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Adsorption of Anionic and Cationic Dyes on Chemically Modified Pomegranate Peel: A Isotherms and Kinetics Studies

T. SENTHILKUMAR[1,2] and LIMA ROSE MIRANDA[1,*]

[1]Carbon Research and Engineering Laboratory, Department of Chemical Engineering, Anna University, Chennai-600 025, India
[2]ICAR-Central Institute for Research on Cotton Technology, Indian Council of Agricultural Research, Matunga (East), Mumbai-400 019, India

*Corresponding author: Tel: +91 44 22359130; E-mail: limamiranda2007@gmail.com

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The dyes used are highly toxic in nature also affecting the aquatic life and causing carcinogenic effects on human beings. Adsorption using activated carbon has received considerable interest from researchers globally due to its high efficiency in the treatment of effluents. In this present study pomegranate peel (*Punica granatum* sp.) was taken as an adsorbent. The methylene blue number, iodine number and surface area of pomegranate peel activated carbon were found to be 175 mg/g and 1360 mg/g and 686 m^2/g, respectively. The anionic and cationic dye adsorption behaviour of pomegranate peel activated carbon (PPAC) was carried out using acid violet 12 (AV12) and basic brown 4 (BB4) onto pomegranate peel activated carbon. The isotherm studies were carried and it was found that the Langmuir isotherms fit well for the adsorption of both acid violet 12 and basic brown 4 on pomegranate peel activated carbon. Adsorption kinetics follows pseudo second order model and the adsorption process endothermic in nature.

Keywords: Pomegranate peel, Activated carbon, Acid violet, Basic brown, Adsorption kinetics.

INTRODUCTION

Textile industries generate highly coloured wastewaters that bear organic and inorganic pollutants, so the removal of dyes from these industrial effluent is important since it pollutes the environment[1]. The discharge of highly coloured wastewater into the ecosystem involves environmental problems like aesthetic pollution (even a small amount of dye is clearly apparent) and perturbation of aquatic life[2]. The wastewater generated from textile and tanning industries contain high amount of exhausted dyes and pigments. It has been estimated that, about 10,000 dyes and pigments were produced and about 7×10^5 tons were used in different industries such as textile, rubber, paper, cosmetic *etc*. Among these various industries, textile ranks first in the usage of dyes for colouration of fibres[3]. Acid dyes are mostly used for dyeing protein fibres such as silk, wool and mohir *etc*. whereas basic dyes are used to dyeing of as acrylic fibre[4]. The textile industry alone accounts for two thirds of the total dyestuff production, about 10-15 % of the dyes are let out into the effluent. Thus, the removal of dyes from coloured effluents, particularly from textile industries, is a major environmental concern[5]. The treatment of dye effluent involves the removal of the colour components from the aqueous solutions. Various physical and chemical methods, such as, dilution, adsorption, oxidation, electrocoagulation and flocculation, chemical precipitation, ion exchange, reverse osmosis and ultra-filtration and biological process have been used[6]. Adsorption process using commercial activated carbon is the most popular and widely used technique in wastewater reuse methodology. However, the cost of this material limits its use[7]. Nowadays a number of researchers are studying the feasibility of using low cost materials such as mango pit[8], rice husk[9], coconut shell[10], orange peel[11], oil palm fibre[12], bamboo[13], coffee husk[14] *etc*. and other sources like marine macro algal biomass[15], olive waste cakes[16], leather wastes[17], chicken waste[18] *etc*., as adsorbents. In the present study, pomegranate peel has been used as precursors for the preparation of activated carbon.

The plant *Punica granatum* is mainly cultivated in Iran which constitutes 47 % of the total world production and the worldwide production of pomegranate is approximated as 1.5 lakh tonnes. In India, the plant is cultivated in large quantities in Maharashtra in about more than 0.1 million hectares of area. The fruit peel is rich in ellagitannins such as punicalagin and its isomers[19]. The present work is pomegranate peel activated carbon adsorption behaviour for anionic and cationic dyes using acid violet 12 and basic brown 4 dye from synthetic aqueous dye solution. The isotherm, kinetics and thermodynamic studies, as well as the effects of initial dye concentration, time, pH and temperature on adsorption were studied.

EXPERIMENTAL

The precursor for the preparation of activated carbon, pomegranate peel, was collected from various parts of Tamilnadu, India. The adsorbates used in this study were acid violet 12 (AV12) (λ_{max} 551 nm) supplied Atul Limited, Mumbai, India. This dye is extensively used in dyeing of textile fabrics such as wool and silk. The chemical nature of the dye is a complex aromatic structure consisting of monoazo, disulphonic groups and basic brown 4 dye (BB4) (λ_{max} = 468 nm) was supplied by Ranbaxy, Mumbai, India. The structural formulae of the acid violet 12 and basic brown 4 dye are shown in Fig. 1. The reagents phosphoric acid, methylene blue dye, potassium iodate, potassium iodide were supplied by CDH (P) Ltd., India. Iodine was supplied by Rankem India Ltd., Hydrochloric acid by MERCK chemicals, India. Sodium thio sulphate, soluble starch and sodium hydroxide by SRL Chem. (P) Ltd., India. All the reagents used for analysis were of analytical grade and double distilled water was used for preparing the adsorbate solutions.

