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Equilibrium and Thermodynamics of Auramine-O Adsorption from Aqueous Solution by Activated Carbons

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ABSTRACT

This paper investigates the efficiency of activated carbons for the removal of Auramine-O (AO) dye from aqueous solution. The effect of pH, carbon dosage, contact time, initial dye concentration and temperature were determined by batch experiments. Influence of carbon-oxygen surface groups present on the carbon surface has also been studied. Calculated thermodynamic parameters indicate endothermic and spontaneous characteristics of the adsorption process. Langmuir and Freundlich adsorption isotherms were applied. Langmuir model gives a better fit than the Freundlich model for granulated carbon samples. Pseudo-first-order kinetic model was found to best represent the kinetic data. In a batch design of an adsorption system it has been calculated that the amount of oxidized carbon required to remove 95 % of the dye is 58% less than the amount of unoxidised carbon.

Keywords: Adsorption, pH effect, Auramine-O, Langmuir isotherm, carbon oxygen surface groups.

INTRODUCTION

The total dye consumption of textile industries worldwide is in excess of 10^7 kg/year [1]. Wastewater containing dyes have high COD. Due to high thermal and photo-stability, dyes cannot undergo biodegradation. Basic dyes are used to dye fabrics such as wool, silk and nylon due to their brightness. Auramine (4,4'-dimethyl-aminobenzophenonimide) is a basic dye used in paper, textile and leather industries. It has also been used as food colorant, fungicide, antiseptic and component in brilliantine. AO can cause liver and lymphatic cancers in animals. It may be carcinogenic for human beings also. Ability of the blood to carry oxygen can be destroyed by AO. Therefore a method to treat AO containing dye wastewater is highly desirable. Among the number of physical and chemical methods, adsorption is considered to be more effective that produces effluents without harmful compounds and with very low levels of dissolved organic compounds [2]. Several types of adsorbents which include superabsorbent polymers [3], poly glutamic acid [4], sesame leaf [5], graphite loaded with Titania [6] have been used. Activated carbons are more efficient adsorbents for removal of dyes because of their large surface area and micro porous structure. Mall et al [7,8], Aber and Esfahlan [9], Kumar and Porkodi [10], performed batch studies for the adsorption of AO by activated carbons prepared from different sources and studied the effect of pH, contact time, temperature, concentration and adsorbent dosage. In this study Auramine-O has been chosen because of its potentiality as carcinogenic agent. Brief perusal of literature shows that influence of surface area and carbon-oxygen surface groups on adsorption of dye has not been reported. The present work describes the adsorption of AO dye from aqueous solutions on activated carbons having different surface areas and associated with varying amounts of different types of carbon-oxygen surface groups. Design of an adsorption system by using Langmuir isotherm equations has also been suggested. Two samples of granulated activated carbons namely I-60, ICEG and fibrous activated carbon cloth were used as adsorbents for equilibrium studies.

MATERIALS AND METHODS

Materials: Investigations have been carried out on two samples of commercial grade granulated activated carbons and a sample of activated carbon cloth. The granulated activated carbons ICEG and Indcarb-60 are coconut shell and wood based materials. The sample of activated carbon cloth (ACC) is a viscose rayon based material obtained from HEG Ltd., Bhopal, India. The activated carbons have been used as such and after modification of their surface by oxidation and degassing.

Oxidation with nitric acid: Oxidation with nitric acid has been carried out by heating 5 g of an activated carbon sample with 200 mL of 50 % nitric acid in a Borosil beaker on a water bath maintained at about 80 ± 5°C. When about 10 mL of the acid is left, the contents are diluted with distilled water and then filtered. The sample is then washed exhaustively with hot distilled water to make it free of nitrate ions. The washed oxidized carbon sample is dried, first in air and then in an electric oven at 120°C and stored in stopperd glass bottles.

Degassing of activated carbons: 5 g of oxidized carbon sample placed in a thin layer in a nickel boat about 5 inches long is placed in a quartz tube furnace. The tube furnace is then connected to a Hyvac. Cenco vacuum pump capable of giving vacuum to the order of 3×10^{-3} mm of Hg. Appropriate voltage is then applied to set the temperature of the furnace at the desired level. The temperature is allowed to rise gradually and complete elimination of the gases at the preceding temperature is ensured before raising the temperature. To avoid reformation of the carbon-oxygen surface groups, the degassed sample is allowed to cool in vacuum. The cooled sample is then transferred to a stopperd bottle flushed with nitrogen [11].

