Liquid phase adsorption of Crystal violet onto activated carbons derived from male flowers of coconut tree

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Abstract

Adsorption of Crystal violet, a basic dye onto phosphoric and sulphuric acid activated carbons (PAAC and SAAC), prepared from male flowers coconut tree has been investigated. Equilibrium data were successfully applied to study the kinetics and mechanism of adsorption of dye onto both the carbons. The kinetics of adsorption was found to be pseudo second order with regard to intraparticle diffusion. The pseudo second order is further supported by the Elovich model, which in turn intensifies the fact of chemisorption of dye onto both the carbons. Quantitative removal of dye at higher initial pH of dye solution reveals the basic nature of the Crystal violet and acidic nature of the activated carbons. Influence of temperature on the removal of dye from aqueous solution shows the feasibility of adsorption and its endothermic nature. Mass transfer studies were also carried out. The adsorption capacities of both the carbons were found to be 60.42 and 85.84 mg/g for PAAC and SAAC, respectively. Langmuir's isotherm data were used to design single-stage batch adsorption model.
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Keywords: Crystal violet; Cellulosic fibre carbons; Adsorption isotherm; Kinetics; Thermodynamics

1. Introduction

As a result of rapid industrialization and population growth environmental pollution is becoming the most challenging threat to human beings. Effluents discharged from dyeing industries are highly coloured. Most of the dyes used in industry are stable to light and oxidation as resistant to aerobic digestion, causing damage to the aquatic life [1].

The various treatment methods for the removal of colour and dye are coagulation using alum, lime, ferric sulphate ferric chloride, chemical oxidation using chlorine and ozone, membrane separation process, adsorption and so on. Among these, adsorption appears to be the best potential for over all treatment. Various agricultural products and byproducts have been investigated to remove dyes from aqueous solutions. These include cotton waste, rice husk, bark, sugar industry mud, palm fruit bunch, jack fruit peel, wood, orange peel, sugar cane dust and peat [2]. Activated carbon adsorption has been found to be an effective and widely employed means of water and wastewater treatment. The adsorption capacities of activated carbons are usually related to their specific surface area and porosity. In addition the adsorption properties of activated carbons are found to strongly depend on the activation process. Crystal violet being a protein dye, it is used to identify the bloody fingerprints. Crystal violet is also used on most types of adhesive taps for latent printing. It is also used in Gram's stain for the demonstration and primary classification of dyes. The brilliant colours are produced using Crystal violet. Crystal violet is toxic. It may cause cancer, severe eye irritation and it is harmful by inhalation, ingestion and through skin contact. Hence the dye removal from the water bodies becomes essential.

The purpose of this study is to study the kinetics and mechanism of adsorption of a basic dye, Crystal violet dye on two different carbons prepared from male flowers of coconut tree using phosphoric acid and sulphuric acid and labeled as PAAC and SAAC, respectively. The influencing parameters such as kinetics and adsorption dynamics were analysed. The influence of temperature on adsorption of Crystal violet was stud-

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Table 1
Characterization of carbonized 'Waste' male flowers of Coconut tree

Parameters	Values	
	PAAC	SAAC
Porosity (%) [29]	72.36	65
pH_{zpc} [30]	6.80	8.03
Surface area (m^2/g)	328.2	556.3
Carboxyl groups (mequiv./g) [31]	0.2	0.15
Phenol groups (mequiv./g) [31]	1.5	1.06

ied at different temperatures (28–48 °C). The equilibrium data were tested with three different models. Mass transfer studies explores the film and pore diffusion models for adsorption of dyes. These fundamental studies will be useful for further applications in designing the batch adsorption for the treatment of dyeing industry wastewaters. Similar studies on the removal of Crystal violet were carried out using adsorbents wollastonite [3], fly ash [4], magnetic charcoal [5], and sludge biomass [6].

2. Materials and methods

2.1. Materials

#### 2.1.1. Preparation of phosphoric acid activated carbon (PAAC)

Sun dried male flowers (MF) of coconut tree were carbonized with 15% phosphoric acid (PA) in the weight ratio 1:3 (MF:PA) and concentrated sulphuric acid (SA) in the weight ratio of 1:2 (MF:SA). The carbonization and activation completed by heating under N_2 atmosphere with a flow rate of 80 ml/min, with a heating rate of 2 °C/min up to 450 °C, residence time of 4 h. The resulting carbons were washed with distilled water until a constant pH of the slurry. The carbons were then dried for 2 h at a 100 °C. The dried materials were ground and sieved to different geometrical sizes and labeled as PAAC and SAAC, respectively. The general characteristics of PAAC and SAAC are presented in Table 1. Approximate FTIR band assignments indicated the presence of carbonyls, carboxyl group, lactone and phenols. 1450–1000 cm^{-1} band was assigned to the C=O stretching and O−H bending modes such as phenols and carboxylic acid.

2.1.2. Adsorbate

The adsorbate, a basic dye, Crystal violet (CV), Fig. 1 (basic dye, C.I. 42555, $\lambda_{max. abs.}$ = 586 nm, and of molecular formula $C_{25}H_{30}N_3Cl$), obtained from Dystar, Mumbai, India was used as received. Doubly distilled water was used. The solution pH was adjusted using 0.1N HCl or 0.1N NaOH obtained from Merck, India. Concentrations of dye solutions were measured by monitoring the maximum absorbance using Schimatzu UV–Vis spectrophotometer (Shimadzu Model: UV 1601).