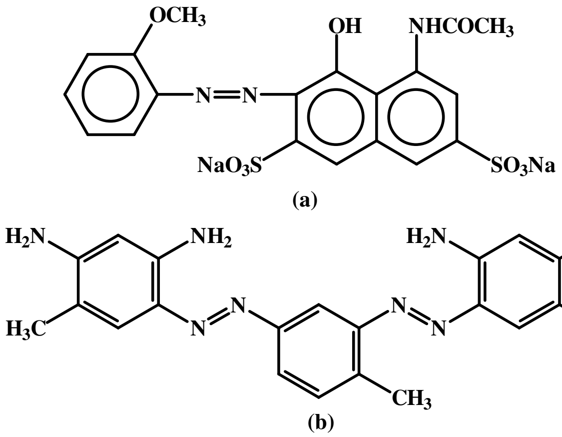

Fig. 1. Chemical Structure of adsorbate (a) acid violet 12 (b) basic brown 4

Preparation of adsorbent: The biomass (pomegranate peel) obtained was cut into approximately uniform pieces, dried and impregnated with phosphoric acid with a impregnation ratio of 1:3 for a period of 24 h. The impregnation ratio is defined as the ratio of weight of the activating agent to weight of the biomass. The acid was decanted and the biomass was carbonized in a Muffle furnace in absence of air at a temperature and activation time of 500 °C and 1 h respectively[20]. The activated carbon thus obtained was washed with distilled water to remove residual acids present in it and then dried in a hot air oven at 110 °C for a period of 4 h. The pomegranate peel activated carbon (PPAC) were crushed and sieved using 170 mesh (BSS) screen to obtain uniform particle size of adsorbents and stored for further use.

Characterization of adsorbent: The proximate and elemental analysis of the raw material (pomegranate peel) and pomegranate peel activated carbon (PPAC) and the characteristics such as iodine number, methylene blue number and surface area of activated carbon are given in earlier paper[20]. The surface morphology and functional group analysis of the pomegranate peel activated carbon before and after adsorption of acid violet 12 and basic brown 4 were studied. The SEM analysis was carried out in scanning electron microscope HITACHI S-3400N having a magnification range of 5-300,000. The surface functional groups of the adsorbents were identified using IR spectrophotometer spectrum RX-1 (Perkin-Elmer).

Batch adsorption studies: Batch adsorption studies were conducted in orbital shaker (Orbitek, Scigenics) using 50 mL of acid violet 12 aqueous solution with 0.1 g pomegranate peel activated carbon and 50 mL of basic brown 4 aqueous solution with 0.05 g of pomegranate peel activated carbon. The difference in the adsorbent dosage was to maintain the constant adsorbate concentration of such as 100 to 500 mg/L in this study. The agitation speed of the shaker was fixed at 180 rpm. The contact time of adsorption varied between time intervals of 0 to 300 min. Further, the samples were centrifuged and the supernatant solutions optical density was analyzed in an UV-visible spectrophotometer (Hitachi). The equilibrium adsorption capacity was calculated using the following formula[21]:

$$q_e = \frac{(C_0 - C_e)V}{M} \qquad (1)$$

where q_e is the equilibrium adsorption capacity (mg/g); C_0 and C_e are the initial and equilibrium concentration of the basic brown and acid violet dye solution (mg/L); V is the adsorbate volume (L); and M is the weight of the pomegranate peel activated carbon (g) taken.

RESULTS AND DISCUSSION

Surface characteristics of pomegranate peel activated carbon: In order to determine the morphological structure of pomegranate peel activated carbon before and after adsorption of acid violet 12 and basic brown 4 the scanning electron microscopic was employed in this study. The SEM micrographs of pomegranate peel activated carbon, acid violet 12 loaded with pomegranate peel activated carbon and basic brown 4 loaded with pomegranate peel activated carbon are shown in the Fig. 2(a-c) respectively. From Fig. 2(a) it is evident that there are many longitudinal voids on the surface of pomegranate peel activated carbon. These pores have clearly uniform dimensions. This is due to the removal of low volatile content, organic by-product and mineral content present in the pomegranate peel. After adsorption, some of the pores of the pomegranate peel activated carbon was irregular due to adsorption of dye molecule on their surface. The adsorbate molecule was packed into the pores of pomegranate peel activated carbon, which is clearly observed from Fig. 2(b) and (c).

Fourier transform infrared spectroscopy (FTIR): The main aim of this analysis was to determine the surface functional groups present in the adsorbent and adsorbate and to find which groups were responsible for the adsorption process. The FTIR spectra for pomegranate peel activated carbon before and after adsorption of both the adsorbates acid violet 12 and basic brown 4 are shown, Fig. 3(a-d) are the FTIR spectrum of pomegranate peel activated carbon, acid violet 12 and basic brown 4, similarly acid violet 12 loaded on pomegranate peel activated carbon and basic brown 4 loaded on pomegranate

