Adsorption of Acid Orange 7 by Activated Carbon Produced from Agriculture Waste: 1. Kinetics

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Summary: Carbon was produced from corncobs waste by physical and chemical activation and evaluated for their physical (bulk density), chemical (ash, pH), surface (surface area, pore size distribution), and adsorption properties for acid orange 7. Activation at 800 °C increased the surface area with increase in pore size distribution. First order and parabolic intraparticle diffusion models were found to apply to the data, indicating the adsorption to be diffusion controlled. Rate constant increased with the increase in both the adsorption temperature and the activation temperature of the carbon. Thermodynamic parameters of adsorption ($\Delta E^{\neq}$, $\Delta H^{\neq}$ and $\Delta S^{\neq}$) were calculated from the kinetic data. The endothermic nature of the adsorption was indicated by the positive values of $\Delta H^{\neq}$. Negative values of $\Delta S^{\neq}$ for adsorption, reflect decrease in the disorder of the system at the solid-solution interface during adsorption.

Introduction

The adsorption efficiency of activated carbon depends not only on its total surface area, but also on its internal porous structure. Pore size determines the adsorption capacity, surface chemical structure influences adsorbent-adsorbate interactions, and active sites determine the type of chemical reactions. For instance, carbons with small pore size may not trap large adsorbate molecules and those, with large pores may not be able to retain small adsorbate molecules. The electrical charge of the surface groups may also enhance or hinder the adsorption of the target molecules on the carbon surface. If the adsorbate has the same electrostatic charge as that of the carbon surface, repulsion will occur, thereby inhibiting the adsorption. Thus, the adsorption of activated carbon cannot be interpreted on the basis of the surface area alone. Another important consideration is that carbons having equal surface areas but have been prepared by different methods or given different activation treatments also show markedly different adsorption characteristics [1]. The effective carbon adsorbent should have a large surface area with the proper pore size and population, and appropriate surface charge to trap the targeted species. The cost effectiveness is also important. Agricultural wastes are cheap and as the surface properties of carbon is basically a function of the precursor, pyrolysis and activation conditions, it is thus essential to characterize carbons from the waste materials, for the number and type of the chemical groups on the surface, pore size distribution and total surface area for their adsorption behavior. We in this study have evaluated carbon produced from corncobs, a cheap agricultural waste. Many investigators have studied the porous structure [2-3] and surface chemistry [4-5] of activated carbons made from a variety of precursors and activation conditions. The objectives of this work was to determine the surface properties such as surface area, pore size distribution and surface functional groups for the activated carbon and to determine the adsorption efficiency of the activated carbon for removing an azo dye acid orange 7 from aqueous solution. As the azo dyes in the effluents can cause problems in several ways. They can have acute and/ or chronic effects on exposed organisms depending on the exposure time and dye concentration. These dyes are inherently highly visible so that their concentrations, as low as 0.005 ppm capture the attention of both the public and the authorities [6-7]. The removal of such colored agents from aqueous effluents is thus environmentally significant [8-13], and as certain industries like textile, paper and pulp produce bulk of colored waste waters, the production of an effective and cheap activated carbon from agricultural wastes is thus of economic and academic interest.

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Results and Discussion

The BET surface area $(m^2.g^{-1})$ method which is the most widely used for the surface area measurements make use of the equation,

$$\frac{1}{W\left(\frac{P_0}{p}-1\right)} = \frac{1}{W_m C} + \frac{C-1}{W_m C}\left(\frac{P}{P_o}\right) \tag{1}$$

Where W is the weight of gas adsorbed at a relative pressure, P/P_0 and W_m is the weight of adsorbate constituting a monolayer coverage. The term C, the BET C constant, is related to the energy of adsorption in the first adsorbed layer and consequently its value is an indication of the magnitude of the adsorbent / adsorbate interactions. The standard multipoint BET method requires a minimum of three points in the appropriate relative pressure range. The weight of a monolayer of adsorbate W_m can then be obtained from the slope and intercept of the BET plot, from equation (1):

$$S = \frac{C-1}{W_m C} \tag{1a}$$

$$i = \frac{1}{W_m C} \tag{1b}$$

Thus, the weight of a monolayer W_m can be obtained by combining equations (1a) and (1b).