2.2. Equilibrium studies

Batch adsorption studies were performed at room temperature. Fifty milliliters of different initial concentrations (10, 20,
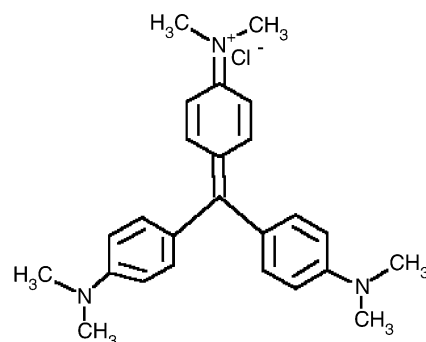
C.I. 42555; λmax.=586nm; $C_{25}H_{30} N_3Cl$ Molecular weight:386

Fig. 1. Crystal violet-dye structure.

30, and 40 mg/l) of the dye solution were taken in 100 ml conical flasks containing 100 mg of PAAC and 25 mg of SAAC separately. The flasks were agitated at room temperature at 120 rpm for a pre-determined time intervals using thermostated water bath rotary orbital shaker with an initial pH 6.0. At time $t = 0$ and equilibrium the dye concentrations were measured using UV/Vis spectrophotometer (Shimadzu Model: UV 1601). The maximum absorbance of colour was read at 586 nm and it was used to calculate the amount of dye adsorbed, q mg/g. Effect of carbon concentration was studied by varying carbon (both PAAC and SAAC) concentration from 10 to 200 mg/50 ml for different dye concentrations (10, 20, 30 and 40 mg/l). Langmuir isotherm studies were carried out by agitating the carbons, PAAC (150 mg/50 ml of Crystal violet dye solutions) and SAAC (100 mg/50 ml of Crystal violet dye solutions) of seven different concentrations, 60, 80, 100, 120, 140, 160 and 180 mg/l for, 10 h. The effect of initial pH on initial dye concentration was studied in the pH range 2–9 with a fixed carbon (both PAAC and SAAC) concentration (50 mg of carbon in 50 ml of 40 mg/l dye solution) agitated for 3 h at room temperature. Fifty milliliters of 40 mg/l of dye solution mixed with fixed carbon concentration (100 mg, PAAC and 25 mg, SAAC) at pH 6.0 were agitated at different temperatures (28–48 °C). Control experiments were carried out for the adsorption of Crystal violet in absence of carbon by the container walls. It was found that there was no degradation or adsorption of Crystal violet by the container walls.

Generally, the carbon (0.15–0.25 mm particle size) concentration of 100 mg of PAAC and 25 mg of SAAC for 50 ml of dye solution at the natural pH 6.0 of the dye solution and room temperature, 28 °C were maintained for all studies unless otherwise stated. All experiments were carried out in duplicate and the mean values are presented. The error obtained was 3.7%.

3. Results and discussions

3.1. Adsorption kinetics study

Successful application of the adsorption demands innovation of cheap, non-toxic, easily available adsorbents of known kinetic parameters and adsorption characteristics. Adsorption kinetics

Table 2
Comparison of kinetic parameters for the adsorption of Crystal violet onto carbon at various concentrations

Conc. (mg/l)	q_e exp. (mg/g)	Pseudo first-order kinetics			Pseudo second-order kinetics			Elovich equation		
		q_e cal. (mg/g)	R^2	SSE	q_e cal. (mg/g)	R^2	SSE	q_e cal. (mg/g)	R^2	SSE
(A) PAAC										
10	4.900	10.299	0.989	0.636	5.7904	0.997	0.445	4.8510	0.978	0.629
20	9.495	12.668	0.979	0.218	10.858	0.999	1.054	9.7582	0.989	0.301
30	14.460	15.137	0.995	1.280	16.474	0.999	0.761	14.596	0.999	0.325
40	18.500	17.582	0.958	1.130	21.231	0.993	0.910	19.236	0.997	0.529

Conc. (mg/l)	q_e exp. (mg/g)	First order kinetics			Second order kinetics			Elovich equation		
		q_e cal. (mg/g)	R^2	SSE	q_e cal. (mg/g)	R^2	SSE	q_e cal. (mg/g)	R^2	SSE
(B) SAAC										
10	11.538	6.1716	0.994	1.239	12.987	0.997	2.655	11.207	0.97	0.231
20	16.134	10.029	0.996	3.466	18.181	0.997	3.414	15.742	0.989	0
30	21.456	11.073	0.991	5.086	23.255	0.999	4.914	21.755	0.993	0
40	24.450	21.890	0.994	7.180	26.315	0.990	4.060	25.095	0.995	0.425

Conditions: (A) PAAC: adsorbent dose: 100 mg/50 ml; temperature: 28 °C; initial pH 6.0. (B) SAAC: adsorbent dose: 25 mg/50 ml; temperature: 28 °C; initial pH 6.0.

can be modeled by pseudo first-order Lagergren equation [7]:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right) t \tag{1}$$

where q_e and q_t are the amounts of dye adsorbed at equilibrium and at time t (mg/g), respectively, and k_1 is the rate constant of pseudo first-order sorption (1 min^{-1}), pseudo second-order

equation [8]:

