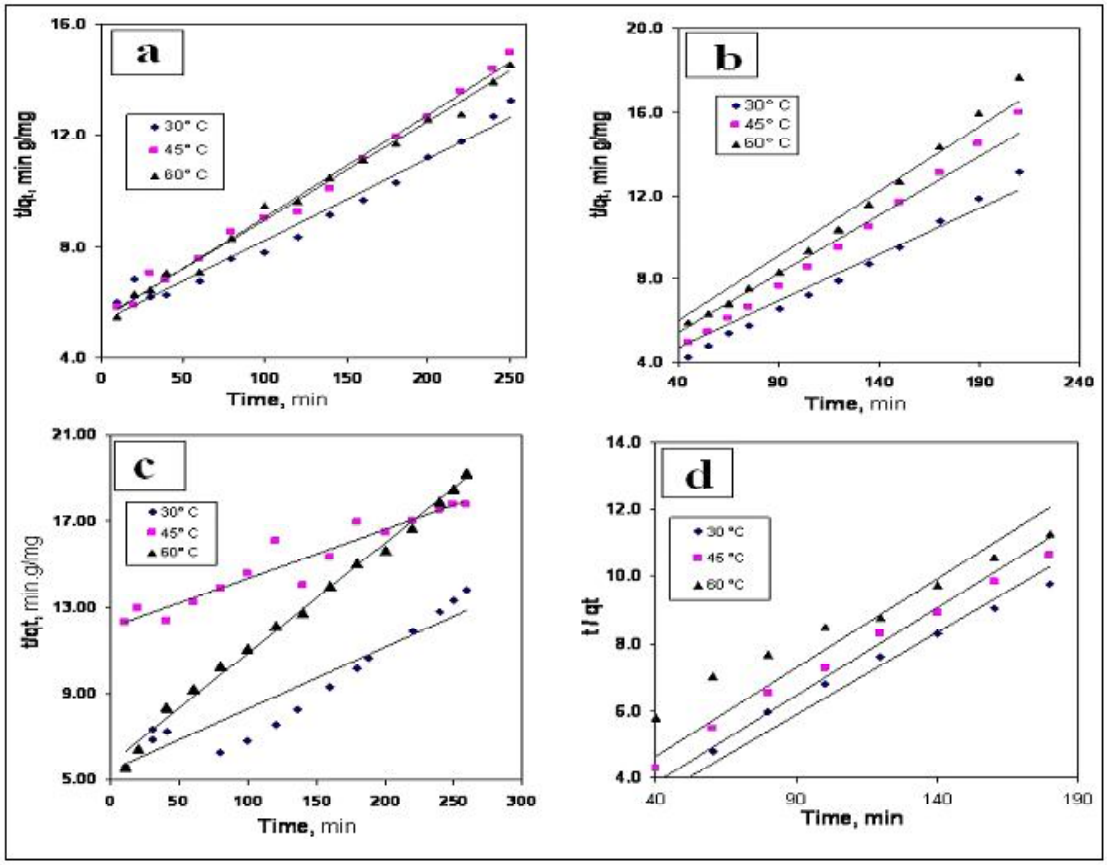

Fig .5 : Pseudo-second order plots for adsorption of Basic Brown dye onto PMWNTs, JCMWNTs, PPMWNTs and CAC at 30°C

On integrating this equation for the boundary conditions, it gives

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \qquad (9)$$

where a and b are the Elovich coefficients that represent the initial adsorption rate (mg g^{-1} min^{-1}) and the desorption constant (g mg^{-1}) respectively. Ifthe adsorption of Basic Brown 4 dye on PMWNTs, JCMWNTs, PPMWNTs and CAC fits to the Elovich model, a plot of q_t versus ln t in Fig. 6 should give a linear relationship with a slope of 1/b and an intercept of 1/b ln (ab). The Elovich constants a and b computed from the slope and intercept of the q_t versus ln t plots were tabulated in Table 3.

2.6.2 Adsorption isotherm

The successful representation of the dynamic adsorptive separation of adsorbate from solution onto an adsorbent depends upon a good description of the equilibrium separation between the two phases. An adsorption isotherm is characterized by certain constant values, which express the surface properties and affinity of the adsorbent for adsorbate. The two well known adsorption isotherm models are Langmuir and Freundlich isotherms. The Langmuir isotherm assumes