$$W_m = \frac{1}{S+i} \tag{1c}$$

The total surface area (S_t) of the sample can be expressed as:

$$S_t = \frac{W_m N A_{CS}}{M} \tag{1d}$$

Where N is Avogadro's number (6.023×10^{23}) and M is the molecular weight of the adsorbate and C is cross sectional area of nitrogen gas $(16.2\ Å^2 / mol)$. Surface area $(S_{BET}\ m^2\ g^{-1})$ of the samples obtained from the plots, $1\ /\ [W\ (P_0/P)\ -1]$ vs P / P_0 of the N_2 adsorption Fig. 1, have values given in the Table 1. Type-I isotherms were obtained which are concave to the P/P_0 axis and N_2 uptake is governed by accessible micropore volume rather than the internal surface area. Such a

Table-1. Surface area and pore size distribution of the Corncobs carbon samples.

Sample	BET surface area (m^2/ g)	Pore size distribution (DR method)		
		Micropore volume (cc / g)	Average Pore width (Å)	Adsorption Energy (kJ / mol)
Raw	68.809	0.010	111.74	2.330
400 °C	140.41	0.070	50.090	5.190
800 °C	412.38	0.210	48.690	5.340

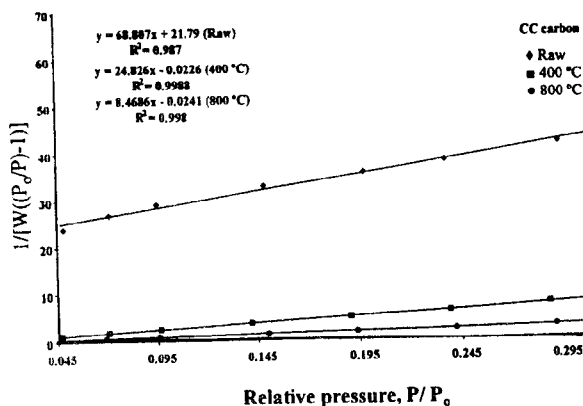

Fig. 1.   BET plots of nitrogen adsorption on Corncobs carbon samples.

behavior was observed for all the samples, indicating mainly the microporous structure. The pore volume $(cm^3\ g^{-1})$ of activated charcoal is also given in Table- 1. The increase in the surface area and pore volume with rise in activation temperature is due to the driving off of the tar in the gaseous form that was trapped in the porous structure [14].

Adsorption Kinetics:

The rate of adsorption of the dye molecules, in the initial 15 seconds, was high at both 10 and 45 °C and then it declined due to the possible diffusion in to the micropores. The increase in temperature has increased adsorption (Fig. 3), indicating the endothermic nature of the process.

Kinetic Equations:

The rate constant for adsorption of acid orange 7 on carbon surface was determined by the first order kinetic equation. Such an equation in the linear form can be expressed as [15]:
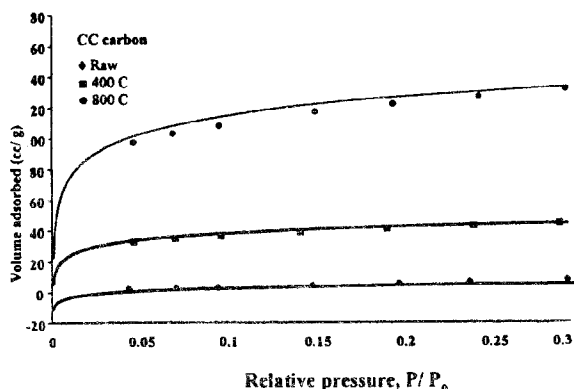
$$\ln D_\sigma = \ln D_o - K_{ad}' \tag{2}$$

Fig. 2.   Adsorption   isotherms   of   nitrogen
adsorption on *Corncobs* carbon samples.