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_t^2} + \frac{1}{q_e}\right) t \tag{2}$$

where q_e is the amount of dyes sorbed at equilibrium (mg/g), k_2 is the equilibrium rate constant of pseudo second-order sorption
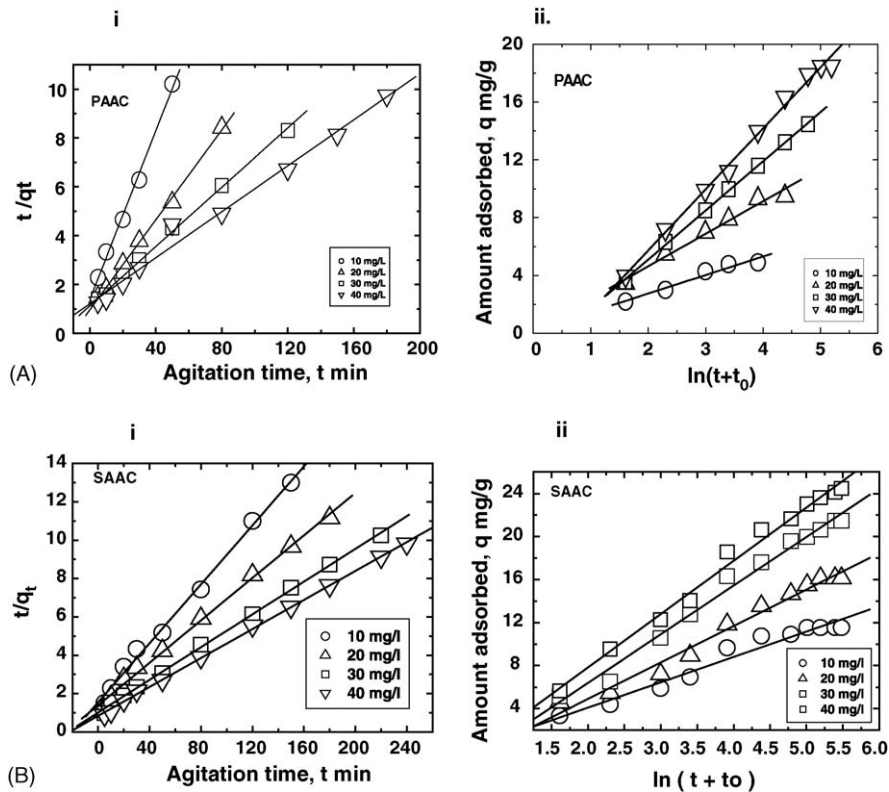

Fig. 2. Kinetic models. (i) Pseudo second-order kinetic model. Conditions: CV concentration = (○) 10 mg/l; (△) 20 mg/l; (□) 30 mg/l; (▽) 40 mg/l; initial pH of CV solution 6.04; adsorbent particle size = 0.150–0.250 mm; temperature = 28 °C; carbon dose: (A) PAAC = 100 mg/50 ml; (B) SAAC = 25 mg/50 ml. (ii) Elovich kinetic model conditions as in (i).

(g/mg min), and Elovich equation [9]:

$$q_t = \left(\frac{1}{b}\right)\ln(t + t_0) - \left(\frac{1}{b}\right)\ln t_0 \qquad (3)$$

the parameter b is related to extent of surface coverage and activation energy for chemisorption (g/mg):

$$q_t = \left(\frac{1}{b}\right)\ln(ab) + \left(\frac{1}{b}\right)\ln t \qquad (4)$$

where a is the initial adsorption rate (mg/g min), $t_0 = (1/ab)$ and $t \gg t_0$.

3.1.1. Selection of the kinetic model

The results of the kinetic studies are presented in Table 2 and Fig. 2. The straight lines for all the initial concentrations (Fig. 2) with extremely high correlation coefficients (<0.998) for pseudo second-order kinetic model compared to those for pseudo first-order model for the adsorption of Crystal violet dye cations onto both the carbons strongly suggest that all the adsorption systems are of pseudo second-order model. Based on the assumption that the rate-limiting step may be chemical adsorption or chemisorptions involving valency forces through sharing or exchange of electrons between the active sites of carbons and polar dye ions. The calculated values of q_e found from pseudo first-order kinetic model gave less reasonable values for both the adsorbents, PAAC and SAAC than those from the pseudo second-order kinetic model. For both the adsorbents, q_e calculated obtained agreed well with the experimental q_e in the pseudo second-order kinetics. This suggests that each dye adsorption systems using PAAC and SAAC follows the pseudo second-order kinetic which provides a better correlation of data. Further, the low SSE, high regression coefficients of the Elovich kinetic model discussed confirms the adsorption of Crystal violet onto both the carbons are chemisorptive in nature. The sums of error squares (SSE) is also calculated using:

$$\mathrm{SSE} = \frac{\sqrt{\sum (q_e \,\mathrm{exp.} - q_e \,\mathrm{cal.})^2}}{N} \qquad (5)$$

where N is the number of data points. Similar observation was reported for dye adsorption onto mixed carbon clay [10], activated clay [11], peat [12], sepiolite [13], peat–resin particle [14].