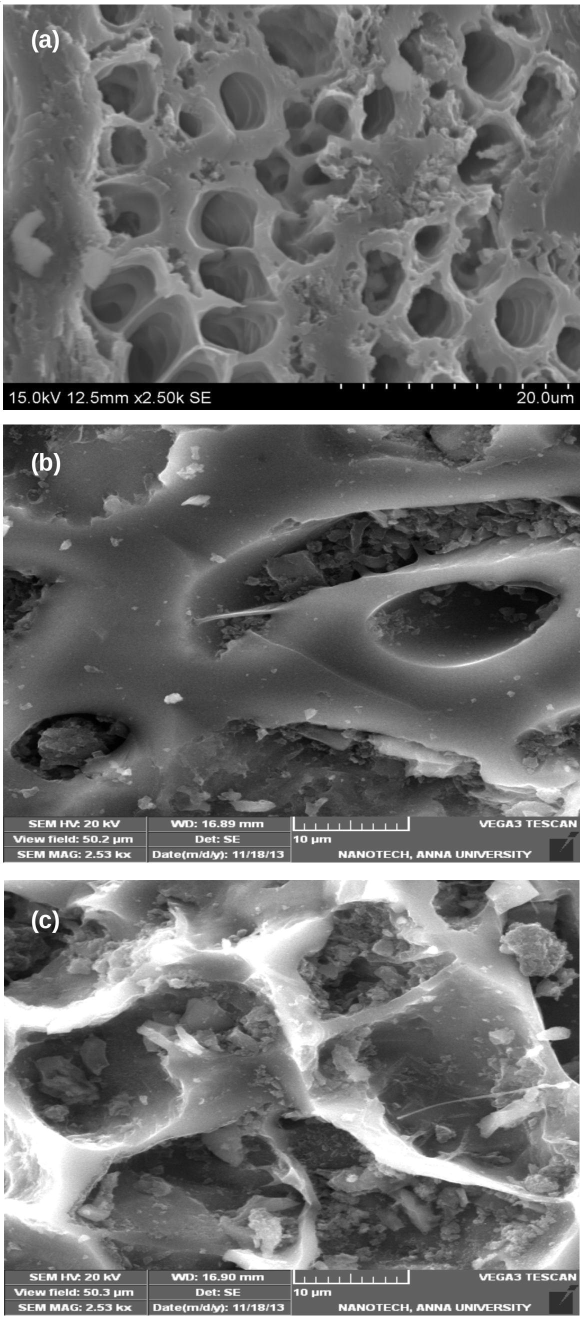

Fig. 2. Scanning electron micrographs of pomegranate peel activated carbon (a) pomegranate peel activated carbon (b) pomegranate peel activated carbon loaded with acid violet 12, (c) pomegranate peel activated carbon loaded with basic brown 4

peel activated carbon are shown in Fig. 3(c) and (e). In Fig. 3(a), the FTIR spectrum of pomegranate peel activated carbon shows the broad band of peaks stretching from 3767 to 3101 cm^{-1} with a maximum at 3447 cm^{-1} corresponds to the stretching of hydroxyl groups. The small bands in the range of 2352 to 1943 cm^{-1} corresponds to the stretching of alkynes group. The stretching of peaks 1584 to 1174 cm^{-1} corresponds to the presence of C-O (carboxyl) and C=O (carbonyl)[22] groups which shows the presence of carbonyl carboxylates on the surface of pomegranate peel activated carbon. From the Fig. 3(b) and (d) the long stretch was observed at the peak 3433 cm^{-1} this corresponds to the primary amino groups present in acid violet 12. Then the small bands in the range of 3067 to 2855 cm^{-1} corresponds to the stretching of strong N-H and C-H groups which confirm the acid violet 12 structure in Fig. 1(a). The small peaks 1600 to 1553 cm^{-1} was observed in Fig. 3(b) and (d) corresponding to –N=N– groups in of both the adsorbate of acid violet 12 and basic brown 4, which confirms the dye structure of both the dye. This azo group was the chromophores of both the dyes. Since acid violet 12 was made up of sodium salt of sulphonic acids which confirm in the FTIR spectrum of Fig. 3(b) there are number of smaller peaks was observed at the range of 1228 to 818 cm^{-1} corresponds to the sulfate ions. Basic brown 4 has the NH_4^+ ion which results the peak was observed at 3170 cm^{-1} in Fig. 3(d). Fig. 3(c) and (e) shows the spectrum after the dye has been adsorbed on the surface of pomegranate peel activated carbon, the intensity of absorption bands have been changed there is interaction of dye both with the hydroxyl as well as with carboxylates present on the surface of the adsorbent.