Here D_0 and D_σ are the solution concentration (mol dm^{-3}) at $t = 0$ and $t = t$ respectively and k_{ad} is the 1st order rate constant. Values of k_{ad} were taken from the linear plots of ln D_σ vs. t and are shown in Table- 2. It was noted that the rate constant increased with the increase in the temperature of adsorption and also in case of the samples activated at high temperature. The energy of activation for the adsorption was calculated using the Arhenius equation in the form:

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right] \tag{3}$$

Where E_a is the activation energy, k_1 and k_2 are rate constants at T_1 and T_2 and R is the gas constant (8.314 J K^{-1} mol^{-1}). The energies of activation for acid orange 7 in case of carbon activated at different temperatures are given in Table- 2. The data showed that samples activated at high temperature have less activation energy of adsorption. The high activation energy of dye adsorption on the less activated sample may be due to the presence of polar functional groups at the pore opening that block the entrance of dye molecules resulting in the energy barrier for

adsorption to occur [16]. From the values of activation energies, thermodynamic parameters such as enthalpy of activation $(\Delta H)^{\neq}$ and entropy of activation $(\Delta S)^{\neq}$ were calculated by using the following equations [15].

$$\Delta H^{\#} = Ea - RT \tag{4}$$

$$\Delta S^{\neq} = R \left[\ln \frac{k_b h}{k_B T} + \frac{\Delta H^{\neq}}{RT} \right] \tag{5}$$

Where

k =   Rate constant
k_B =   Boltzmann constant (1.3806×10^{-23} J K^{-1})
$\Delta H^{\neq}$ =   Enthalpy change of activation.
h =   Plank's constant (6.626×10^{-34} J s)

The enthalpy of activation, $\Delta H^{\neq}$, calculated from the energy of activation, was found to decrease with the increase in the adsorption temperature indicating the process to be endothermic in nature. Negative values of the entropy of activation, $\Delta S^{\neq}$, reflects the affinity of the dye toward the carbon which decreased with the increase in adsorption temperature (Table- 2) meaning that the dye molecules have more stable oriented position on the carbon surface [17].

The intraparticle diffusion was analyzed by applying the parabolic diffusion equation to the data. For a solid liquid adsorption process, the solute transfer is usually characterized by either external mass transfer (boundary layer diffusion) or intraparticle diffusion or both. Adsorption dynamics can be described by the three consecutive steps i.e. transport of the solute from bulk solution through liquid film to the adsorbent exterior surface; solute diffusion into the pores of adsorbent except for a small quantity of adsorption on the external surface; parallel to this is the intraparticle transport mechanism of the surface diffusion and

Table- 2. Thermodynamic parameters for the adsorption of acid orange 7 on the
Corncobs carbon samples.