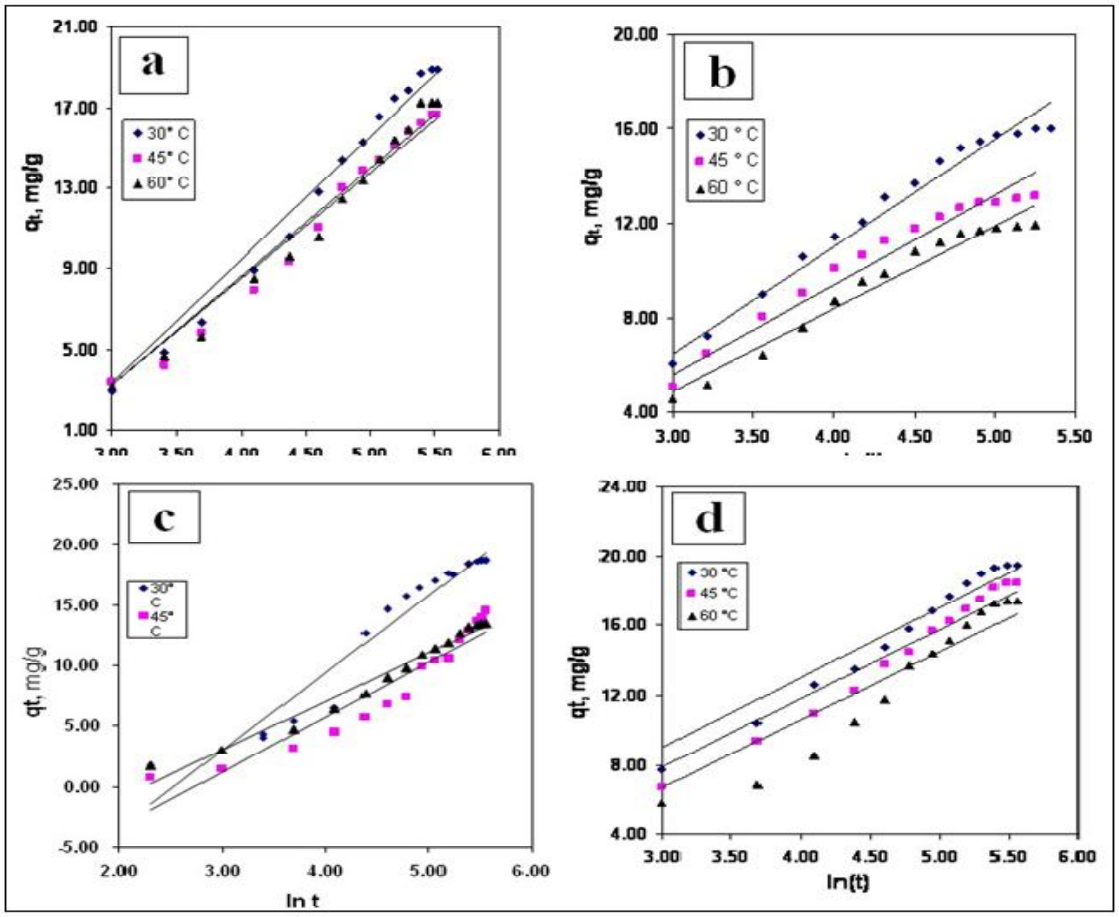

Fig .6 : Elovich plots for adsorption of Basic Brown dye onto PMWNTs, JCMWNTs, PPMWNTs and CAC at 30°C

monolayer adsorption of adsorbate onto a surface containing a finite number of adsorption sites, while the Freundlich isotherm model assumes heterogeneous surface energies (Fytianos *et al.* 2000). In this study, Langmuir and Freundlich employed for the treatment of the equilibrium adsorption data. The applicability of the isotherm equation is compared by judging the correlation coefficient R^2.

2.6.2.1 Langmuir isotherm

Isotherms were determined at three different temperatures viz. 30, 45 and 60 °C. The linear regression analysis of Langmuir plots were drawn using the following equation

$$C_e / q_e = (C_e / Q_0) + (1 / Q_0 b_L) \qquad (10)$$

where q_e is the amount adsorbed at equilibrium (mg g^{-1}); Q_0, the monolayer adsorption capacity (mg g^{-1}); C_e, the equilibrium concentration of adsorbate (mg L^{-1}); and b_L, the Langmuir constant related to energy of adsorption. Fig.7 represents variation of C_e/q_e with C_e for three different temperatures viz. 30, 45, and 60 °C. The respective data were shown in Table 4. The essential characteristics of Langmuir isotherm can be

Table 3. Kinetic parameters for the removal of Basic Brown dye by the chosen adsorbents PMWNTs, JCMWNTs, PPMWNTs and CAC at different temperatures

		PMWNTs			JCMWNTs			PPMWNTs			CAC		
		30 °C	45 °C	60 °C	30 °C	45 °C	60 °C	30 °C	45 °C	60 °C	30 °C	45 °C	60 °C
Pseudo-First Order	k_1 min^{-1}	0.018	0.013	0.011	0.025	0.027	0.029	0.013	0.011	0.020	0.011	0.015	0.013
	R^2	0.982	0.981	0.980	0.989	0.996	0.986	0.926	0.915	0.889	0.979	0.985	0.938
	SE	0.0521	0.0423	0.0413	0.0532	0.0473	0.0398	0.0673	0.0761	0.0802	0.0472	0.0359	0.0578
Pseudo-Second Order	k_2 X 10^{-4} $g\,mg^{-1}\,min^{-1}$	1.588	2.552	2.265	6.655	9.899	10.948	1.440	3.997	4.293	16.114	15.064	10.641
	h $mg\,g^{-1}\,min^{-1}$	0.189	0.186	0.185	0.344	0.316	0.285	0.184	0.826	0.172	0.671	0.557	0.394
	R^2	0.973	0.991	0.992	0.905	0.926	0.957	0.851	0.917	0.993	0.979	0.977	0.928
	SE	0.0234	0.0122	0.0157	0.0134	0.0176	0.0145	0.0176	0.0124	0.0127	0.0132	0.0145	0.0148
Elovich	α $mg\,g^{-1}$ min^{-1}	0.530	0.489	0.490	0.939	0.819	0.701	0.515	0.297	0.433	0.49764	0.46510	0.39263
	β $g\,mg^{-1}$	0.164	0.192	0.188	0.220	0.262	0.285	0.157	0.222	0.251	0.249	0.254	0.256
	R^2	0.765	0.834	0.873	0.912	0.921	0.924	0.936	0.904	0.907	0.936	0.904	0.907
	SE	0.0954	0.0921	0.0932	0.0915	0.0974	0.0913	0.0885	0.0953	0.0915	0.0935	0.017	0.0893