Porous characteristics: BET surface area, total pore volume, average pore radius and pore size distribution of activated carbon samples have been determined from nitrogen adsorption-desorption isotherms measured at 77 K by using a Quantachrome Nova 2200e Surface area and Pore size analyzer.
The chemical structure of the carbon surface has been determined by evacuation procedure [12] of carbons at temperature upto 950°C.

Adsorption procedure: The adsorption equilibrium experiments were carried out by placing the 0.1 g of dried activated carbon sample in contact with 20 mL solutions of the dye of different concentrations between 100 and 1000 mg L^{-1}. The suspension are agitated intermittently for 24 h and then allowed to stand. The effect of time of contact on the adsorption of AO dye at a concentration of 500 mg L^{-1}, has been studied by shaking 1 g of the adsorbent with 100 ml of dye solution at different temperatures of 30, 40, 50 and 60°C. The sample was taken at different time intervals and analyzed spectrophotometrically at a wavelength of 432.8 nm.

RESULTS AND DISCUSSION

Effect of pH: The effect of pH with blank dye solutions of C_0 = 500 mg L^{-1} over a pH_0 range of 2–12 shows that the colour intensity remains stable below pH_0 7 and get reduced in the basic range. pH_0 of solutions is adjusted by dilute HCl and NaOH. Colour removal due to pH change alone may be due to the structural changes taking place in the dye molecules [13, 14]. Effect of pH in range of 3-7 on the adsorptive removal of AO by I-60 shows slight increase in the removal of dye with the increase in pH. Further studies on adsorptive removal of AO by activated carbons were carried out at a pH_0 7.0.

Adsorption Isotherm: Adsorption isotherms of Auramine-O on three samples of as-received activated carbons are shown in Fig.1.The adsorption isotherms are Type 1 of the BET classification. The adsorption increases rapidly as the concentration of the aqueous solution is increased but tends to increase slowly at higher concentrations. It is seen that the amount adsorbed is different for different carbons which have different surface area, pore size dimension and carbon-oxygen surface groups. The amount adsorbed is maximum in case of I-60 which has largest surface area (1090 m^2 g^{-1}) as compared to other carbon samples.

The amount of dye adsorbed at equilibrium q_e (mg/g) was calculated from the following equation:

$$q_e = \frac{(C_o - C_e)V}{W} \tag{1}$$

Where C_0 and C_e (mg/l) are the liquid phase concentrations of dye at initial and equilibrium, respectively, V (L) the volume of the solution, and W (g) is the mass of adsorbent used. Adsorption data has been modelled by using Langmuir and Freundlich adsorption isotherm equations which in their linear form can be expressed as:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{1}{q_m} C_e \qquad \textit{Langmuir} \tag{2}$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \qquad \textit{Freundlich} \tag{3}$$

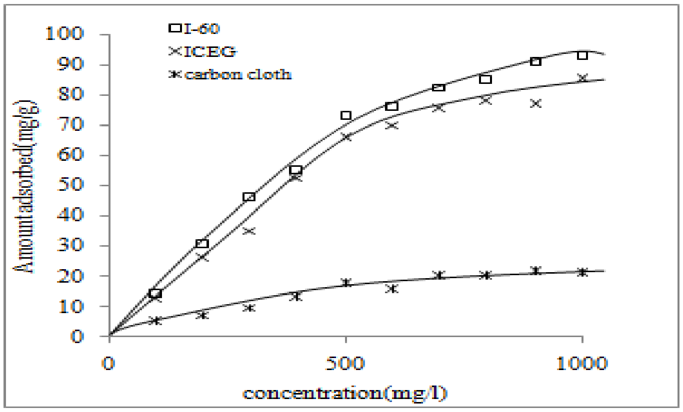

Fig.1: Adsorption isotherms of Auramine-O on different as received activated carbons

where C_e (mg/l) is the equilibrium concentration, q_e (mg g^{-1}) the amount of adsorbate adsorbed per unit mass of adsorbent, q_m and b are Langmuir constants related to adsorption capacity and rate of adsorption, respectively. K_f and n are Freundlich constants. The Langmuir and Freundlich constants were calculated from the isotherms (Not shown here) and their values are listed in Table.1.

