Nature Environment and Pollution Technology
An International Quarterly Scientific Journal

ISSN: 0972-6268	Vol. 12	No. 3	pp. 397-405	2013

Original Research Paper

Adsorption of Reactive Blue and Direct Red Dyes on Powdered Activated Carbon (PAC) - Equilibrium, Kinetics and Thermodynamic Studies

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Nat. Env. & Poll. Tech.
Website: www.neptjournal.com
Received: 28-1-2013
Accepted: 19-2-2013

Key Words:
Dye adsorption
Powdered activated carbon
Chemical kinetics
Thermodynamic studies

ABSTRACT

The present study deals with the adsorptive removal of Reactive Blue 19 (RB19) and Direct Red 81(DR81) from their aqueous solutions. Powdered Activated Carbon (PAC) was used as an adsorbent. Batch studies were performed to analyse various experimental parameters like adsorbent dose, pH, contact time and initial dye concentration. Optimum PAC doses for RB19 and DR81 were found to be 0.2 g/L and 0.3 g/L, respectively. Effective pH for RB19 and DR81 removal was found to be 2 and 7, respectively. In addition, high percent removal with decrease in initial dye concentration was observed. Quasi-equilibrium was attained in 3h for both dyes. Pseudo-second-order rate equation satisfactorily represented the adsorption kinetics for both the dyes. Langmuir and Temkin isotherms were found to best represent the equilibrium data for DR 81-PAC system whereas for RB19-PAC system Langmuir isotherm was found to be best suited. Furthermore, thermodynamic studies showed that the adsorption of both the dyes onto PAC was exothermic in nature.

INTRODUCTION

In textile industry, dyeing process requires large volumes of water for dyeing, fixing and washing purposes (Rajkumar et al. 2007). In turn, increased consumption of dyes is associated with wastewater generation. Colour is the most obvious indicator of water pollution (Ergene et al. 2009). The discharge of coloured wastewater into receiving streams causes toxicity to aquatic flora and fauna (Khaled et al. 2009). It also interferes with transmission of sunlight into streams and reduces the photosynthetic activity (Eren & Acar 2006). Without a suitable treatment, these dyes are stable and can remain persistent in the environment.

Reactive and Direct dyes are most abundantly used in textile industry. These dyes, owing to their toxic nature, need to be removed from the effluent discharged from such industries (Sivakumar et al. 2010). Adsorptive removal of Reactive and Direct dyes has been studied earlier (Eren & Acar 2006, Purkait et al. 2007, Al-Degs et al. 2008). Reactive Blue 19 (RB 19) is found to be resistant to chemical oxidation due to its aromatic anthraquinone structure and is highly stabilized by resonance (Lizama et al. 2002) with about 46 years of half life of hydrolysed RB19 at pH 7 and 25°C (Santos et al. 2007, Siddique et al. 2011). Adsorptive removal of Remazol synthetic dye effluent containing RB19 on activated carbon was studied by Vijayaraghavan et al. (2009). *Balsamodendron caudatum* (BAC), a wood waste based activated carbon was employed for the removal of Direct Red 81 (DR81) (Sivakumar et al. 2010).

The present study is concerned with the equilibrium, thermodynamics and kinetics of adsorptive removal of two dyes RB 19 and DR 81. PAC has been used as an adsorbent for dye removal. To our knowledge, studies based on adsorption isotherm experiments and estimation of thermodynamic parameters have not been conducted so far. A number of kinetic models have been employed to understand the mechanism of adsorption and potential rate controlling steps. A comparative analysis for the treatment of these dyes has also been made.

MATERIALS AND METHODS

Adsorbates*:* RB19 dye A.R. grade, Make: Fisher Scientific, Mumbai and DR81 dye A.R. grade, Make: Colortex Industries, Surat (India) were used as adsorbates in present study. The characteristics, structures and chemical formulae for these dyes are given in Table 1.

Adsorbent and its characterization: Powdered Activated Carbon (PAC) A.R. grade, Make: Merck was used as an adsorbent in the present study. Table 2 gives the general characteristics of PAC.