Table 4. Isotherm parameters for the adsorption of Basic Brown dye on to the chosen adsorbents PMWNTs, JCMWNTs, PPMWNTs and CAC at different temperatures

		PMWNTs			JCMWNTs			PPMWNTs			CAC		
		30 °C	45 °C	60 °C	30 °C	45 °C	60 °C	30 °C	45 °C	60 °C	30 °C	45 °C	60 °C
Langmuir Isotherm	Q_0 $mg\,g^{-1}$	118	111	100	142	58.8	45.4	200	198	125	76.9	32.2	22.7
	B $L\,mg^{-1}$	0.048	0.029	0.027	0.065	0.052	0.063	0.024	0.021	0.034	0.148	0.392	0.234
	R^2	0.994	0.991	0.988	0.973	0.975	0.975	0.988	0.991	0.947	0.921	0.965	0.948
	SE	0.062	0.074	0.067	0.066	0.077	0.086	0.093	0.064	0.062	0.086	0.088	0.089
Freundlich Isotherm	h	3.906	4.219	7.143	1.883	2.66	3.39	1.916	1.689	1.908	1.377	1.376	2.012
	K_f $L\,g^{-1}$	21.429	11.803	10.56	14.125	9.016	8.886	8.67	6.916	6.683	6.761	5.834	5.12
	R^2	0.942	0.986	0.797	0.962	0.99	0.993	0.951	0.961	0.974	0.948	0.956	0.982
	SE	0.0954	0.0921	0.0932	0.0915	0.0974	0.0913	0.0885	0.0953	0.0915	0.0935	0.017	0.0893

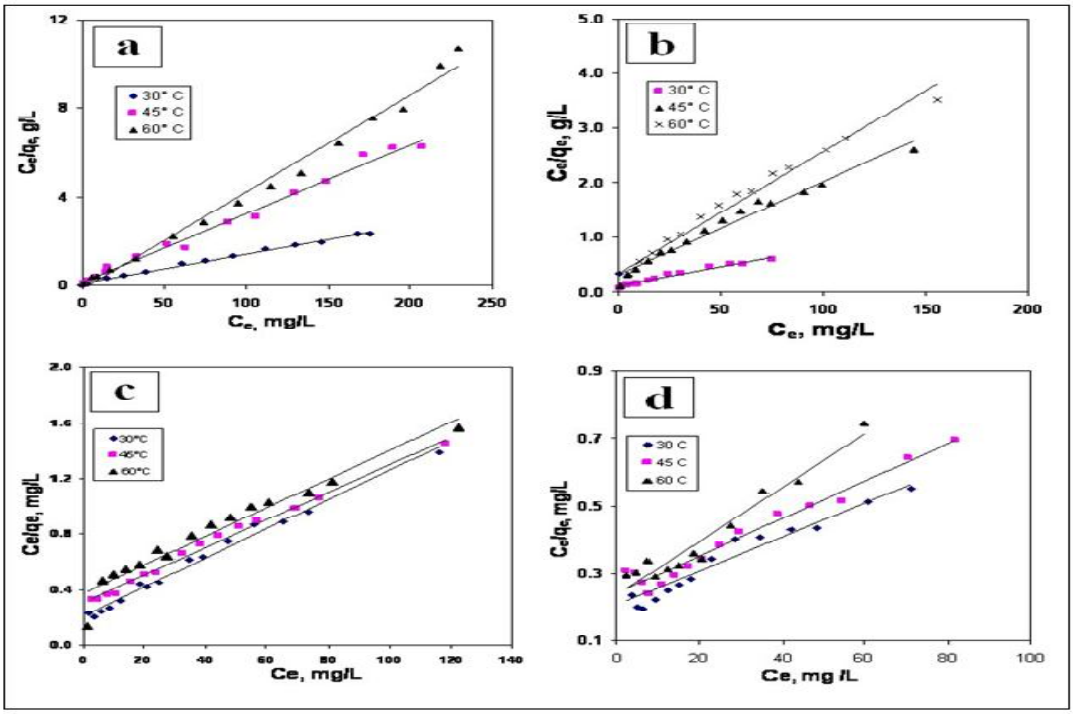

Fig. 7 : Langmuir isotherms for adsorption of Basic Brown 4 dye onto PMWNTs, JCMWNTs, PPMWNTs and CAC

expressed in terms of dimension less constant, separation factor (R_L) (Yang *et al*. 1993) which is defined by

$$R_L = 1 / (1 + b_L C_0) \quad (11)$$

The R^2 value of langumuir model for adsorption of Basic Brown 4 dye molecule on PMWNTs, JCMWNTs, PMWNTs and CAC are shown in table 4, where C_0 is the initial concentration of dye (mg L^{-1}). The value of R_L ranged from 0 and 1,conforms that the adsorption process is favourable.