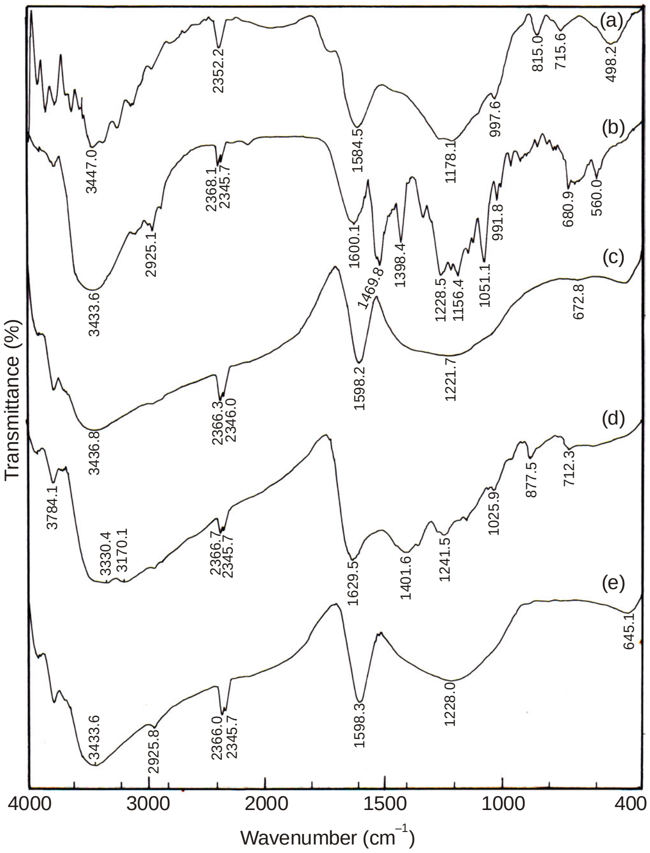

Fig. 3. FTIR spectra for adsorbate and adsorbent before and after adsorption (a) pomegranate peel activated carbon, (b) basic brown 4, (c) basic brown 4 loaded with pomegranate peel activated carbon, (d) acid violet 12, (e) acid violet 12 loaded with pomegranate peel activated carbon

Effect of initial concentration and contact time: The effect of initial dye concentration and contact time on the removal of acid violet 12 and basic brown 4 are shown in Fig. 4(a) and 4(b). The adsorption of pomegranate peel activated carbon for both the dyes acid violet 12 and basic brown 4 increases as the initial dye concentration increases. Increase in initial concentration increased the driving force for mass transfer resulting in higher adsorption of the dyes[23]. In both the cases, low concentration of 100 mg/L of acid violet 12 and basic brown 4 aqueous solution attained equilibrium is less than 25 min, whereas, at higher concentrations of 200 to 500 mg/L equilibrium time was observed at 120 min for basic brown 4 and 180 min for acid violet 12 respectively. However, the experiments were carried out upto 240 min to make sure that complete equilibrium was attained. During the adsorption of dyes, the dye molecules initially reach the outer surface boundary layer, pass through finally diffuse into the porous structure of the adsorbent, both the boundary layer pore to offer resistance to the movement of the adsorbate, hence, this phenomenon requires a relatively longer contact time[24]. The amount of acid violet 12 adsorbed increased from 48 to 140 mg/g when the initial concentration was increased from 100 to 500 mg/L. whereas the adsorption of basic brown 4 onto pomegranate peel activated carbon increased from 90 to 350 mg/L when the initial dye concentration was increased from 100 to 500 mg/L.

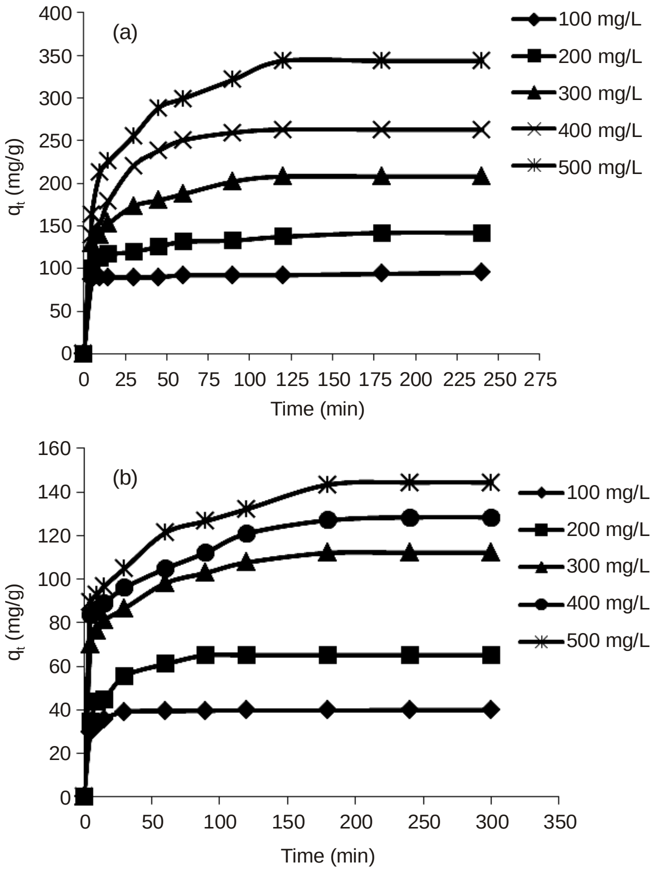

Fig. 4. Effect of initial dye concentration and contact time on adsorption (a) basic brown 4 on pomegranate peel activated carbon, (b) acid violet 12 on pomegranate peel activated carbon