3.2. Effect of agitation time and initial concentration of dye on adsorption

Adsorption rate of Crystal violet on both the carbons at different time intervals and different initial dye concentrations (10, 20, 30 and 40 mg/l) are shown in Fig. 3. It was observed that the removal of dye was rapid in the initial stages of contact time and gradually decreased with lapse of time until equilibrium. The equilibrium time was 50, 80, 120 and 180 min for PAAC and 120, 150, 180 and 220 min for SAAC for the initial concentration, 10, 20, 30 and 40 mg/l, respectively. For both the carbons the equilibrium time of adsorption of Crystal violet were found to decrease with increase in concentration. The time profile of
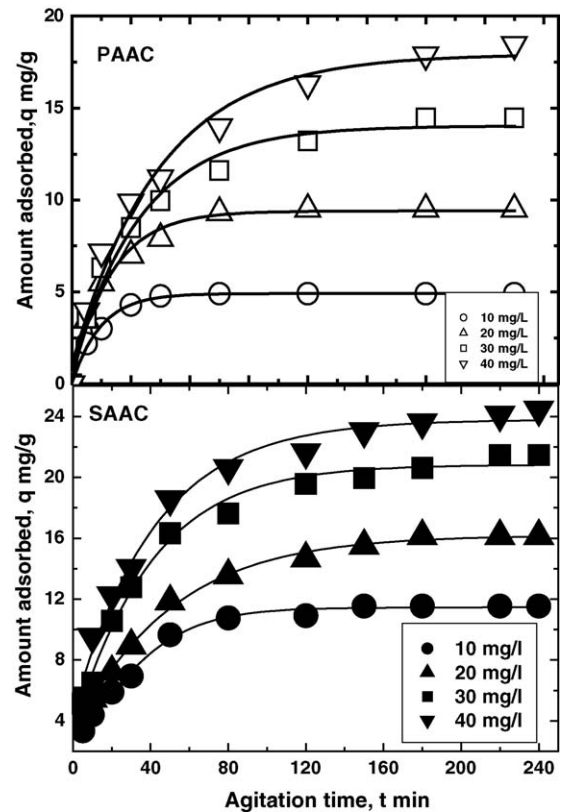

Fig. 3. Effect of agitation time and initial concentration of Crystal violet PAAC conditions: CV concentration = (○) 10 mg/l; (△) 20 mg/l; (□) 30 mg/l; (▽) 40 mg/l; initial pH of CV solution 6.04; adsorbent dose = 100 mg/50 ml; adsorbent particle size = 0.150–0.250 mm; temperature = 28 °C. SAAC conditions: conditions: CV concentration = (●) 10 mg/l; (▲) 20 mg/l; (■) 30 mg/l; (▼) 40 mg/l; adsorbent dose = 25 mg/50 ml; initial pH of CV solution 6.04; adsorbent particle size = 0.150–0.250 mm; temperature = 28 °C.

dye uptake is a single, smooth and continuous curve (Fig. 2) leading to saturation, suggesting the possible monolayer coverage of dye on the surface of adsorbent.

3.3. Effect of carbon concentration

For both carbons, it was observed that the uptake of the dye increased with the increase in carbon concentration (figure not shown), at different carbon concentrations (10–200 mg/50 ml) at fixed equilibrium time of 3 h with different initial dye concentration (10, 20, 30 and 40 mg/l) at an initial pH 6.0. This can be attributed to increase in carbon concentration increase, the available carbon surface area and availability of more adsorption sites [15,16].

3.4. Adsorptions Isotherms

Adsorption isotherms were analysed according to the linear form of Langmuir isotherm [17]:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L}C_e \qquad (6)$$

Table 3
Fitting results of Langmuir model

Carbon	b	R	Q_0 (mg/g)	Average R_L
PAAC	1.0521	0.992	60.42	0.0095
SAAC	0.8642	0.994	85.84	0.0095

where K_L and a_L are Langmuir constants. Eq. (6) can be modified as

$$\left(\frac{C_e}{q_e}\right) = \left(\frac{1}{bQ_0}\right) + \left(\frac{C_e}{Q_0}\right) \tag{7}$$

where C_e is the concentration of the dye solution (mg/l) at equilibrium, q_e is the amount of dye adsorbed per unit weight of adsorbent (mg/g) and b is related to the energy of adsorption (l/mg). The values of Q_0 and b were calculated from the slope and intercept of the linear plot, C_e/q_e versus C_e with $R^2 = 0.97$ and 0.99 for PAAC and SAAC, respectively, gives an accurate description of Langmuir equation (figure not shown). The fitting results are presented in Table 3. Q_0 represents practical limiting adsorption capacity. When the surface is fully covered with dye molecules and assists in the comparison of adsorption performance. The adsorption capacities, Q_0 were found to 60.42 and 85.84 mg/g for PAAC and SAAC, respectively. For comparison, the Q_0 values for other non-conventional materials from literature are compared: wollastonite −0.83 mg/g [3], fly ash −3.76 mg/g [4], magnetic charcoal −10 mg/g [5], and sludge biomass −113.6 mg/g [6]. The essential characteristics of Langmuir equation can be expressed in terms of a dimensionless separation factor R_L [18]:

$$R_L = \frac{1}{1 + bC_0} \tag{8}$$

where C_0 is the initial dye concentration (mg/l) and R_L values indicate the shape of the isotherm. The R_L values were found between 0 and 1 for both the dyes confirm the on going adsorption process are favourable. The adsorption isotherm assumes that intermolecular forces decrease rapidly with distance and consequently predicts the existence of monolayer of adsorbate at the outer surface of the adsorbent. It also assumes that adsorption takes place at specific sites within the adsorbent. It is believed that once the adsorbate occupies a site, no further adsorption take place at that site.