Applicability of these isotherm equations was compared by calculating a correlation coefficient, R^2. It can be seen that the Langmuir model fits well for adsorption of Auramine-O on granulated activated carbons

Table.1: Langmuir and Freundlich constants for adsorption of AO on different as-received activated carbons

carbon sample	**Langmuir Parameters**			**Freundlich Parameters**		
	q_m (mg/g)	**b (l/mg)**	**R^2**	**n**	**K_f (l/ mg)$^{1/n}$**	**R^2**
I-60	120.48	0.0070	0.964	1.76	1.659	0.863
ICEG	120.48	0.0043	0.914	1.54	1.242	0.885
Carbon cloth	34.25	0.0019	0.906	1.63	0.642	0.962

Influence of carbon-oxygen surface groups on the adsorption: In order, to understand the influence of carbon-oxygen surface groups on the adsorption of AO, I-60 was oxidized with nitric acid to enhance the amount of carbon-oxygen groups on the carbon surface and then degassed at 400°, 650° and 950° temperatures to gradually remove these surface groups. The adsorption isotherms on the degassed samples are shown in Fig.2. It is seen that the adsorption of AO increases on oxidation of carbon with nitric acid and decreases when the oxidized samples were degassed. The adsorption results can be explained on the basis of electrostatic attractive and repulsive interactions.

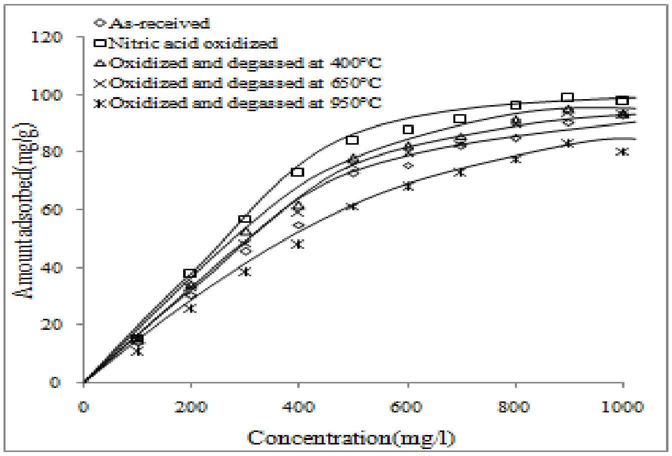

Fig.2: Adsorption isotherms of Auramine-O on nitric acid oxidized I-60 after degassing at different temperature

The oxidized activated carbons are associated with acidic carbon-oxygen surface groups that ionized in solution to produce H^+ ions. Which are directed toward the liquid phase, leaving the carbon surface with a negative charge. The negative charge of the carbon surface depends on the amount of the acidic-surface groups present on the carbon surface. Negative charge of the carbon surface attracts positively charged dye. As the acidic surface groups are removed gradually on degassing at increasing temperatures the carbon surface tends to become less negatively charged. This decreases the adsorption of Auramine-O.

Effect of temperature: Effect of time of contact for the removal of AO by I-60 at different temperatures (30°, 40°, 50°and 60° C) is shown in Fig.3 indicates rapid adsorption of dye in about two hours because large numbers of vacant surface sites are available initially and thereafter, the adsorption rate decreases gradually and becomes almost constant. The equilibrium reached for adsorption in about 300 min at 30°C.

Temperature has a pronounced effect on the adsorption capacity of the adsorbents. Adsorptive capacity increases with an increase in temperature due to increase in the mobility of the ions.

For the characterization of the temperature effect, thermodynamic parameters such as the Gibbs free energy change (ΔG), enthalpy change (ΔH), and Entropy (ΔS) were calculated by using following equations and listed in Table.2

$$K_c = \frac{q_e}{C_e} \qquad (4)$$

$$\Delta G = -RT \ln(K_c) \qquad (5)$$

$$\log Kc = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \qquad (6)$$

Where q_e and C_e are the equilibrium concentrations (mg L^{-1}) of dye adsorbed on adsorbent and in solution respectively. K_c is the adsorption distribution coefficient, R is gas constant and T is absolute temperature (K). ΔH and ΔS of an adsorption reaction were determined from the van't Hoff plot $\log K_c$ vs. 1/T. The negative values of ΔG indicate the spontaneous nature of dye adsorption. More negative values of ΔG at higher temperatures imply the greater driving force of adsorption at high temperatures than at low. The change in enthalpy for adsorption on activated carbon was found to be positive. The positive values confirm the endothermic nature of adsorption. This is supported by the increase in amount of adsorption of AO with temperature. The positive values of entropy show the increased randomness at solid solution interface [15].