Particle size analysis: Particle size distribution of PAC as an adsorbent was determined by particle size analyser (Make: Malvern Instruments, Model: Mastersizer 2000E). Fig. 1 shows the particle size distribution curve of PAC used in the present work. The specific surface area calculated by particle size analyser was 0.294 m^2/g and surface weighted mean and volume weighted mean diameters were 20.385 µm and 39.481 µm, respectively.

Scanning electron microscopy (SEM): To study the surface

Table 1: Physical and chemical characteristics of dyes RB19 and DR81 (As supplied by manufacturer).

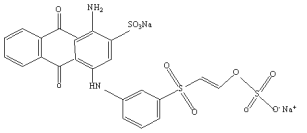
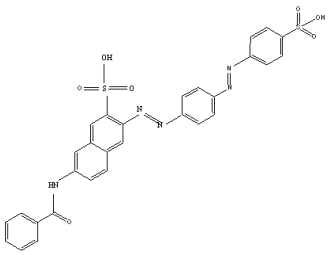
Dye	Dye structure	Generic name	Chemical formula	λ_{max}	C.I.	M.W.
Reactive Blue 19		Remazole Brilliant Blue	$C_{22}H_{16}N_2Na_2O_{11}S_3$	592	61200	626.54
Direct Red 81		Direct	$C_{29}H_{19}N_5Na_2O_8S_2$	508	28160	675.60

Table 2: Characteristics of powdered activated carbon (PAC)*.

Particulars	% Composition
Substance soluble in water	1
Substance soluble in HCl	3
Chloride (Cl)	0.2
Sulphate (SO_4)	0.2
Heavy metals (as Pb)	0.005
Iron (Fe)	0.1
Incomplete carbonization	Present
Methylene blue adsorption	180 mg/g
Loss on drying(120°C)	10
Residue on ignition (600°C)	5

*as supplied by manufacturer

morphology, surface images of PAC were captured by scanning electron microscope JEOL, JSM-6610LV at an accelerating voltage of 20 kV. The SEM microscopy carried out at Malaviya National Institute of Technology Jaipur, India, yielded micrographs of the adsorbent particles as shown in Fig. 2.

From Fig. 2, PAC appears to be an amorphous and highly porous structure with wide range of cracks and crevices reaching molecular dimensions.

Pore characterization: Micromeritics ASAP 2000 (Folio Instruments Inc.) was used for BET analysis. The following parameters were estimated:

BET surface area = 1062.6 m^2/g; Langmuir surface area = 1417.81m^2/g

Micro pore area = 646.5 m^2/g; Micropore volume = 0.2998 cc/g

Average pore diameter = 16.6 Å; External surface area = 416.05 m^2/g

Total pore volume at P/P_0 (0.9846) = 0.578876 cc/g

Perkin Elmer Elemental was used in CHNS analysis at University of Saskatchewan, Canada and results obtained are as follows:

C = 81.39%, H = 1.774%, N = 0.212%, S = 0.028%.

Analytical measurement: Dye concentrations were determined by measuring the absorbance at characteristic wavelength using UV spectrophotometer (Model: UV-1800, Make: Shimadzu, Japan). Calibration curves were plotted between absorbance and concentration of the dye solutions.

Batch studies: The percent removal of dyes and equilibrium adsorption uptake, q_e (mg/g), were calculated using the following relationships:

$$\text{Percent Removal} = \frac{(C_0 - C_e)}{C_e}100 \quad ...(1)$$

$$\text{Amount adsorbed, } q_e = \frac{(C_0 - C_e)V}{W} \quad ...(2)$$

For optimal amount of PAC per unit mass adsorbate, a 100 mL dye solution was agitated with different amounts of PAC in conical flasks till equilibrium was attained. Kinetics of adsorption was determined by analysing adsorptive uptake of dye from aqueous solution at different time intervals. For adsorption isotherms, dye solutions of different concentrations were agitated in a conical flask with known amount of PAC till equilibrium was achieved. The residual dye concentration was then determined. Blank runs (without dye) were conducted simultaneously at similar conditions to account for any colour leached by PAC and adsorption by glass containers.

Adsorption kinetics: In order to understand the adsorption mechanism, the kinetic parameters of adsorption of RB19 and DR81 on PAC were determined. These include pseudo-first order equation, pseudo-second order equation; intra-particle diffusion model, Elovich kinetic model and Bangham's equation.