3.5. Effect of pH on the removal of Crystal violet

The adsorption of Crystal violet onto both the carbons over a pH range of 2–9 were studied and shown in Fig. 4. The adsorption of Crystal violet, basic dye increases with increasing pH. This can be explained by considering the zeta potential of both the carbons and found to be 6.80 and 8.03 for PAAC and SAAC, respectively. Thus it seems that for pH values above the zeta potential of carbon, negative charge density on the surface increases. The charge developed in the acid medium does not favour association of the cationic dye. However, for pH values above the zeta potential of carbon, as the carbon surface slowly becomes negatively charged, favours the adsorption of
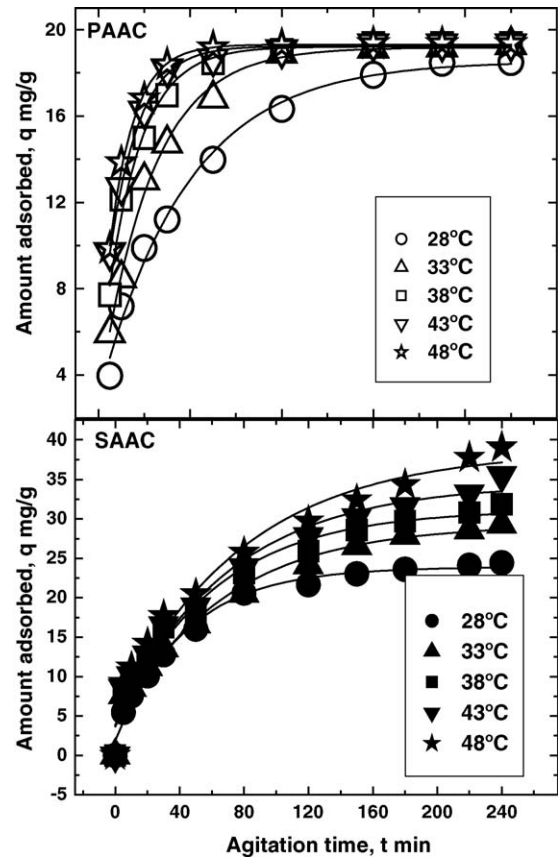

Fig. 4. Effect of temperature on the removal of dyes PAAC conditions: temperature = (○) 28 °C; (△) 33 °C; (□) 38 °C; (▽) 43 °C; (☆) 48 °C; CV concentration = 40 mg/l; initial pH of CV solution 6.04; adsorbent dose = 100 mg/50 ml; adsorbent particle size = 0.150–0.250 mm. SAAC conditions: temperature = (●) 28 °C; (▲) 33 °C; (■) 38 °C; (▼) 43 °C; (★) 48 °C; adsorbent dose = 25 mg/50 ml; initial pH of CV solution 6.04; adsorbent particle size = 0.150–0.250 mm.

cationic dye. Also, the Crystal violet dye molecules become protanated in the acid medium with deprotanation likely taking place at higher pH. Consequently, the positive charge density would be found more on the dye molecule at pH less than the zeta potential on carbon and this accounts for the higher uptake of dye onto negatively charged surface of carbon [4]. Obviously, poorer adsorption of Crystal violet at pH less than zeta potential of both the carbons, resulting an unfavourable condition for the adsorption of Crystal violet. In our previous study [19], similar trend on the effect of solution pH on the adsorption of a basic dye, Methylene blue onto jute fibre carbon was observed.

3.6. Temperature effect

The influence of effect of temperature on Crystal violet adsorption is shown in Fig. 4. The effect of temperature on the adsorption rate was studied by carrying out a series of experiments at 28, 33, 38, 43 and 48 °C for both the carbons. The adsorption of Crystal violet on PAAC and SAAC increased from 19.8 to 96.80% and 7.02 to 48.83%, respectively. This suggest that the adsorption process is endothermic in nature when temperature was increased from 28 to 48 °C
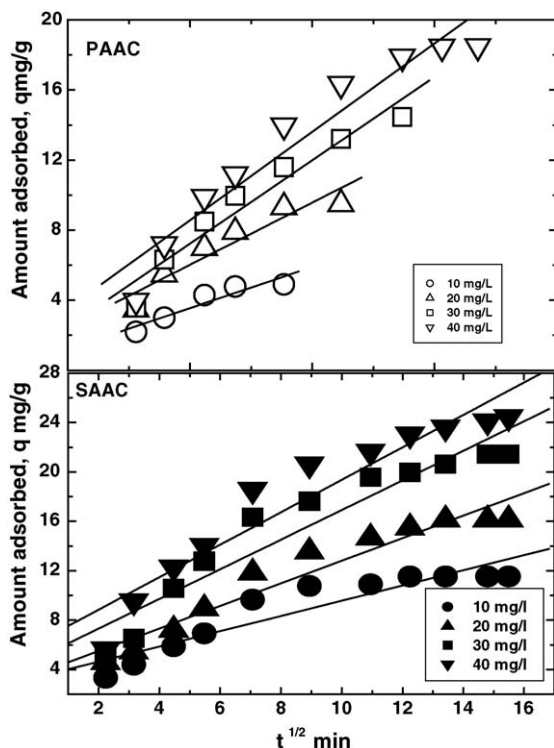
Fig. 5. Intraparticle diffusion PAAC conditions: CV concentration = (○) 10 mg/l; (△) 20 mg/l; (□) 30 mg/l; (▽) 40 mg/l; initial pH of CV solution = 6.04; adsorbent dose = 100 mg/50 ml; adsorbent particle size = 0.150–0.250 mm; temperature = 28 °C. SACC conditions: CV concentration = (●) 10 mg/L; (▲) 20 mg/l; (■) 30 mg/l; (▼) 40 mg/l; initial pH of CV solution 6.04; carbon dose: SAAC = 25 mg/50 ml; adsorbent particle size = 0.150–0.250 mm; temperature = 28 °C.