The activation energy for adsorption of dye was determined by using Arrhenius equation.

$$\ln K_1 = \ln A - \frac{E_a}{RT} \qquad (7)$$

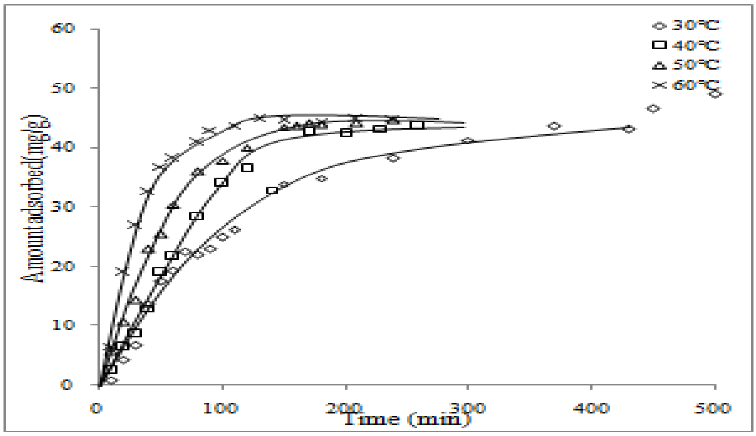

Fig.3: Effect of contact time and temperature on adsorption of Auramine-O on I-60

where A is Arrhenius constant, K_1 is first order rate constant and E_a is the activation energy. From Arrhenius plot ln K_1 vs 1/T, activation energy is calculated and listed in Table.2. The magnitude of activation energy indicated that the adsorption had a low potential barrier which is in the domain of physisorption.

Table.2: Thermodynamic parameters for adsorption of Auramine- O

Adsorbent	**T(°C)**	**ΔG (kj/mol)**	**ΔH(kj/mol)**	**ΔS(j/mol/K)**	**E_a (Kj/mol)**
I-60	30°C	-3.904	16.77	68.11	38.64
	40°C	- 4.531			
	50°C	- 5.084			
	60°C	-6.013			

Adsorption Kinetics: Adsorption processes of Auramine-O have been analyzed by pseudo-first-order, pseudo-second-order and intra-particle diffusion kinetic models.
The pseudo-first-order model was described by Lagergren [16]

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \tag{8}$$

Where q_e and q_t refer to the amount of dye adsorbed (mg/g) at equilibrium and at any time, t (min), respectively. K_1 is the equilibrium rate constant of pseudo-first-order adsorption ($\min^{-1}$). Integration of eq. (8) for the boundary conditions t=0 to *t* and q_t =0 to q gives:

$$\log(q_e - q_t) = \log(q_e) - \frac{K_1}{2.303}t \tag{9}$$

The pseudo-second-order model [17] can be represented in the following form:

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \tag{10}$$

where K_2 is the pseudo-second-order rate constant (g mg^{-1} $\min^{-1}$). Integrating Eq. (10) and noting that q_t=0 at $t = 0$, the following equation is obtained:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e 2} + \frac{1}{q_e}t \tag{11}$$

Values of first order rate constant (K_1), second-order rate constant (K_2) equilibrium adsorption capacity (q_e) and the correlation coefficient (R^2) at 30, 40, 50 and 60°C were calculated from linear plots are presented in Table.3.
The calculated equilibrium adsorption capacities agree well with experimental values for pseudo first order kinetic model. The calculated correlation coefficients are also closer to unity for pseudo-first-order kinetics than that for the pseudo-second-order kinetic model. This indicates that the adsorption of dye onto activated carbon is an ideal pseudo-first-order reaction.