2.6.2.2 Freundlich isotherm

The Freundlich model brings out the relation between log (x/m) and log C_e. The Freundlich isotherm was determined at three different temperatures viz 30, 45 and 60 °C. The linear plot of Freundlich isotherm model was drawn using the following equation.

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (12)$$

where k_f is the measure of adsorption capacity; and n the adsorption intensity.

2.6.3 Thermodynamic parameter

The thermodynamic parameters like ΔG, ΔH and ΔS provide in-depth information to determine the spontaneity and energetic changes associated with adsorption. The Langmuir isotherm equation is applied to calculate the thermodynamic parameters as follows (Inbaraj *et al.* 2002).

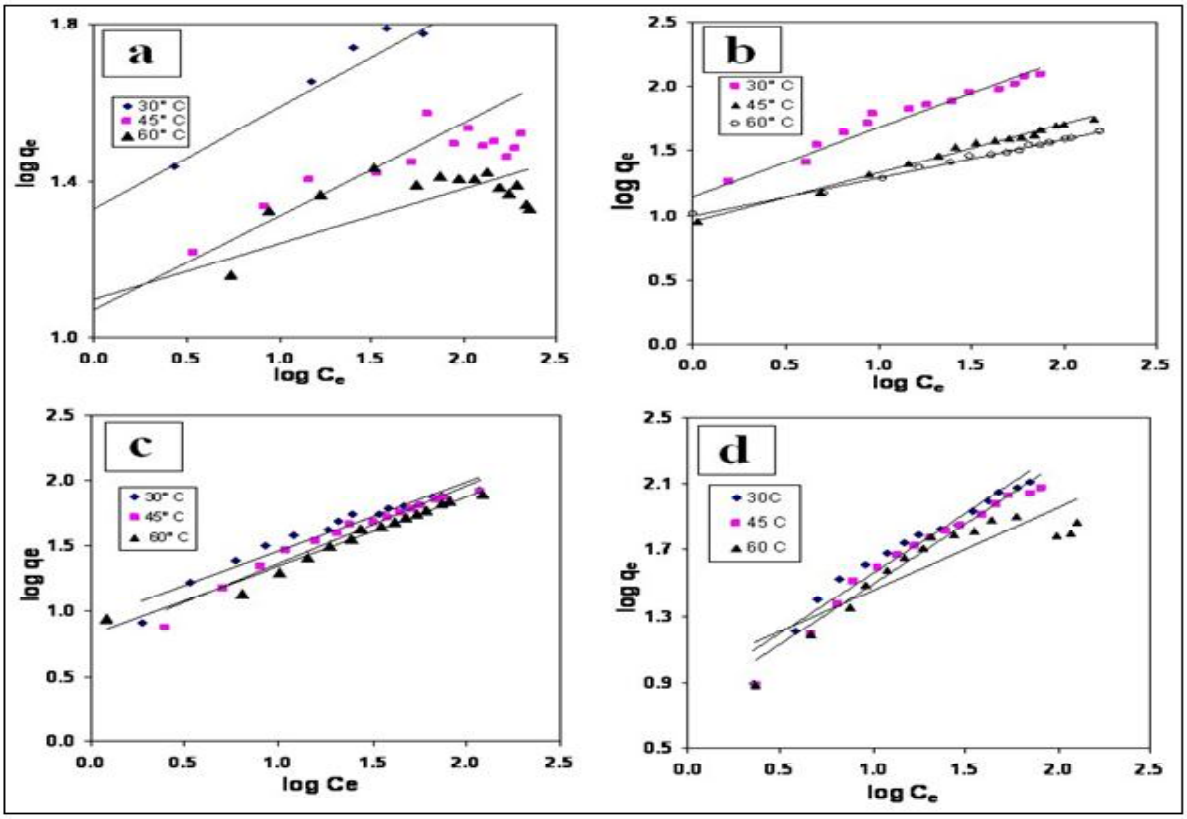

Fig 8. Freundlich isotherms for adsorption of Basic Brown dye onto PMWNTs, JCMWNTs, PPMWNTs and CAC

$$K_c = \frac{C_{Ae}}{C_e} \quad (13)$$

$$\Delta G = -RT \ln K_c \quad (14)$$

$$\log K_c = \frac{\Delta S}{2.303\,R} - \frac{\Delta H}{2.303\,RT} \quad (15)$$

K_c is the Langmuir equilibrium constant; ΔS is entropy change; ΔH the enthalpy change; C_{AC} and C_c are the equilibrium concentration of Basic Brown 4 dye adsorbed on the adsorbent (mg g^{-1}) and in the solution (mg L^{-1}) respectively; R is the gas constant (8.314 J mol^{1} K^{-1}); and T is the solution temperature in Kelvin. The thermodynamic parameters were obtained from the slope and intercept of Vant Hoff plot (1/t versus logKc). Table 5 gives the value of ΔH, ΔS and ΔG for the removal of Basic Brown 4 dye by the chosen adsorbents.