Pseudo-first order kinetic model: The pseudo-first-order equation is given as:

$$\frac{dq_1}{dt} = k_1(q_e - q_t) \qquad ...(3)$$

The integration of eq. (3) with initial condition, $q_t = 0$ at t = 0 leads to

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

The values of k_1 and q_e can be obtained from the intercept and slope of log (q_e-q_t) vs. t.

Pseudo-second order kinetic model: The pseudo-second order model is represented as:

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

Integration of eq. (5) for the boundary condition: $q_t(0) = 0$ and $q_t(t) = q_t$, gives

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \qquad ...(6)$$

Eq. (6) can be rearranged to obtain a linear form,

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

The initial sorption rate at $t = 0$ is defined as

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

If pseudo-second-order kinetics is applicable, the plot of t/q_t versus t should be linear.

Intra-particle diffusion model: The possibility of intra-particle diffusion resistance affecting adsorption was explored by using the Weber and Morris intra-particle diffusion model using following relationship,

$$q_t = k_p t^{1/2} + C \qquad ...(9)$$

Elovich kinetic model: The Elovich equation is based on the adsorption capacity, given by the following equation.

$$\frac{dq_t}{dt} = a \ \exp(-b q_t) \qquad ...(10)$$

Simplifying by applying the boundary conditions, $q_t(0) = 0$ and $q_t(t) = q_t$, eq. (10) can be rewritten as:

$$q_t = \frac{1}{b}\ln(ab) + \frac{1}{b}\ln(t) \qquad ...(11)$$

The applicability of the Elovich equation to the kinetics of RB19 and DR81 dye sorption on to PAC may be tested using eq. (11).

Bangham's equation: Kinetic data were further employed to determine the slow step using Bangham's equation (Mane et al. 2007):

$$\log\log\left(\frac{C_0}{C_0 q_t m}\right) = \log\left(\frac{k_0 m}{2.303V}\right) + a\ \log(t) \qquad ...(12)$$

Fig. 10, presents a plot of log t versus log log [C_0/ (C_0-$q_t m$)] for Bangham's equation for RB19 and DR81 dye on PAC.

Adsorption Isotherms

Langmuir isotherm: The Langmuir equation is suitable to describe the adsorptive behaviour of homogeneous surface. The Langmuir isotherm model can be expressed as follows (Khaled et al. 2009).

$$q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \qquad ...(13)$$

Eq. (13) can be rearranged to obtain a linear form,

$$\frac{C_e}{q_e} = \frac{1}{q_m k_L} + \frac{C_e}{q_m} \qquad ...(14)$$

Freundlich isotherm: The Freundlich isotherm endorses the heterogeneity of the surface and assumes that the adsorption occurs at sites with different energy of adsorption (Onal et al. 2007). Following equation shows the linear equation of Freundlich isotherm.

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \qquad ...(15)$$

The value of K_F is related to the adsorption capacity of the adsorbent and value of $1/n$ is related to the adsorption intensity.

Temkin isotherm: Temkin isotherm assumes that: (i) heat of adsorption of all molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and (ii) adsorption is characterized by a uniform distribution of binding energy. Temkin isotherm is represented by following equation (Khaled et al. 2009).

$$q_e = \frac{RT}{b}\ln(K_T C_e) \qquad ...(16)$$

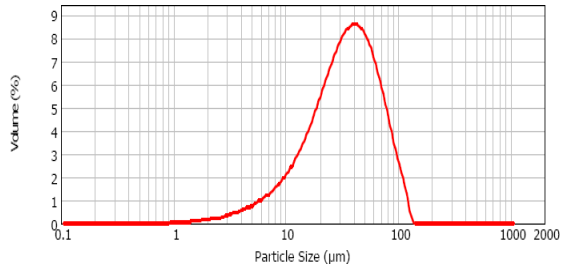


Fig. 1: Particle size distribution curve of PAC.

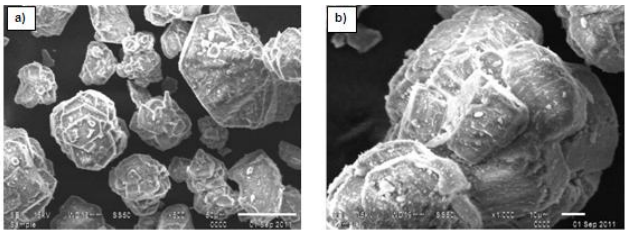


Fig. 2: Scanning electron micrographs of PAC: a) 500X, b) 1000X.