Table 3 . Kinetic parameters for the adsorption of Auramine-O on I-60

T(°C)	**q_e(exp) (mg/g)**	**Pseudo First Order Model**			**Pseudo Second Order Model**		
		q_e(cal) (mg/g)	**K_1 ($\min^{-1}$)**	**R^2**	**q_e(cal) (mg/g)**	**K_2 (g/mg min)**	**R^2**
30°C	41.25	45.49	0.009	0.964	62.5	0.000116	0.992
40°C	42.54	54.95	0.016	0.982	76.92	0.000079	0.873
50°C	43.45	51.52	0.021	0.992	76.92	0.000119	0.939
60°C	44.88	55.21	0.037	0.986	55.56	0.000543	0.966

The possibility of intra-particle diffusion resistance affecting adsorption was explored by using the intraparticle diffusion Weber and Morris model [18] as:

$$q_t = K_{id}t^{1/2} + I \tag{12}$$

Where k_{id} (mg/g $\min^{1/2}$) is the intra-particle diffusion rate constant. Fig.4 shows the intraparticle diffusion plot for the adsorption of AO on I-60. The shape of Fig. confirms that the intraparticle diffusion is not the only rate-limiting step. Macro pore diffusion is depicted by first line and the second represents micro pore diffusion until equilibrium was achieved.

Effect of adsorbent Dose: The effect of varying adsorbent dose between 0.1-0.8 g on dye adsorption shows that amount of dye adsorbed per unit mass of adsorbent decreases with increase in adsorbent dose.. This decrease in adsorption may be due to the reduction in effective surface area available due to aggregation of adsorption sites [19].

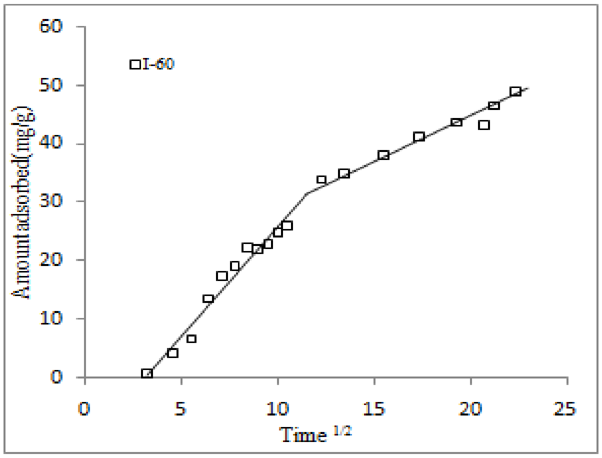

Fig.4: Intraparticle diffusion plot for Auramine-O adsorption on I-60

Design of Batch Adsorption from Equilibrium Data: A single-batch absorber design [20] requires equilibrium data. The design objective is to reduce the dye concentration from C_o to C (mg L^{-1}).The mass balance for dye adsorption system is given by:

$$V(C_o - C) = W(q_1 - q_o) = Wq_1 \tag{13}$$

Where *V* is the volume of dye solution. *W* is the amount of the activated carbon added to the solution when the amount of the dye adsorbed on carbon changes from q_0=0 to q_1.
At equilibrium $C \to C_e$ and $q_1 \to q_e$

$$V(C_o - C_e) = Wq_e \tag{14}$$

From adsorption studies it was found the Langmuir model gave better fit to equilibrium data from I-60. Rearrangement of the above equation on substituting the value of q_e from Langmuir equation gives adsorbent/solution ratio as

$$\frac{W}{V} = \frac{(C_o - C_e)}{q_e} = \frac{C_o - C_e}{q_m bC_e/(1 + bC_e)} \tag{15}$$

Fig.5 shows the predicted amounts of as-received and oxidized I-60 carbon to remove 95% of 500mg/l of AO solution from different volumes of dye solutions in a single-batch absorber. It can be seen, that the amount of oxidized I-60 as adsorbent is less by about 58% compared to the amount of as-received I-60 for the removal of 95% Auramine-O from the solution.