3. RESULTS & DISCUSSION

The correlation coefficient (R^2) values show that the Elovich model does not fit for the adsorption of Basic Brown 4 dye onto the chosen adsorbents. The Elovich model is mainly applicable for chemisorptions

kinetics (Palanisamy *et al.* 2009). The unsuitability of Elovich model to describe the adsorption of Basic Brown 4 dye on the chosen PMWNTs, JCMWNTs, PPMWNTs and CAC adsorbents at operating conditions shows that the adsorption of the Basic Brown 4 dye on the chosen adsorbents is physisorption in nature.

The pseudo-first -order kinetic plot of $\log(q_e-q_t)$ versus t shown in Fig. 4 for the adsorption of Basic Brown 4 onto the chosen four different adsorbents viz. Pine oil (PMWNTs), methyl ester of *Jatropha curcas* oil (JCMWNTs) and methyl ester of *Pongamia pinnata* oil (PPMWNTS) at three different temperatures (30, 45 and 65 °C) under investigation, indicates the experimental data fit to the linearized equation with correlation coefficient (above 0.978) for all the linear lines Table 3. The pseudo-first-order model, although does not give clear explanation, it has been proved suitable for heterogeneous system of which the adsorption of Basic Brown 4 dye onto the chosen adsorbents are undoubtedly such a case. The same experimental data have been used for pseudo secondorder equations Fig. 5. This has been performed to ensure which of the model describes better the sorption kinetics. The plot shows the pseudo-second order fit better to the experimental values with good correlation coefficients (above 0.984) for all the four adsorbents. It is worth to compare the obtained rates with literature data. The direct comparison may be ambiguous, because researchers use sorbents with various textural and surface properties and wide range of experimental conditions. However, in some cases the direct comparison might be reasonable. Sakthivel *et al.* (2013) studied the adsorption kinetics of azo dye onto nanoporous activated carbon from *Jatropha curcas* stem and multi-walled carbon nanotubes synthesized from *Jatropha curcas* oil. They fitted their results to the pseudo-first-order model and pseudo-second-order model and the rates obtained were 3.6×10^{-3} sec^{-1} and 2.85×10^{-3} sec^{-1} for the nanoporous activated carbon. Similarly, for multi-walled carbon nanotubes the rates obtained using pseudo-first-order model and pseudosecond-order model were 2.018×10^{-3} sec^{-1} and $2.096 \times 10^{-3} sec^{-1}$. Kartikeyan *et al.* (2011) also reported a similar observation with adsorption of Basic Brown 4 dye adsorption onto activated carbon. This shows fair agreement with our results. Nevertheless, as the applied models do not properly describe the adsorption process, it is difficult to conclude which adsorption mechanism actually occurred. Therefore, other sources of information were viewed in an attempt to identify the specific adsorption mechanism. The Langmuir adsorption capacities vary from 118mg g^{-1} to 100mg g^{-1} for PMWNTs, from 142mg g^{-1} to 45.4mg g^{-1} for JCMWNTs, from 200mg g^{-1} to 125mg g^{-1} for PPMWNTs and from 76.9mg g^{-1} to 22.7mg g^{-1} for CAC for Basic Brown 4 dye in aqueous solution with increase in temperature from 30 °C to 60 °C. It is evident that adsorption capacities are high at high solution temperature. A similar result was reported for removal of acid blue 161 by MWNTs (Geyikci, 2013). It is concluded from the values that the maximum adsorption corresponds to a saturated mono layer of Basic Brown 4 dye molecule on the chosen adsorbent surface with constant energy and there is no transmission of dye molecules on the adsorbent surface. The R^2 value of langumuir model for adsorption of Basic Brown 4 dye molecule on PMWNTs, JCMWNTs, PPMWNTs and CAC are 0.994,0.973, 0.988 and 0.921 respectively. It shows Langmuir isotherm provides a better correlation with experimental data. The experimental data show that Freundlich rate constant (K_f) value decreases with increasing temperature for Basic Brown 4 dye adsorption onto chosen adsorbents. It implies that the adsorption process may be exothermic in nature under the experimental conditions. The value of 1/n is a measure of surface heterogeneity, ranging between 0 and 1, becoming more heterogeneous as its value gets closer to zero. The negative values of ΔG at all tested temperatures viz. 30, 45 and 60 °C indicate the adsorption of Basic Brown 4 dye on the chosen adsorbents were spontaneous and thermodynamically favorable. The negative ΔH values indicated that the adsorption of Basic Brown 4 dye on the chosen adsorbents were exothermic in nature.