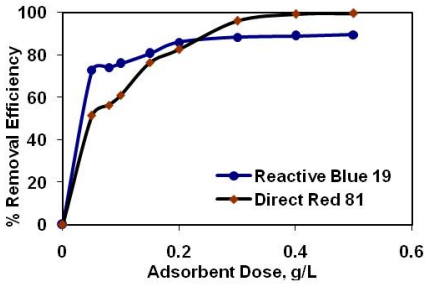


Fig. 3: Effect of adsorbent dose on the adsorption of dyes by PAC (Temperature = 298 K, contact time =180 min, initial dye concentration = 50 mg/L)

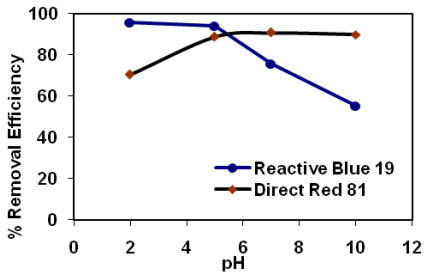


Fig. 4: Effect of pH on the adsorption of dyes by PAC (Temperature = 298K, contact time = 180 min, initial dye concentration = 50 mg/L, PAC dose = 0.2 g/L (RB19); 0.3 g/L (DR 81)

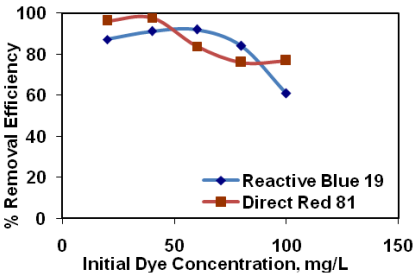


Fig. 5: Effect of initial dye concentration on the adsorption of dyes by PAC (Temperature = 298 K, contact time = 180 min, initial, PAC dose = 0.2 g/L (RB19); 0.3 g/L (DR 81)

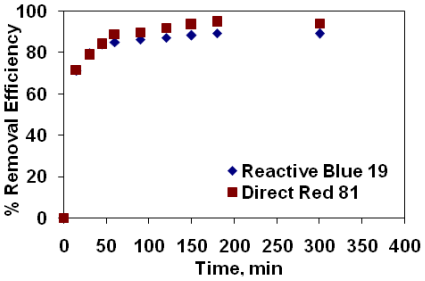


Fig. 6: Effect of contact time on the adsorption dyes by PAC (Temperature = 298 K, initial dye concentration = 50 mg/L, PAC dose = 0.2 g/L (RB19); 0.3 g/L (DR 81).

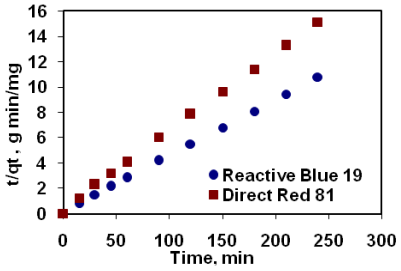


Fig. 7: Pseudo-second order kinetic plots for removal of dyes by PAC (Temperature = 298 K, contact time = 180 min, initial dye concentration = 50 mg/L PAC dose = 0.2 g/L (RB19); 0.3 g/L (DR 81).

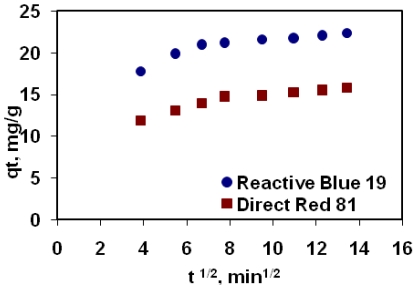


Fig. 8: Weber and Morris intra-particle diffusion plot for removal of dyes by PAC (Temperature = 298 K, contact time = 180 min, initial dye concentration = 50 mg/L PAC dose = 0.2 g/L (RB19); 0.3 g/L (DR 81).