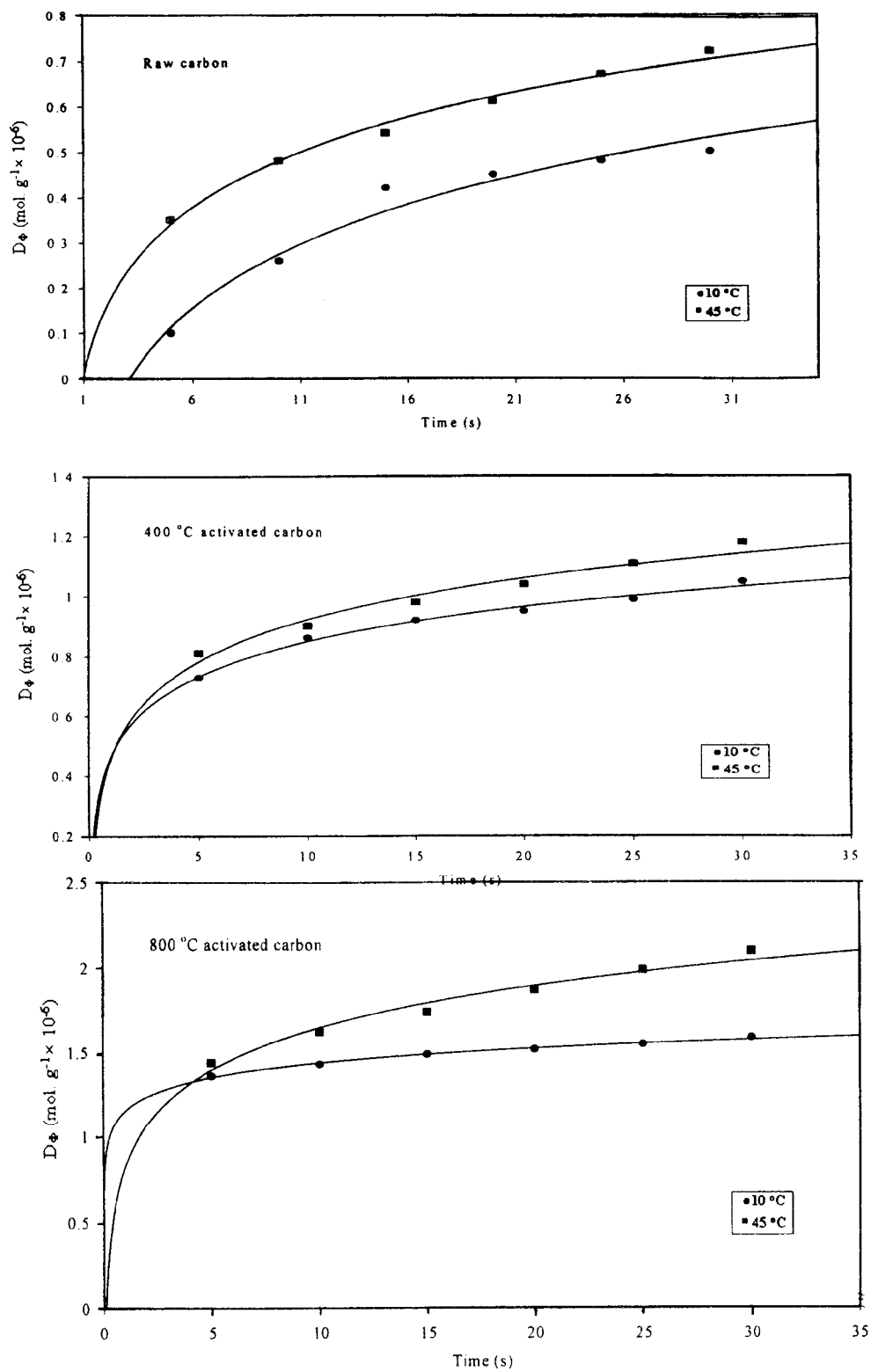| Sample | k_{ad} (s^{-1}) | | E_a | $\Delta H^{\neq}$ (kJ.mol^{-1}) | | $\Delta S^{\neq}$ (J.mol^{-1} K^{-1}) | |
	10 °C	45 °C	(kj.mol^{-1})	10 °C	45 °C	10 °C	45 °C
Raw	0.00420	0.00580	6.901	4.547	4.256	-273.9	-274.9
400°C	0.00550	0.00730	6.052	3.699	3.408	-274.7	-275.6
800°C	0.01810	0.02160	3.78	1.426	1.135	-272.7	-273.7

Fig. 3.   Adsorption kinetics of acid orange 7 on   the *Corncobs* carbon samples.

adsorption of solute on the interior surfaces of the pores and capillary spaces of the adsorbent. Of the three steps, the third step is assumed to be rapid and negligible to be considered. The overall rate of adsorption will be controlled by the slowest step, which would be either film diffusion or pore diffusion. However, the controlling step might be distributed between intraparticle and external transport mechanisms. In both cases the external diffusion is involved in the adsorption process. The adsorption of dyes onto charcoal particles may be controlled by the film diffusion at earlier stages and then as the adsorbent particles are loaded with dye ions, the adsorption then be controlled by the intraparticle diffusion. Literature shows that the plot of D_Φ versus $t^{1/2}$ (eq. 6) represents multi-linearity, which characterizes the two or more steps involved in the sorption process. According to Weber and Morris [18 - 19] intraparticle diffusion is defined by the equation:

$$D_\Phi = K_{ad} t^{1/2} + B \qquad (6)$$

The K_{ad} value can be obtained from the slope of the plot of D_Φ (amount adsorbed in mol / g) vs. $t^{1/2}$. The intraparticle diffusion coefficient, K_{ad}, given in Table- 3 increased with the increase in adsorption temperature and the activation temperature of the samples.
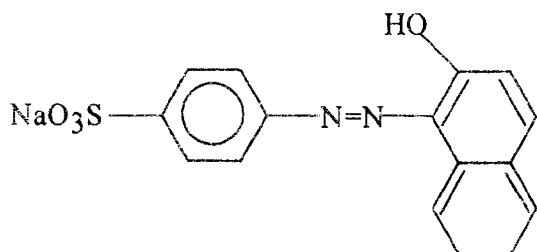
Table-3. Intraparticle diffusion constants for the adsorption of acid orange 7 on the Corncobs carbon samples

Sample	K_{ad}		B	
	10 °C	45 °C	10 °C	45 °C
Raw	0.1339	0.3496	0.0280	0.0253
400 °C	0.7426	0.7900	0.0208	0.0255
800 °C	1.3590	1.4057	0.0156	0.0460

Experimental

Acid Orange 7:

The dye used was supplied by *Sigma-Aldrich* (Catalogue No. =19, 523-5, dye contents = 90 %, formula weight =350.33, λ_{max} 483 nm),
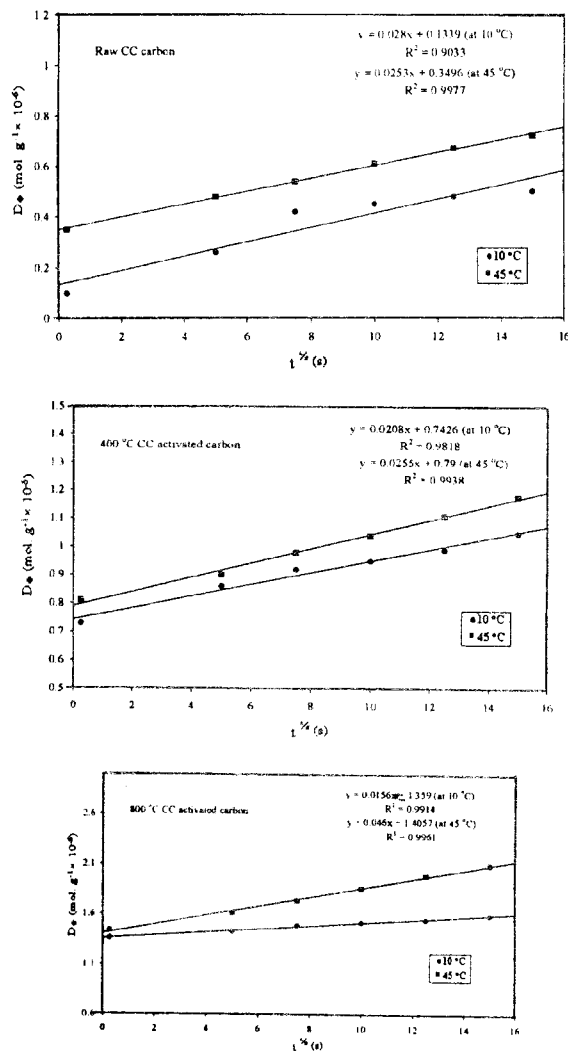
Scheme 1: Chemical Structure of Acid orange 7

Fig. 4.   Parabolic diffusion plots for the acid orange 7 adsorption on *Corncobs* carbon samples.

Preparation of Carbon:

Corncobs were collected from agricultural fields and heated (400-500 °C) continuously for 8 hours on a flame burner in a specially designed iron container with an outlet for the emission of volatile matter. Carbon obtained (about half of the mass of wood used) was cooled in the container and ground with the help of pestil and mortar and screened with US standards mesh 150-180 μ m. It was then treated with 0.5 M aqueous solution of KOH for 24 hours with occasional stirring. The mixture was then filtered and washed with double distilled water for the complete removal of basicity. The carbon was

then leached with 0.2 N solution of HNO_3 : HCl (1 : 1) and allowed to stand for 24 hours at room temperature with regular mixing. It was then filtered and washed with double distilled water until free from Cl^- and NO_3^- ions. The carbon thus obtained was then air-dried in an oven at 105 ± 2 °C. This treated carbon was then extracted with n-hexane for two hours in a soxhlet extractor and allowed to dry for 8 hours in a vacuum oven. The sample was then degassed by placing in silica (SiO_2) tubes and heated at 400 and 800 °C in a tube furnace (FS. 215 Gallenkamp England) with a vacuum facility. The samples thus obtained were allowed to cool and stored under nitrogen atmosphere.