(Fig. 5) at pH 6 and $C_0 = 40$ mg/l. Increasing temperature may also produce a swelling effect within the internal structure of the carbons enabling more dye molecules diffusion into carbon [20].

Several researchers [4,21] reported the similar observation and suggested that this is due to the possibility of an increase in the porosity and in the total pore volume of the adsorbent with the increase of temperature. Further, it is also believed that the possibility of increase of the number of active sites for the adsorption with the increase of temperature. This may also be a result of an increase in the mobility of the dye molecule with the rise of temperature. It is still not get well established, became several variables such as molecular volume of the dye, its pla-

narity and its ability to bind to the adsorbents, among others may affect the degree of adsorption. The curves in Fig. 4 are found to be smooth and continuous suggesting monolayer coverage of Crystal violet onto both the carbons.

Thermodynamic parameters, $\Delta H°$ and $\Delta S°$ for the adsorption process are also determined using the Eyring's plot, $\ln K_c$ versus $1/T$ (figure not shown) as per Eq. (9):

$$\ln K_c = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \qquad (9)$$

where ($K_c = C_{ad}/C_e$) is the ratio of the amount of dye adsorbed on the adsorbent, C_{ad} to that in the adsorbate, C_e. From the values evaluated $\Delta S°$ and $\Delta H°$ at different temperatures (28–48 °C), $\Delta G°$ are also calculated using Eq. (10) and presented in Table 4:

$$\Delta G° = \Delta H° - T\Delta S° \qquad (10)$$

The negative free energy values indicate the feasibility of the process of adsorption and its spontaneous nature. It may also be noted from Table 2 the decrease in free energy values with increasing temperature with increasing adsorption capacity. The positive values of enthalpy change ($\Delta H°$) for the processes further confirm the endothermic nature of the process whereas the positive values of entropy change ($\Delta S°$) reflect good affinity of the dye towards both the carbons [22]. When the adsorbate gets adsorbed on the surface of the adsorbents, water molecules previously bonded to the dye cation get released and dispersed in the solution; this results in an increase in the entropy.

3.7. Mass transfer effects

The intraparticle diffusion model used here refers to the theory proposed by Weber and Morris [23]. The initial rate of intraparticle diffusion can be obtained by linearization of the curve (Fig. 5) $q_t = f(t^{1/2})$ [29]. A good correlation of q_e experimental with q_e calculated, $R^2 > 0.9$ and low SSE values in this model (Table 5) supports the mass transfer mechanism for the diffusion of dyes. The fractional approach to equilibrium changes according to a function of $(Dt/r^2)^{1/2}$, where r is the particle radius and D is the diffusivity of solutes within the particle. As the double nature of intraparticle diffusion plot confirms the presence of both film and pore diffusion, in order to predict the actual slow step involved, the kinetic data were further analysed using the Boyd kinetic expression [24] and observations of Reichenberg [25]. This kinetic expression Eq. (11) predicts the actual slowest step involved in the sorption process for different

Table 4
Thermodynamic parameters for the removal of Crystal violet by carbons

$1/T \times 10^{-3}$ K^{-1}	$-\Delta G_{ads}$ (kJ mol^{-1})		R^2		ΔS_{ads} (J K^{-1} mol^{-1})		ΔH_{ads} (J K^{-1} mol^{-1})	
	PAAC	SAAC	PAAC	SAAC	PAAC	SAAC	PAAC	SAAC
3.322	77.815	32.403	0.968	0.982	258.76	107.896	71.490	73.382
3.268	79.109	32.942						
3.215	80.403	33.482						
3.165	81.697	34.022						
3.155	82.990	34.561						