Effect of pH on adsorption: The pH of the dye solution affects not only the surface charge of the adsorbent, the degree of ionization of the materials and the dissociation of functional groups on the active sites of the adsorbent, but also the structure of the dye molecule[25]. The effects of pH on the adsorption of acid violet 12 and basic brown 4 on to pomegranate peel activated carbon were studied by changing the pH of the adsorbate solution from 2 to 8 for the adsorbate concentration of 200 mg/L using HCl and NaOH. The operating condition of this study was 0.05 g of pomegranate peel activated carbon in 50 mL of basic brown 4 solution for 120 min and 0.1 g of pomegranate peel activated carbon in 50 mL of acid violet 12 solution for 180 min respectively. Fig. 5 showed that acid violet 12 an anionic dye showed a decrease in the adsorption capacity with increase in pH. However, basic brown 4 showed an increase in the adsorption capacity with increase in pH. In both cases increase in pH more than 8 showed that the dye molecules precipitated. Hence results obtained for pH more than 8 have not been reported. At acidic pH the H^+ ions concentration in the solution increases imparting a positive change on the surface of the activated carbon. As the carbon surface is positively charged, a significantly strong electrostatic attraction appears between the positively charged carbon surface and negatively charged anionic dye (acid violet 12) molecule leading to maximum adsorption of dye at lower pH. However, lowering the pH creates a competition between the H^+ ions generated an the positively charged cationic dye (basic brown 4) molecule adsorb on the surface of the activated carbon lowering the adsorption capacity. As the pH is increased the mechanism is reversed leading to higher adsorption of basic brown 4 since the surface of the activated carbon acquires negatively charged. While acid violet 12 an anionic dye experiences electrostatic repulsion. The similar observation was reported[26,27] for the adsorption of direct dyes on mahogany saw dust activated carbon and of malachite green dye on baggase fly ash and activated carbon.

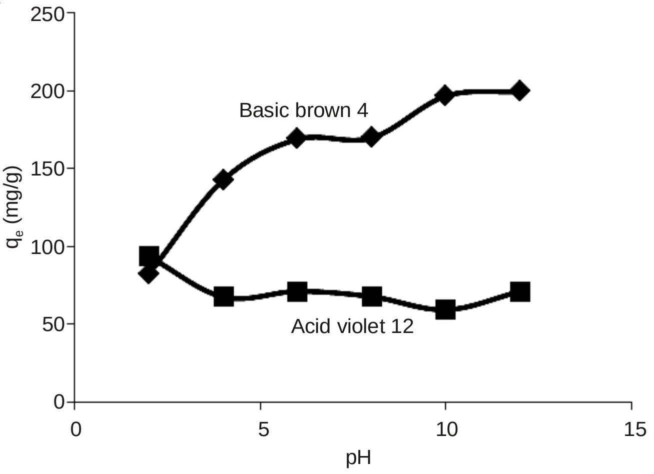

Fig. 5. Effect of pH on adsorption of basic brown 4 and acid violet 12 on pomegranate peel activated carbon

Effect of temperature on adsorption: The effect of temperature on adsorption of acid violet 12 and basic brown 4 on pomegranate peel activated carbon were studied for an adsorbate concentration of 200 mg/L for acid violet 12 and basic brown 4 and their respective equilibrium time. The temperature varied from 20 to 60 °C. The adsorbent dose and adsorbate volume taken were 0.1 g pomegranate peel activated carbon and 50 mL of acid violet 12 and 0.05 g pomegranate peel activated carbon and 50 mL of basic brown 4. It was observed from Fig. 6(a) that increase in temperature, increase the adsorption capacity of both acid violet 12 and basic brown 4 on pomegranate peel activated carbon which shows endothermic nature of adsorption process[28]. This indicates that there is an increase in the rate of the intra particle

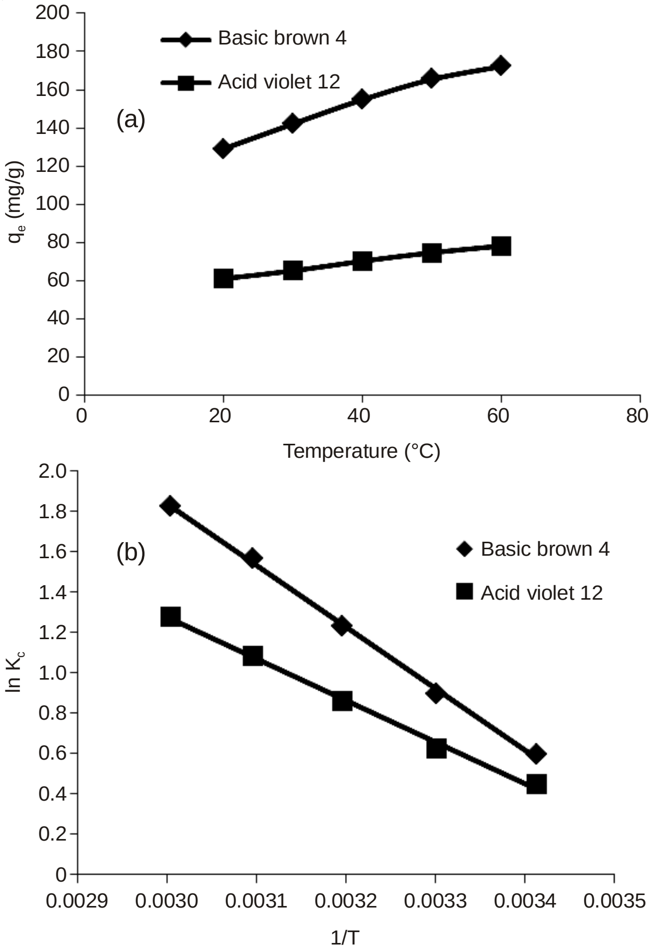

Fig. 6. Effect of temperature on adsorption, (a) basic brown 4 and acid violet 12 on pomegranate peel activated carbon (b) van't Hoff plot for the adsorption of basic brown 4 and acid violet 12 on pomegranate peel activated carbon

diffusion of dye molecules into the pores of the adsorbent at higher temperature.