Characterization:

The FTIR, XRD, SEM and EDS analysis of the prepared carbon are reported earlier [20]. BET-N_2 adsorption experiments were carried out manometrically at -196 °C using Quantachrome NOVA 2200 surface area and pore size analyzer. Surface area was obtained by applying the standard BET equation to the adsorption data in the relative pressure (P/P_o) range: 0.05 - 0.350. The values of 0.81 g cm^{-3} and 16.2×10^{-20} m^2 were used for the density of liquid nitrogen and the molecular area of adsorbate nitrogen at -196 °C, respectively. The pore size distribution was determined by DR method using the NOVAWin2 data analysis software.

Adsorption Kinetics:

0.2 g of activated carbon and 20 mL of acid orange 7 (3×10^{-5} *mol. dm*$^{-3}$) was shaken in a laboratory syringe (Hamilton CO.) for 5 - 30 seconds at 10 °C and 45 °C and filtered through 0.2 μm filter paper fitted in the syringe adopter (Hamilton CO.; Reno Nevada). The residual concentration of the dye in the filtrate was determined by uv-visible spectrophotometer. pH of the dye was noted as 8.10 before starting the experiment. The experiment was carried out in triplicate.

References

1. R. C. Bansal, J. B. Donnet and F. Stoeckli, *Active Carbon*, Marcel Decker, New York, 1988.
2. T. Wigmans, *Carbon*, **27**, 13 (1989).
3. F. R. Reinoso and M. M. Sabio, *Carbon*, **30**, 1111 (1992).
4. A. Contescu, C. Contescu, K. Putyera and J. A. Schwarz, *Carbon*, **35**, 83 (1987).
5. F. K. Bangash and S. Alam, *J. Chin. Chem. Soc.* **53**, 1091, (2006).
6. J. Pierce and J. Soc. Dyers *Colour*, **110**, 131 (1994).
7. Y. M. Slokar. A. Majcen and L. Marechal, *Dyes Pigments*, **37**, 335 (1998).
8. Y. Guo, S. Yang, W. Fu, J. Qi, R. Li, Z. Wang and H. Xu, *Dyes Pigments*, **56**, 219 (2003).
9. G. McKay. *J. Chem. Technol. Biotechnol.*, **32**, 759 (1982).
10. F. K. Bangash and A. Manaf, *Jour. Chem. Soc. Pak.*, **26**, 111 (2004).
11. F. K. Bangash and S. Alam, *Tenside Surf. Det.*, **43**, 299 (2006).
12. F. K. Bangash and S. Alam, I. Ahmad, *Chin. J. Chem.*, **25**, 596, (2007).
13. V. Meshko, L. Markovska, M. Mincheva and A. E. Rodrigues, *Wat. Res.*, **35**, 3357 (2001).
14. J. W. Hassler, *Purification with Activated Carbon*, Chemical Publishing CO. Inc. New York, p. 176. (1974).
15. K. L. Laidler, *Chemical Kinetics*, McGraw-Hill, New York, pp 54. (1965).
16. Y. Iqbal, M. A. Khan and N. A. Ihsanullah. *Inter. J. Envi. Stud.*, **62**, 47 (2005).
17. T. Vickerstaff, *The Physical Chemistry of Dyeing*, Interscience, New York, p 100 (1954).
18. V. Vadivelan and K. V. Kumar, *J. Colloid Interf. Sci.*, **286**, 90 (2005).
19. J. W. J. Weber and J. C. Morris, *Kinetics of adsorption on carbon from solution. J. Sanit. Eng.*, Div. ASCE 89 (SA2), p. 31 (1963).
20. F. K. Bangash and S. Alam, *J. Chin. Chem. Soc.*, **54**, 1 (2007).