The endothermic nature of adsorption is substantiated by the increase of adsorption with respect

to temperature. Furthermore, the negative ΔS indicated that randomness decreased at the solid-liquid interface during adsorption of Basic Brown 4 dye on the chosen adsorbents. Generally, ΔG for physisorption is less than -40 kJ mol^{-1} and for chemisorption it is between -80 kJ mol^{-1} and -400 kJ mol^{-1} (Jaycock *et al*.1981. The determined ΔG values shown in Table 5, confirms that the adsorption of Basic Brown 4 dye onto the chosen adsorbents is physisorption in nature. Further to this, the adsorption process with an activation energy less than 40 KJ mol^{-1}, evidences the main interaction between the Basic Brown 4 dye molecule and the chosen adsorbents were physisorption. This suggests that the chosen adsorbent adsorbate system were probably physisorption (Chen *et al*. 2009).

3.1 Mechanism for sorption of Basic Brown onto chosen adsorbents

Because of the significant correlation coefficients obtained using pseudo first order and pseudo second order models, it was difficult to conclude which adsorption mechanism actually occurred. In an attempt to identify the specific adsorption mechanism, other sources of information are reviewed. The morphology, defects and active sites of carbon nanotubes played an important role in the adsorption of the dyes onto surface of carbon nanotubes. If it consists of multiple concentric tubes then it is called multi-walled carbon nanotubes (MWNTs). The outer layer of MWNTs consist of graphitic sheets or graphene, which exhibiting a special sidewall curvature and possessing a π-conjugative structure with a highly hydrophobic surface. These unique properties and the hexagonal arrays of carbon atoms in graphite sheets of MWNTs surface have strong interactions which allow them to interact with other molecules or atoms through π-π electronic and hydrophobic interactions which make MWNTs a promising adsorbent material (Stafiej *et al.* 2007; Li *et al*. 2004). The adsorption on MWNTs is relatively higher as compared to such widely used materials as activated carbons due to the unique properties exhibited by MWNTs (Simonyan *et al*. 2001). The possible adsorption sites for binding of dye molecule on MWNTs and activated carbon are shown as schematic diagram in Fig. 9 (Cruz *et al*. 2010).

1) Internal sites – these sites are found within the hollow structure of tubes and available only when ends of the tube are open;
2) Interstitial channels – these sites are easily accessible for the adsorbate species and found in the interior space of the bundle;
3) External grooves – the grooves present on the periphery of a nanotube where two adjacent parallel tubes meet and
4) Exposed surface site or outside surface – outside surface site are highly accessible for the adsorbate and found on the curved surface of individual nanotubes.

The radius of gyration of organic vapors and common organic molecules are too large to be adsorbed between the interlayer spacing of MWNTs which is 0.34 nm. Therefore, adsorption can occur on the external wall surface or through capillary condensation in the MWNTs pores (Shih *et al*. 2008). The inner sites would also be inaccessible for adsorbate molecules because these cavities would be blocked. Generally, the surface with various defects is able to exhibit relatively high surface reactivity toward the adsorption and activation of adsorbate. In addition, from experimental point of view, it is quite difficult to accurately study the adsorption process at defect sites of solid surface (Xu *et al*.2004). The nature of adsorbate also played a crucial role in the adsorption onto CNTs. In adsorption process of dye on the solid surface, the dye species migrate towards the surface of the adsorbent. This type of migration proceedstill the concentration of the adsorbate species on the surface of the adsorbent becomes saturated.

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 theliquid and solid phases. The magnitude of this kind of

Table 5. Thermodynamic parameters for adsorption of Basic Brown dye onto the chosen adsorbents

	$\Delta G \times 10^4$ KJ mol^{-1}			ΔH KJ mol^{-1}	ΔS KJ mol^{-1}
	30 °C	45 °C	60 °C		
PMWNTS	-3.10	-1.85	-2.19	-28.87	-0.07
JCWNTS	-1.52	-7.41	-4.68	-28.17	-0.08
PPMWNTS	-2.97	-1.14	-0.88	-56.06	-0.16
CVC	-3.94	-2.82	-2.27	-48.19	-0.13

Table 6. D_p and D_f values for the chosen adsorbent-adsorbate system

	PMWNTs			JCMWNTs			PPMWNTs			CAC		
	30 °C	45 °C	60 °C	30 °C	45 °C	60 °C	30 °C	45 °C	60 °C	30 °C	45 °C	60 °C
$t_{1/2}$ s	4364	2715	3059	1041	700	632	4812	1733	1614	430	460	651
D_p cm^2/sec	1.81×10^{-9}	2.91×10^{-10}	2.59×10^{-11}	7.61×10^{-9}	0.11×10^{-10}	0.12×10^{-11}	1.6×10^{-9}	4.57×10^{-10}	4.9×10^{-11}	8.06×10^{-9}	7.53×10^{-10}	5.32×10^{-11}
D_f cm^2/sec	0.14×10^{-8}	6.8×10^{-9}	7.5×10^{-10}	0.14×10^{-8}	0.1×10^{-9}	8.7×10^{-10}	0.11×10^{-8}	5.81×10^{-9}	4.82×10^{-10}	0.002×10^{-8}	0.62×10^{-9}	0.25×10^{-10}