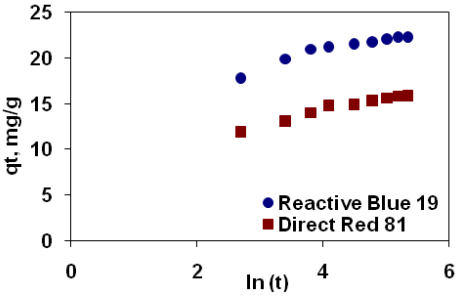


Fig. 9: Elovich kinetic plot for removal of dyes by PAC (Temperature = 298 K, contact time = 180 min, initial dye concentration = 50 mg/L PAC dose = 0.2 g/L (RB19); 0.3 g/L (DR 81).

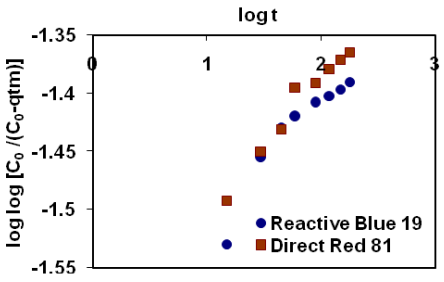


Fig. 10: Bangham's equation plot for removal of dyes by PAC (Temperature = 298 K, contact time = 180 min, initial dye concentration = 50 mg/L PAC dose = 0.2 g/L (RB19); 0.3 g/L (DR 81).

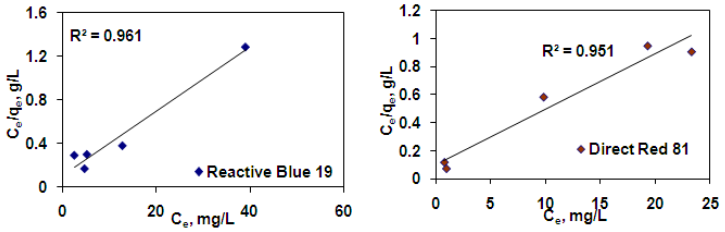


Fig. 11: Langmuir isotherm plots for the removal of dyes on PAC (temperature = 298 K, contact time = 180 min).

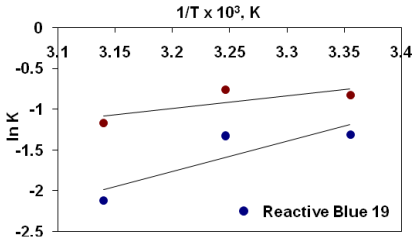


Fig. 12: Van't Hoff plot for the adsorption of RB 19 and DR 81 onto PAC.

Eq. (16) can be expressed in its linear form as:

$$q_e = B_1 \ln K_T + B_1 \ln C_e \quad ...(17)$$

Where,

$$B_1 = \frac{RT}{b} \quad ...(18)$$

Dubinin-Radushkevich (D-R) isotherm: The linear form of Dubinin-Radushkevich isotherm equation can be expressed as (Mane et al. 2007):

$$q_e = q_s \exp(Be^2) \quad ...(19)$$

Eq. (19) can be written as:

$$\ln q_e = \ln q_s - B e^2 \quad ...(20)$$

Where, q_s is the D-R constant and e can be correlated as

$$e = RT \ln\left(1 + \frac{1}{C_e}\right) \quad ...(21)$$

The constant B gives the mean free energy E of sorption per molecule of sorbate when it is transferred to the surface of the solid from infinity to solution and can be computed using the following relationship:

$$E = \frac{1}{\sqrt{2B}} \quad ...(22)$$

Thermodynamics: The thermodynamic analysis determines the properties of adsorption system such as activation energy, activation parameters, Gibb's free energy change, enthalpy and entropy which cannot be measured directly (Saha et al. 2010). Thermodynamic parameters such as change in free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) were calculated using the following equations.

$$\Delta G^0 = -RT \ln K \quad ...(23)$$

According to thermodynamics, the Gibb's free energy change is also related to the entropy change and heat of adsorption at constant temperature by the following equation.

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad ...(24)$$

Combining the above two equations, we get,

$$\ln K = \frac{-\Delta G^0}{RT} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad ...(25)$$

Table 3: Kinetic parameters for the removal of dyes by PAC at 298K.