Thermodynamic studies: Thermodynamic parameters such as standard Gibbs free energy (ΔG^o), enthalpy (ΔH^o) and entropy change (ΔS^o) of adsorption were evaluated using equations (2-4):

$$\Delta G^\circ = -RT \ln K_c \tag{2}$$

where K_c is the equilibrium constant, given by

$$K_c = \frac{C_{Be}}{C_{Ae}} \tag{3}$$

where C_{Ae} and C_{Be} are the equilibrium concentration of the dye in the solution and on the adsorbent, respectively. Standard enthalpy (ΔH°) and entropy (ΔS°) were determined from the vant Hoff equation:

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{4}$$

where, ΔG^o, ΔH^o and ΔS° are changes in Gibbs free energy (kJ/mol), enthalpy (kJ/mol) and entropy (J/mol/K), respectively. R is the gas constant (8.314 J/mol/K), T is the temperature (K). ΔG^o values were calculated using the eqn. 2. ΔH° and ΔS° were obtained from the slope and intercept of the plot of ln K_c *vs.* 1/T as shown in Fig. 6(b). The values of enthalpy change (ΔH°) and entropy change (ΔS°) recorded from this work are presented in the Table-1. The negative ΔG^o indicates the process be feasible and spontaneous in nature for adsorption. The positive values of ΔS° show the affinity of the adsorbent for the acid violet 12 and basic brown 4 dye and the increasing randomness at the solid-liquid interface[29].

Adsorption isotherms: In order to optimize the design of an adsorption system to remove the dye, it is important to establish the most appropriate correlations for the equilibrium data for each system[30] Four isotherm models have been tested in the present study; Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms were studied for the adsorption of both acid violet 12 and basic brown 4 on pomegranate peel activated carbon. The isotherm parameters were determined using the MATLAB software, Fig. 3(a) and (b), which shows the plot of C_e *versus* q_e for the different isotherms for acid violet 12 and basic brown 4 on pomegranate peel activated carbon respectively.

Langmuir isotherm: Langmuir theory was based on the assumption that adsorption was a type of chemical combination or process and the adsorbed layer was unimolecular (Navine, 2008). The Langmuir isotherm is given by the following equation[31]:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{5}$$

where, q_m is the maximum monolayer adsorption capacity (mg/g), K_L is the equilibrium constant related to free energy (L/mg), C_e is the concentration of the supernatant dye solution at equilibrium (mg/L) and q_e is the amount of dye adsorbed at equilibrium (mg/g).

Freundlich isotherm: Freundlich adsorption model stipulates that the ratio of solute adsorbed to the solute concentration is a function of the solution. The empirical model was shown to be consistent with an exponential of active centres, characteristic of heterogeneous surfaces. The amount of solute adsorbed is related to the equilibrium concentration of solute in solution[27]. The Freundlich isotherm is given by the following equation[32]:

$$q_e = K_F (C_e)^{1/n} \tag{6}$$

where, K_F is the adsorption capacity related to multilayer (mg/g), 1/n is the adsorption intensity (L/g) and n is the measure of deviation from linearity of adsorption.

TABLE-1
THERMODYNAMIC PARAMETERS FOR THE ADSORPTION OF ACID VIOLET 12 AND BASIC BROWN 4 ON POMEGRANATE PEEL ACTIVATED CARBON

Adsorbate	ΔH° (kJ/mol)	ΔS° (kJ/mol/K)	ΔG° (kJ/mol)				
			293 K	303 K	313 K	323 K	333 K
Acid violet 12	17.09	0.06	-1.10	-1.58	-2.24	-2.91	-3.54
Basic brown 4	25.38	0.09	-1.46	-2.26	-3.20	-4.21	-5.06

Temkin isotherm: Temkin isotherm model contains a factor that explicitly takes into account adsorbing species-adsorbate interactions. This model assumes the following: (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions and that (ii) the adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy[33]. Temkin isotherm is given by the following equation[32]:

$$q_e = \frac{RT}{B}\ln(AC_e) \tag{7}$$

where, A is the equilibrium binding constant (L/g), B is the constant related to heat of adsorption, R is the general gas constant (kJ/mol K) and T is the absolute temperature (K).

Dubinin-Radushkevich isotherm: This model is often employed for estimating the characteristic porosity and the apparent free energy of adsorption of pollutant on the adsorbent[34]. Dubinin-Radushkevich isotherm is given by the following equation[32]:

$$q_e = q_m e^{(-K\varepsilon^2)} \tag{8}$$

where K is the constant related to mean free energy of adsorption, q_m is the theoretical saturation capacity (mg/g) and ε is the Polanyi potential, where ε is given by:

$$\varepsilon = RT\ln\left(1+\frac{1}{C_e}\right) \tag{9}$$

where R is the gas constant (kJ/mol K) and T is the absolute temperature (K). The value of sorption energy E_S (kJ/mol) can be calculated from the equation,

$$E_S = \frac{1}{\sqrt{2K}} \tag{10}$$

The calculated constants for the above said isotherms together with the regression values are given in Table-2. Langmuir, Freundlich and Temkin isotherms fit the data for adsorption of acid violet 12 on pomegranate peel activated carbon reasonably as shown in the Fig. 7(a). In the case of adsorption of basic brown 4 on pomegranate peel activated carbon, the Langmuir and Freundlich isotherms fit the equilibrium adsorption data well as shown in the Fig. 7(b). From Dubinin-Radushkevich isotherm the sorption energy value of acid violet 12 and basic brown 4 on pomegranate peel activated carbon was found to be 170.60 kJ/mol and 1202.47 kJ/mol respectively which conclude that the adsorption takes place by chemical means. The maximum monolayer adsorption capacity of acid violet 12 and basic brown 4 on pomegranate peel activated carbon given by Langmuir isotherm was found to be 185.3 mg/g and 444.6 mg/g respectively. However, the adsorption capacity of various acid and basic dyes on activated carbon from various sources available in the literature is given in the Table-5.