Table 7. D_i, E_a, D_0 and $\Delta S^{\#}$ values for the chosen adsorbent-adsorbate system

	$D_i \times 10^{-9}$ cm^2 sec^{-1}			Ea KJ mole^{-1}	$D_0 \times 10^{-9}$ cm^2 sec^{-1}	$\Delta S^{\#}$ KJ mole-1
	30 °C	45 °C	60 °C			
PMWNTS	1.93	53.5	67.01	8.54	56.84	0.018
JCWNTS	1.18	120.51	183.33	12.78	0.32	0.022
PPMWNTS	0.48	49.12	80.33	2.565	51.48	0.020
CVC	13.39	29.16	33.16	9.562	0.0031	0.022

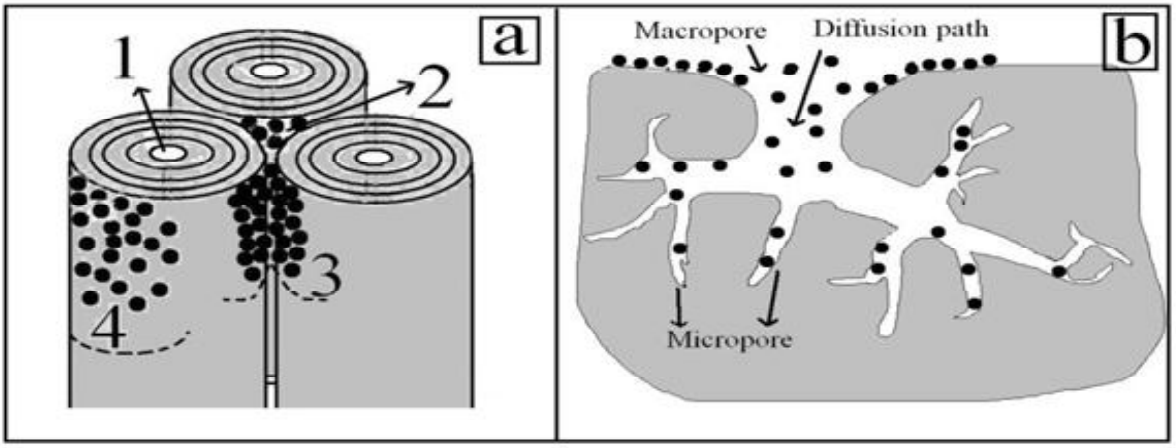

Fig 9: Possible adsorption sites for binding of dyes on (a) MWNTs (b) Activated carbon

distribution is a measure of the efficiency of the chosen adsorbent. When a powdered solid adsorbent material is made in contact with a solution containing dye, the dye first migrates 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 adsorp tion 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. It is now well established, that during the adsorption of dye over chosen adsorbent, the following four consecutive steps were taken place (Gupta *et al.* 2005; Bystzejewski *et al*. 2011).

(i) External mass transport of the adsorbate from the bulk liquid to the sorbent particle.

(ii)Transport of the adsorbate through the liquid film that surrounds the sorbent surface (film diffusion),

(iii)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) and

(iv)Adsorption of the ingoing adsorbate ions on the interior surface of the adsorbent.

Out of these four processes, the first process can be neglected, because the batch mode contact time studies included vigorous shacking. The fourth process is also considered to be very fast and is not the rate limiting step in the uptake of organic compounds (Weber *et al.* 1963). Thus, the steps (ii) and (iii) may affect the adsorption mechanism and it should be distinguished which of them determine the overall rate of Basic Brown 4 dye removal. The two steps impart the following three possibilities:

Case 1: External transport > internal transport, where rate is governed by film diffusion.

Case 2: External transport < internal transport, where the rate is governed by particle diffusion.

Case 3: External transport $\approx$ internal transport, which accounts for the transport of the adsorbate 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.

As rapid stirring was maintained, the transport of the adsorbed species, in this study Basic Brown 4, from the solution to the pores of the adsorbent material 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 be 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 onto chosen adsorbent, attempts were made to calculate the diffusion coefficient 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 diffusion coefficient in accordance with the expression,

$$t_{1/2} = 0.03 \frac{r_0^2}{D_p} \quad (16)$$

or to the film diffusion coefficient in accordance with

$$t_{1/2} = 0.23 \frac{r_o^{\partial}}{D_f} \times \frac{\overline{C}}{C} \quad (17)$$