Pseudo-first-order model						
Dye	$q_{e\ expt.}$, mg/g	k_1, min^{-1}	$q_{e\ calc.}$, mg/g		R^2 (linear)	SSE %
RB19	22.31	5.2×10^{-3}	1.91		0.2847	10.20
DR81	15.89	18.0×10^{-3}	1.41		0.1374	7.24
Pseudo-second-order model						
Dye	$q_{e\ expt.}$, mg/g	k_2, g/ mg min	$q_{e\ calc.}$, mg/g	h, mg/g min	R^2, linear	SSE %
RB19	22.31	10.0×10^{-3}	22.72	5.24	1.0	0.205
DR81	15.89	8.60×10^{-3}	16.39	2.31	0.99	0.250
Intra-particle diffusion						
Dye	k_p, mg/g min$^{1/2}$		C, mg/g		R^2, linear	
RB19	0.3901		17.54		0.7979	
DR81	0.374		11.45		0.8921	
Elovich kinetic model						
Dye	β, g/mg		α, mg/g		R^2, linear	
RB19	1.5543		14.39		0.9086	
DR81	1.478		8.197		0.966	
Bangham's constants						
Dye	k_0, mL/(g/L)		α, mg/g		R^2, linear	
RB19	0.2235		0.1158		0.881	
DR81	0.1514		0.1182		0.9632	

Table 4: Isotherm parameters for the removal of RB 19-PAC system.

RB 19-AC	Temperature		
	298 K	308 K	318 K
Langmuir isotherm			
K_L, L/mg	0.268	0.265	0.120
q_m, mg/g	13.12	35.21	52.08
R_L	0.157-0.035	0.158-0.036	0.294-0.076
R^2	0.9691	0.9628	0.9469
Freundlich isotherm			
K_F, (mg/g) (mg/L)$^{1/n}$	9.4593	8.989	8.584
$1/n$	0.3902	0.4128	0.583
R^2	0.549	0.9628	0.8709
Temkin isotherm			
K_T, L/mg	10.58	0.922	0.074
B_1	5.9281	7.9705	12.215
R^2	0.9143	0.6636	0.9644
Dubinin-Radushkevich isotherm			
q_s, mg/g	33.48	8.20	26.91
B	-2×10^{-6}	0.317	-2×10^{-6}
R^2	0.8695	0.8108	0.993

Table 5: Isotherm parameters for the removal of DR 81-PAC system.

DR 81-PAC	Temperature		
	298 K	308 K	318 K
Langmuir isotherm			
K_L, L/mg	0.437	0.466	0.312
q_m, mg/g	25.18	24.93	34.01
R_L	0.102-0.022	0.096-0.021	0.138-0.031
R^2	0.9515	0.9795	0.964
Freundlich isotherm			
K_F, (mg/g) (mg/L)$^{1/n}$	9.311	8.989	8.602
$1/n$	0.287	0.3105	0.4784
R^2	0.7941	0.8219	0.9287
Temkin isotherm			
K_T (L/mg)	2.481	2.174	1.209
B_1	4.0108	4.3317	7.2451
R^2	0.8385	0.9087	0.96
Dubinin-Radushkevich isotherm			
q_s, mg/g	22.05	17.99	23.93
B	-2×10^{-7}	-7×10^{-8}	-3×10^{-7}
R^2	0.7169	0.3002	0.9443

RESULTS AND DISCUSSION

Effect of adsorbent dose: The effect of adsorbent dose on the removal of RB19 and DR81 dye solution is shown in Fig. 3. It is evident that at adsorbent dose > 0.2 g/L for RB19 and adsorbent dose > 0.3 g/L for DR81, the adsorbent surface becomes saturated with PAC and the residual dye concentration in the solution is large (Eren and Acar 2006). Therefore, optimum PAC doses for RB19 and DR81 removal were found to be 0.2 g/L and 0.3 g/L of dye solutions, respectively.

Effect of pH: The adsorption of RB19 and DR81 by PAC was studied over a pH range of 2-10 at 298 K and the studies were conducted for 3 h. Fig. 4 shows the effect of pH on the adsorptive removal of RB19 and DR81 on PAC.

From Fig. 4, it is evident that the percent removal of RB19 is maximum at acidic pH (pH 2) and decreased with further increase in pH though up to a pH of 5.0 the difference was negligible. For an actual system, based on the pH of the wastewater, this range of 2-5 may be adopted for minimum requirement for neutralization. For DR81, the maximum removal was found at neutral pH (pH 7). Change of pH affects the adsorptive process through dissociation of functional groups on the adsorbent surface active sites (Kumar et al. 2008). This subsequently leads to a shift in reaction kinetics and equilibrium characteristics of adsorption process (Mall et al. 2006).