Adsorption kinetics: Adsorption kinetic studies are significant since they not only provide valuable insights into the reaction pathways, but also describe the solute uptake rate which in turn controls the residence time of sorbate at the solid-liquid interface[32]. In order to investigate the mechanism of adsorption and to determine the rate-controlling step, the

TABLE-2
ISOTHERM CONSTANTS FOR ADSORPTION OF ACID VIOLET 12 AND BASIC BROWN 4 ON POMEGRANATE PEEL ACTIVATED CARBON

Isotherm model	Parameters	Acid violet 12	Basic brown 4
Langmuir	q_m (mg/g)	185.3	444.6
	K_L (L/mg)	0.0156	0.0096
	R^2	0.9908	0.9847
Freundlich	K_F ((mg/g)(L/mg)$^{(1/n)}$)	12.09	42.78
	n (g/L)	2.131	2.837
	R^2	0.978	0.9233
Temkin	A (L/mg)	0.1375	1.198
	B	18.52	21.21
	R^2	0.9949	0.7854
Dubinin-Radushkevich	q_m (mg/g)	131.6	238.5
	K ((mol K/kJ)^2)	1.718×10^{-5}	3.458×10^{-7}
	Es (kJ/mol)	170.5978	1202.4651
	R^2	0.9413	0.4348

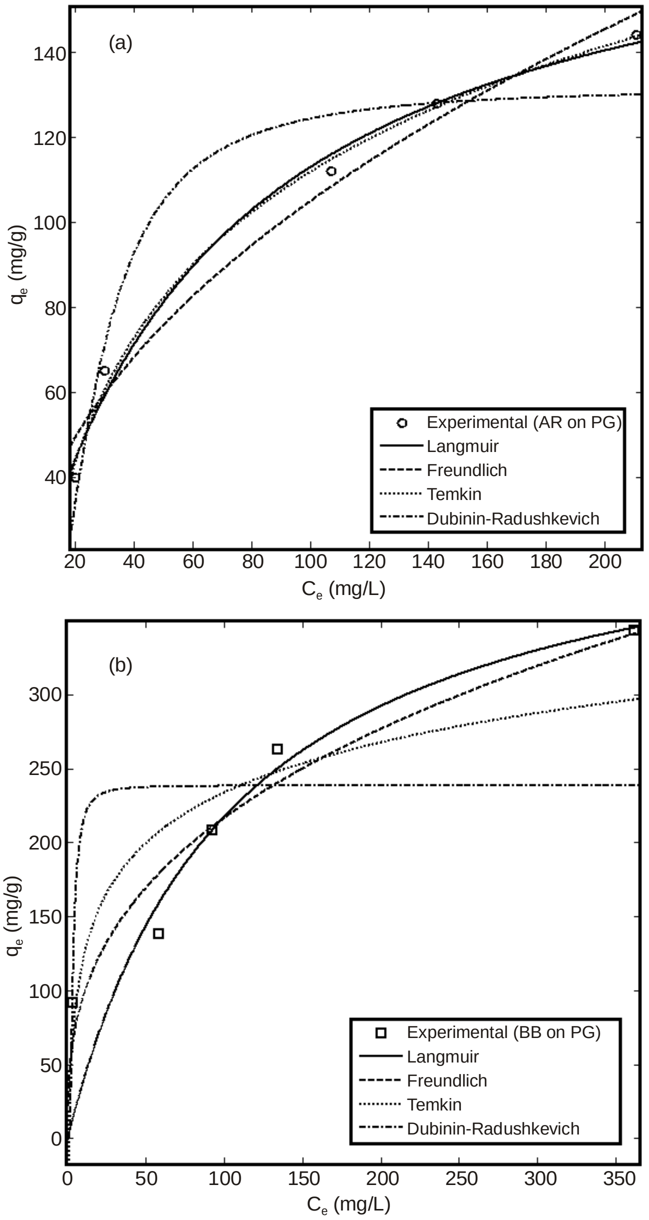

Fig. 7. Non-linear plot of adsorption isotherms for pomegranate peel activated carbon, (a) acid violet 12 on pomegranate peel activated carbon and (b) basic brown 4 on pomegranate peel activated carbon