where, r_0 is radius of the sorbent (cm) since, one dimensional and the three dimensional carbon nanoparticles used were of the size 50 and 180-250 microns respectively, the corresponding average diameter of the particles were taken as 50 and 215 microns; D_p and D_f are pore diffusion coefficient (cm^2/sec) and film diffusion coefficient (cm^2/sec) respectively, C/C is equilibrium loading of the adsorbent, ∂ is the film thickness (cm) and $t_{1/2}$ is the time for half change (sec) were calculated using the expression $0.693/K_2$. The values of D_p and D_f were calculated using the equation 16 and 17 taking the film thickness (∂) as 10^{-3}cm under the given set of operating conditions, and are presented in Table 6. The present study indicated the D_p and D_f values were in the order of 10^{-9} to 10^{-11} cm sec^{-1} and 10^{-8} to 10^{-10}cm sec^{-1} respectively for each adsorbents, The results are in good accordance with the reports by Sakthivel *et al.* (2013). In the study of sorption of Acid Orange 7 onto one and three dimensional carbon nano structured materials prepared from *Jatropha curcas*, they suggested that both intra particle diffusion and film transport were considered important in controlling the rate of the adsorption process. Hence, the author concludes that the mechanism of the removal of Basic Brown 4 dye in the present study by the chosen adsorbents is complex. It indicates the probable occurrence of both film diffusion and intra particle diffusion. Therefore, the sorption data were further analyzed by the kinetic expression given by Boyd *et al.* (1947) as

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

$$B_t = \pi^2 D_i / r^2 \quad (19)$$

$$F = 1 - \frac{6}{\pi^2} \sum_{N-1}^{\alpha} \frac{1}{n^2} \exp\left[-n^2 \beta_t\right] \quad (20)$$

where F is the fractional attainment of equilibrium at time t, n is the integer value, D_t is the effective diffusion coefficient of adsorbate in the adsorbed phase and r is the radius of the adsorbent particle. On the basis of F values, corresponding values of B_t were obtained (Reichenberg, 1953). The linearity test of B_t versus time plots was employed to distinguish between the film diffusion and particle diffusion controlled adsorption. The B_t versus time plots represented in Fig 10. for the sorption of Basic Brown 4 dye onto chosen MWNTs were found to be linear but did not pass through the origin. Thus the process involved can be interpreted as film diffusion. The B_t versus time plot Fig. 10 for the sorption of Basic Brown 4 dye over the CAC was found to be linear and pass through the origin. Therefore, under the experimental conditions, particle diffusion mechanism as the rate-controlling step occurs. The value of B was calculated from the slope of the straight

line obtained from the plot of B_t versus time. The value of effective diffusion coefficient D_i calculated at different temperatures using the following equation.

$$B = \pi^2 D_i / r^2_o \quad (21)$$

here, r_0 is the radius of the adsorbent particle.

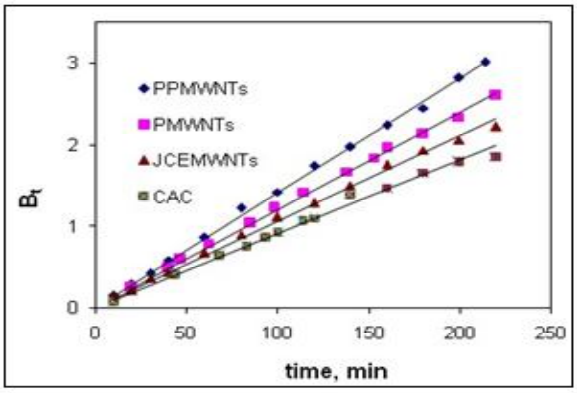

Fig. 10 : Time Vs. B_t plot for adsorption of Basic Brown dye onto PMWNTs, JCMWNTs, PPMWNTs and CAC at 30 °C

The D_i values are given in the Table 7. 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 pre-exponential constant D_0 and entropy of activation $DS^{\#}$ were calculated using following equations.

$$\log D_i = \log D_i - [(/2.303)* 1/r)] \quad (22)$$

$$D_0 = (2.72\ d^2 k_T/h\ )\exp\Delta S^{\#}/R] \quad (23)$$

where, d is the average distance between the successive exchange sites and is taken as 5A°. and h are the Boltzmann and Planck constants respectively. The values of D_i, D_0 and $\Delta S^{\#}$ are given in Table 7. The postive value for entropy of activation $DS^{\#}$ indicates that there is no significant change in the internal structure of chosen adsorbents.

4. CONCLUSION

A comparative study for adsorption of Basic dye (Basic Brown 4) on MWNTs synthesized from three different natural precursors in comparison with commercial activated carbon was evolved. The adsorption of Basic Brown 4 dye on each of the chosen adsorbents was found to be dependent on pH, temperature and concentration. The experimental kinetic data were fitted to the pseudo-first-order and pseudo-second order models. Despite obtaining high R^2 values, both models poorly described the sorption kinetics at early contact times. The sorption kinetics was properly characterized in the whole range of contact time using the B_t versus time plot for the sorption of Basic Brown 4 dye onto the different adsorbents. Thermodynamic parameters such as enthalpy change, free energy change and entropy change indicate that the process is endothermic, spontaneous and decreased disorder at the solid-liquid interface respectively. The sorption mechanism in the case of PMWNTS, JCMWNTS and PPMWNTs were limited by film diffusion whereas particle diffusion were observed for CAC. The results suggest that MWNTs have good potential applications in dye adsorption.

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