Effect of initial dye concentration: It is well known that a given mass of adsorbent can adsorb only a fixed amount of adsorbate. Thus, initial concentration of dye solution is important. The adsorption of RB19 and DR81 by PAC was studied over initial dye concentration of 20-100 at 298 K for about 3 h. The effect of initial RB19 and DR81 dye concentrations for their removal by PAC is shown in Fig. 5.

From Fig. 5, it is evident that for both the dyes, a high percent removal was observed at lower initial dye concentration. However, the amount of dye adsorbed per unit adsorbent increased with increase in initial dye concentration due to decrease in resistance to the uptake of solute from the dye solution.

Effect of contact time: The effect of contact time for adsorption of RB19 and DR81 by PAC was studied for initial dye concentration of 50 mg/L at 298 K. PAC dose was 0.2 g/L and 0.3 g/L of dye solution for RB19 and DR81, respectively, without pH adjustment. Although, dye solutions were kept in contact with PAC for 24 h, no significant variation in residual dye concentration was detected after 3 h of contact time. Thus, after 3 h of contact, a steady-state approximation may be assumed and a quasi-equilibrium situation is accepted. The effect of contact time on RB19 and DR81 dyes for their removal by PAC is shown in Fig. 6.

Fig. 6 presents that the curves of contact time are smooth and continuous leading to saturation. The curves indicate that the dye removal was rapid in the first 15 min. These curves also indicate the possible monolayer coverage of dye on the surface of PAC (Lata et al. 2008).

Adsorption kinetics: Various kinetic models were analysed to predict the adsorption mechanism. The results were analysed for pseudo-first order model, pseudo-second order model, intraparticle diffusion model, Elovich model and Bangham's plot. The results are presented in Table 3. It may be observed that pseudo-second order kinetics well describes

Table 6: Thermodynamic parameters for different dyes on activated carbon.

Adsorbent/Adsorbate	Temperature, K	ΔG^0, kJ/mol	ΔH^0, kJ/mol	ΔS^0, J/K	References
Activated Carbon/Malachite Green	298	10.93	60.16	238	Onal et al. (2007)
	313	14.97			
	323	16.81			
Activated Carbon/Congo Red	303	2.86	51.09	118.1	Purkait et al. (2007)
	313	4.64			
	323	6.42			
Activated Carbon/Reactive Orange dye	298	-3.2	8.59	-14.2	Abdelwahab et al. (2008)
	313	-2.9			
	323	-2.3			
Agro Waste/Reactive Red 198	303	-4.57	-9.74	-17.04	Akar et al. (2009)
	310	-4.40			
	320	-4.23			
Powdered Activated Carbon/RB19 dye	298	3.260	-1.37	-4.6	This study
	308	3.400	-3.85	-12.5	
	318	5.604	-6.07	-19.1	
Powdered Activated Carbon/DR81 dye	298	2.04	-3.13	-10.5	This study
	308	1.953	-3.08	-10.0	
	318	3.077	-4.23	-13.3	

the adsorption process. The calculated q_e values are found to be equal with experimental data. Fig. 7 represents the plot of pseudo-second order kinetics. Besides the value of R^2, the applicability of both pseudo-first order and pseudo-second order kinetic models has been verified through the sum of the squares of the errors (Mane et al. 2007). The validity of each model was determined by the sum of error squares (SSE %) given by:

$$\text{SSE (\%)} = \sqrt{\frac{\sum (q_{e.\exp} - q_{e.calc})^2}{N}} \qquad ...(26)$$

Where, N is the number of data points. The higher the value of R^2 and lower the value of SSE; the better will be the goodness of fit (Lata et al. 2008). Table 3 also shows that values of SSE are lower for pseudo-second-order kinetic model for both the dyes, thereby confirming the applicability of pseudo-second-order kinetic model.