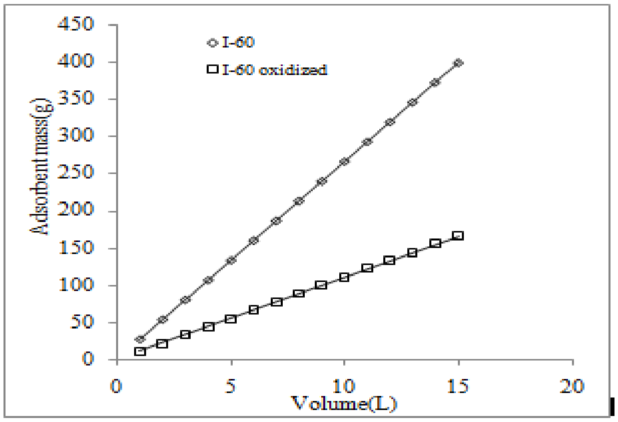

Fig.5: Adsorbent mass against treated volume of water for 95% removal of Auramine-O by as-received and oxidized activated carbon

APPLICATIONS

The present study shows the applicability of as received and modified activated carbons for the removal of Auramine-O a carcinogenic dye, from aqueous solution. Modification of activated carbon with nitric acid increases the removal of dye. In a batch design, it has been shown that the amount of oxidized carbon required to remove 95 % of the dye is 58% less than the amount of unoxidised carbon.

CONCLUSIONS

Adsorption of Auramine-O on the activated carbon surface increases after oxidation of carbon with nitric acid and decreases on degassing. Dye removal increases with increase in temperatures. Thermodynamic parameters indicate spontaneity of process. Maximum dyes adsorption occurred at pH= 7. The adsorption kinetics is better represented by first order rate law. Langmuir model fits well for the adsorption of Auramine-O. To treat a certain volume of waste water requirement of modified carbon is 58% less as compared to as received activated carbons.

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REFERENCES

[1] N. Saadatjou, M.H. Rasoulifard, A. Heidari, S. Mohammad and M.D. Mohammadi, *Int. J. Phys. Sci.* **2011**, 6(22), 5181-5189.
[2] T.C. Chandra, M.M. Mirna, Y. Sudaryanto, and S. Ismadji, *Chem. Eng. J.* **2007**, 127, 121-129.
[3] N.B. Shukla and G. Madras, *J. Appl. Polym. Sci.* **2012**, 124, 3892–3899.
[4] B.S. Inbaraj, J.T. Chien, G.H. Ho, J. Yang and B.H. Chen, *Biochem. Eng. J.* **2006**, 31, 204–215.
[5] L. Liu, F. Yu, j. Liu, X. Han, H. Zhang and B. Zhang, *Asian J. Chem.* **2013**, 25(4),1991-1998.
[6] X. Pang, *Int. J. Chem. Tech. Res.* **2010**, 2(2), 1281-1288.
[7] I.D. Mall, V.C. Srivastava, and N.K. Agarwal, *J. Hazard. Mater.* **2007**, 143, 386–395.
[8] I.D. Mall, V.C. Srivastava, G.V.A. Kumar and I.M. Mishra, *Colloids Surf., A* **2006**, 278, 175–187.
[9] S. Aber and F.H. Esfahlan, G*lobal Nest J.* **2011**, 13(3), 246-254.
[10] K.V. Kumar and K. Porkodi, *Indian Chem. Eng.* **2008**, 50 (3), 227-238.
[11] R.C. Bansal, T.L. Dhami and S. Parkash, *Carbon* **1977**, 15, 157.
[12] R.C. Bansal, N. Bhatia and T.L. Dhami, *Carbon* **1978**, 16, 65.
[13] I.D. Mall, V.C. Srivastava, N.K. Agarwal and I.M. Mishra, Colloids Surf., A **2005**, 264, 17–28.
[14] I.D. Mall, V.C. Srivastava, N.K. Agarwal and I. M. Mishra, *Chemosphere* **2005**, 61, 492–502.
[15] M.J. Iqbal and M.N. Ashiq, *J.Chem.Soc.Pak*, **2010**, 32(4), 419.
[16] S. Lagergren, *Handlingar* **1898**, 24, 1.
[17] Y.S. Ho and G. McKay, *Chem. Eng. J.* **1998**, 70, 115-24.
[18] W.J. Weber, and J.C Morris, *J. San. Eng. Div.* **1963**, 89, 31-60.
[19] B.S. Inbaraj and N. Sulochana, *Indian J. Chem. Technol*. **2006**, 13, 17.
[20] E.I. Unuabonah, K.O. Adebowale and F.A. Dawodu, *J. Hazard. Mater.* **2008**,157, 397.