Table 5
Intraparticle diffusion parameters

Carbon	q_e exp. (mg/g)	q_e cal. (mg/g)	R^2	SSE
PAAC	4.900	5.349	0.939	0.0018
	9.495	10.401	0.946	0.0034
	14.460	15.492	0.968	0.0056
	18.500	18.962	0.973	0.6826
SAAC	11.538	10.959	0.927	0.903
	16.134	15.930	0.965	0.919
	21.456	22.667	0.953	0.647
	24.450	26.572	0.954	0

adsorbent–adsorbate systems:

$$F = \frac{1}{-6/\pi^2} \sum_t^\infty \left(\frac{1}{n^2}\right) \exp(-n^2 Bt) \tag{11}$$

where F is the fractional attainment of equilibrium at time, t and n is a constant:

$$F = \frac{q_t}{q_\infty} \tag{12}$$

where q_t and q_∞ are amounts adsorbed after time t and infinite time, respectively:

$$B = \frac{\pi^2 D_i}{(r_0)^2} = \text{time constant} \tag{13}$$

where D_i is the effective diffusion coefficient of adsorbates in adsorbent phase, r_0 is the radius of adsorbent particle, assumed to be spherical. For every calculated value of F, corresponding values of Bt (ion exchange rate constant), already documented in the Reichenberg's table [25] is taken into consideration. In each case, the plot of Bt versus time (Fig. 6) distinguishes between the film diffusion and particle diffusion-controlled rates of adsorption. From Fig. 6, it was observed that the plots were linear but do not pass through the origin for the carbon, PAAC and pass through the origin for SAAC. The above observations indicate that dye adsorption rate is governed by film diffusion and particle diffusion for PAAC and SAAC, respectively. The adsorbed dye fraction decreases with the increase in initial concentrations of dyes was the fact derived from Fig. 6. Initially the amount of Crystal violet adsorbed onto both the carbon surfaces increases rapidly, but then the process slows down and reaches equilibrium. This behavior was attributed to the fact that the reduction in immediate solute adsorption due to the lack of available sites to adsorb high initial concentrations of dye which in turn supports film diffusion. The D_i values for the adsorption of Crystal violet onto both the carbons were found to decrease with the increase in initial concentration of the dyes.

The energy of activation E_a, pre-exponential factor (D_0) analogous to the Arrhenius frequency factor [26] were also evaluated
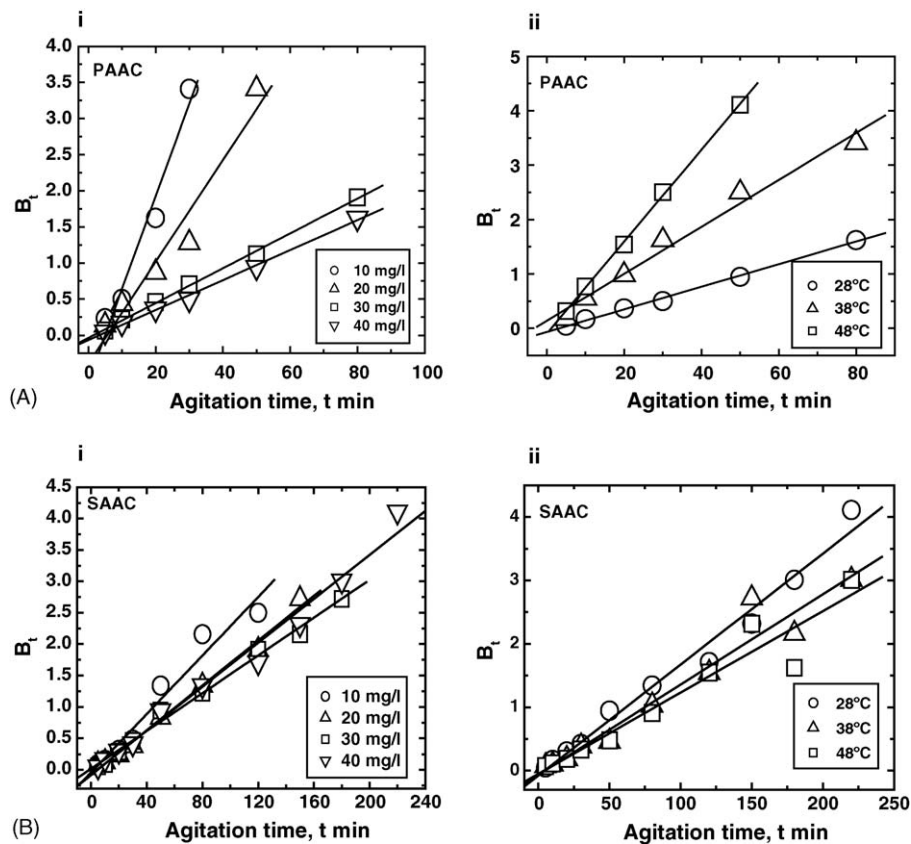

Fig. 6. Reichenberg's plot for the diffusion of dyes. (A): PAAC (i) conditions: CV concentration = (○) 10 mg/l; (△) 20 mg/l; (□) 30 mg/l; (▽) 40 mg/l; initial pH of CV solution 6.04; adsorbent dose = 100 mg/50 ml; adsorbent particle size = 0.150–0.250 mm; temperature = 28 °C, (ii) conditions: temperature = (○) 28 °C; (△) 38 °C; (□) 48 °C; CV concentration = 40 mg/l; initial pH of CV solution 6.04; adsorbent dose = 100 mg/50 ml; adsorbent particle size = 0.150–0.250 mm. SAAC (B): (i) and (ii) conditions: as in Fig. 6(i) and (ii), respectively. Adsorbent dose = 25 mg/50 ml.