In Fig. 8, a plot of $t^{1/2}$ versus q_t is presented for intraparticle diffusion plot for RB19 and DR81 dye on PAC. It may be observed that straight lines did not pass through the origin. This implies that the intraparticle diffusion is not the sole rate controlling step for the adsorption of dyes on PAC, but other processes may also control the rate of adsorption. There are two separate areas, first portion describes the bulk diffusion process and second describes the intra-particle diffusion process (Mane et al. 2007, Khaled et al. 2009). Fig. 9, presents a plot of q_t versus *ln (t)* for Elovich equation for RB19 and DR81 dye on PAC.

A good regression correlation coefficient value (R^2) for DR81 indicates that the Elovich kinetic model is more favourable for DR81 dye than RB19 dye solution.

A plot of log t versus log log $[C_0/(C_0 - q_t m)]$ is presented for Bangham's equation for RB19 and DR81 dye on PAC (Fig. 10). From Fig. 10, the non-linear double logarithmic plots confirm that intra-particle diffusion of adsorbate is not the sole controlling step as shown earlier by intraparticle diffusion model.

Adsorption equilibrium: The isotherm studies mainly identify the conditions for which high adsorption capacities are obtained and estimate the shape of the isotherm curve (Sohn & Kim 2005). Among the different isotherm models studied, in both cases of dyes, Langmuir isotherm was found to best represent the sorption on PAC. Fig. 11 shows, a linear plot of C_e/q_e versus C_e for the removal of RB19 and DR81 on PAC, respectively.

The Fig. 11 indicates the applicability of the Langmuir isotherm model. The values of q_m and K_L and correlation coefficients for Langmuir isotherm for RB19-PAC and DR81-PAC systems are presented in Tables 4 and 5, respectively. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter R_L which is defined as:

$$R_L = \frac{1}{1 + k_L C_0} \qquad ...(27)$$

$R_L > 1$ Unfavourable, $R_L = 1$ Linear, $0 < R_L < 1$ Favourable, $R_L = 0$ Irreversible

In Tables 4 and 5, the values of R_L were found to be in

the range of 0-1, indicating that the adsorption process is favourable for both the adsorbents (Eren & Acar 2006). In Table 4, the value of q_m increases with increasing temperature confirming that the adsorption process is favoured at higher temperatures (Abdelwahab 2008). Therefore, the Langmuir isotherm model estimates the maximum adsorption capacity produced from complete monolayer coverage on the adsorbent surface (Khaled et al. 2009).

Thermodynamics: The values of ΔH^0 can be determined by the slope of the linear Van't Hoff plot as $ln\ K$ versus $1/T$ (Fig. 12). A comparative analysis of the thermodynamic parameters with the values reported in literature is presented in Table 6.

The positive values of ΔG^0 indicated that the process is not spontaneous in nature. The similar findings have been reported in the literature (Onal et al. 2007, Purkait et al. 2007). The negative value of ΔH^0 indicated the exothermic nature of the process. The similar findings have also been reported by Akar et al. (2009). The negative value of $\Delta S°$ also suggests decreased randomness at the solution interface during the adsorption of dyes onto PAC. The similar findings have been reported by Abdelwahab et al. (2008) and Akar et al. (2009).

CONCLUSIONS

In the present study, a comparative study of adsorptive removal of two dyes, viz., RB19 and DR81 has been presented. PAC was found as an effective adsorbent for the removal of RB19 and DR81 from their aqueous solutions. The specific surface area of PAC calculated by particle size analyser was 0.294 m^2/g with surface weighted mean and volume weighted mean diameters as 20.385 µm and 39.481 µm, respectively.

High percent removal of RB19 and DR81 by PAC is possible, provided the concentration of dyes in the solution is low. Optimum PAC dose for RB 19 and DR 81 was found to be 0.2 g/L and 0.3 g/L respectively with an optimal equilibrium time for both dyes to be 3 h. Sorption of both the dyes onto PAC was found to follow pseudo second-order rate expression. Langmuir and Temkin isotherm were found to best represent the equilibrium data for DR81-PAC system while the equilibrium adsorption data for RB19-PAC system were best represented by the Langmuir isotherm. Moreover, the adsorption of dyes is favourably influenced by increase in temperature indicating the exothermic nature of the adsorption process. Overall, it may be concluded that both RB19 and DR81 are excellently adsorbed by PAC from their aqueous solutions. The study may further be extended for the design of wastewater treatment plants for dye removal.

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