Table 6
Diffusion parameters and energy of activation

Dyes	Diffusion coefficient, $D_i \times 10^{-10}$ (m²/s)				Diffusion coefficient, $D_i \times 10^{-10}$ (m²/s)			D_0 (m²/s)	E_a (KJ/mol)
	10 mg/l	20 mg/l	30 mg/l	40 mg/l	28 °C	38 °C	48 °C		
PAAC	8.657	4.766	1.6302	1.405	1.405	2.918	5.713	1.834	58.685
SAAC	1.568	1.209	1.014	1.183	1.183	0.962	0.868	6.991×10^{-13}	−5.603

using Eq. (14) as

$$D_i = D_0 \exp\left[\frac{-E_a}{RT}\right] \tag{14}$$

Further, using Eq. (14) for diffusion phenomena, a plot of $1/T$ versus $\log D_i$ was made for both carbons (Table 6). The plots were found to be linear with $R^2 > 0.9$ (figure not shown). The values of E_a and D_0 for the diffusion of Crystal violet in activated carbon are calculated from the slope and intercept of the plot, $\log D_i$ versus $1/T$ and presented in Table 6. In PAAC, the value of E_a was found to be positive and the value was above 30 KJ/mol. This confirms the film-controlled diffusion of CV in PAAC. Al-Ghoute et al. [27] also reported the similar positive E_a value for the film diffusion of dyes onto modified diatomite. The diffusion of CV in SAAC was a particle diffusion process; the E_a value was negative, hence lower energy was required for CV to diffuse into SAAC for the diffusion into the interior of SAAC was a slow process. Apart from that the D_i values do not show appreciable change with rise of temperature. This is reflected in the negative value of E_a of diffusion in the diffusion of CV in SAAC. Hence the D_0 values derived from the plot $\log D_i$ versus $1/T$ also shows a very low value as compared to that of PAAC. A negative value of E_a of diffusion shows the failure of film diffusion model. The significance of negative value of E_a of diffusion is giving strength to the particle diffusion of CV in SAAC, which was distinguished from film diffusion by Reichenberg's plot [28]. Similar results were obtained for the diffusion coefficient, D_i in the adsorption of reactive red onto CFC and JFC [16], and the removal of dyes by fly ash [4].

3.8. Designing batch adsorption from isotherm data

Adsorption isotherm can be used to predict the design of single-stage batch adsorption systems [17]. Consider an effluent containing V liter of solvent (water) and the dye concentration reduced from C_0 to C_1 g dye per liter solvent. The amount of adsorbent is M g and the solute loading changes from q_0 to q_1 mg dye per g adsorbent. When fresh adsorbent is used, $q_0 = 0$ and the mass balance equates the dye removed from the liquid to that picked up by the solid:

$$V(C_0 - C_1) = M(q_0 - q_1) = Mq_1 \tag{15}$$

If the system is allowed to come to equilibrium, then:

$$C_1 \rightarrow C_e \text{ and } q_1 \rightarrow q_e$$

In case of the adsorption of CV onto PAAC and SAAC Langmuir isotherm gives the best fit to experimental data. Consequently, the Langmuir equation can be best substituted for q_1

in the rearranged form of Eq. (16), giving adsorbent/solution for a given change in dye concentration, $C_0 - C_e$, at this particular system:

$$\frac{M}{V} = \frac{C_0 - C_e}{q_1} = \frac{C_0 - C_e}{q_e} \equiv \frac{C_0 - C_e}{\frac{K_L C_e}{1 + a_L C_e}} \tag{16}$$

where K_L and a_L are Langmuir constants from Eq. (9) an initial dye concentration of 100 mg/l is assumed and the required amount of PAAC and SAAC to reduce the colour content by 90% at various volumes of effluents can be calculated. For example, 10 l of the solution is to be treated. The required masses of PAAC and SAAC are 15.565 and 1.340 g for CV, respectively, for 90% dye removal.

4. Conclusion

The results of present study suggests that the recycling of an agricultural waste byproduct as adsorbent for the treatment of dyeing industry wastewater.

- 'Waste' male flowers of coconut tree were chemically activated to non-toxic carbonaceous material.
- The kinetics of the adsorption of a basic dye, Crystal violet onto both the carbons (PAAC and SAAC) to pseudo second-order chemical reaction kinetics.
- This pseudo second-order kinetics is further supported by Elovich kinetic model.
- The adsorption of Crystal violet increased with decrease in initial concentration of the dye molecules.
- Equilibrium data agreed well with Langmuir isotherm model suggests the monolayer coverage of the dye onto PAAC and SAAC with adsorption capacity as 60.42 and 85.84 mg/g, respectively.
- For both the carbons, the dye removal increases with increase of initial solution pH (2–9).
- The rate of adsorption of Crystal violet increased with increasing temperature. Adsorptions of Crystal violet onto both the carbons were spontaneous and endothermic in nature.
- The mass transfer diffusion of dye molecules follows, film diffusion in PAAC and pore diffusion in SAAC.

From designing of single-stage batch adsorption, the required mass of carbons, PAAC and SAAC to achieve a fixed percentage of Crystal violet removal from wastewater can readily be calculated.

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