TABLE-3
KINETIC CONSTANTS FOR THE ADSORPTION OF ACID VIOLET 12 ON POMEGRANATE PEEL ACTIVATED CARBON

Kinetic model	Parameters	Concentration of acid violet 12 (mg/L)				
		100	200	300	400	500
Pseudo first order	q_e, exp mg/g)	40	65	112	128	144
	q_e, calc (mg/g)	4.7	19	46	57	85
	K_1 (1/min)	0.0281	0.0213	0.0205	0.0192	0.0212
	R^2	0.8363	0.8117	0.99203	0.9778	0.9220
Pseudo second order	q_e, exp mg/g)	40	65	112	128	144
	q_e, calc (mg/g)	40	67	114	128	144
	K_2 (1/min)	0.0154	0.0026	0.0013	0.0012	0.00081
	R^2	0.9999	0.9995	0.9980	0.9982	0.9947
Elovich model	α (mg/g/min)	43.07×10^3	6.9×10^3	1.03×10^3	1.50×10^3	6.45×10^2
	β (g/mg)	0.3568	0.1454	0.1020	0.0789	0.0647
	R^2	0.8459	0.9683	0.9901	0.9614	0.9572
Intra-particle diffusion model	K_{id} (mg/(g $min^{0.5}$))	0.791	2.012	3.095	4.0094	5.0085
	Integral constant, C	31.464	58.403	58.887	77.574	77.679
	R^2	0.6634	0.9694	0.9577	0.9479	0.9887

TABLE-4
KINETIC CONSTANTS FOR THE ADSORPTION OF BASIC BROWN 4 ON POMEGRANATE PEEL ACTIVATED CARBON

Kinetic model	Parameters	Concentration of acid violet 12 (mg/L)				
		100	200	300	400	500
Pseudo First Order	q_e, exp mg/g)	92	137	208	264	344
	q_e, calc (mg/g)	9	37	108	165	225
	K_1 (1/min)	0.0065	0.0173	0.0353	0.0421	0.0411
	R^2	0.7760	0.9649	0.9610	0.7428	0.9687
Pseudo Second Order	q_e, exp mg/g)	92	137	208	264	344
	q_e, calc (mg/g)	92	138	217	277	357
	K_2 (1/min)	0.01690	0.00218	0.00073	0.00048	0.00031
	R^2	0.9999	0.9990	0.9976	0.9988	0.9956
Elovich Model	α (mg/g/min)	1.8×10^{22}	2.8×10^4	7.3×10^2	1.9×10^2	2.3×10^2
	β (g/mg)	0.5835	0.0906	0.0413	0.0293	0.0229
	R^2	0.8522	0.9760	0.9909	0.9778	0.9924
Intra-particle diffusion model	K_{id} (mg/(g $min^{0.5}$))	0.5799	3.7864	9.0560	14.931	19.166
	Integral constant, C	86.734	98.673	115.51	119.31	144.9
	R^2	0.7954	0.9208	0.9664	0.9130	0.9557

following kinetic models are generally used to test the experimental data.

Pseudo first order kinetics model: This model is represented by the following equation[35]

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \tag{11}$$

which on integration with the boundary conditions 1) at t = 0, q_t = 0 and 2) at t = t, q_t = q_t gives the following equation:

$$\ln(q_e - q_t) = \ln(q_e) - K_1 t \tag{12}$$

where q_e is the amount of dye adsorbed at equilibrium (mg/g), q_t is the amount of dye adsorbed at any time t (mg/g) and K_1 is the adsorption rate constant for pseudo first order kinetics (min^{-1}). The value of $q_{e,calculated}$ and K_1 can be found out from a plot of $\ln(q_e\text{-}q_t)$ *vs.* t as shown in the Fig. 8(a) and (b). The rate constants, $q_{e,calculated}$ and regression values for pseudo first order kinetics for different concentration of the aqueous dye solution are given in Tables 3 and 4. It was found from the regression values, $q_{e,calculated}$ and the rate constant values that the adsorption of acid violet 12 and basic brown 4 on pomegranate peel activated carbon did not follow the pseudo first order kinetic model.

Pseudo second order kinetics model: This model is represented by the following equation[35]:

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \tag{13}$$

which on integration with the boundary conditions 1) at t = 0, q_t = 0 and 2) at t = t, q_t = q_t gives the following equation:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{14}$$

where K_2 is the adsorption rate constant for pseudo second order kinetics (g mg^{-1} min^{-1}). The value of $q_{e,calculated}$ and K_2 can be determined from a plot of t/q_t against t as shown in the Fig. 9(a) and (b) for basic brown 4 and acid violet 12, respectively on pomegranate peel activated carbon. The rate constants, $q_{e,calculated}$ and regression values for pseudo second order kinetics for different concentration of the aqueous dye solution are given in Tables 3 and 4. It is evident from Tables 3 and 4, that the experimental data can be explained by the pseudo second order kinetics model, also $q_{e,calculated}$ values are approximately equal to $q_{e,experimental}$ values. The rate constants for pseudo second order kinetics decreases with increase in adsorbate concentration. Also, it was found from the rate constant values

TABLE-5
COMPARISON OF MAXIMUM ADSORPTION CAPACITY OF SOME ACID AND BASIC DYES ON VARIOUS ADSORBENTS

Adsorbate	Adsorbent	q_{max} (mg/g)	Reference
		Acid dye	
Acid violet 12	Pomegranate peel	185.3	Present work
Acid yellow 36	Saw dust	183.8	[9]
Acid green 25	Activated palm ash	123.4	[29]
Acid violet 17	Sunflower seed hull	116	[36]
Acid yellow 36	Rice husk	86.9	[9]
Acid green 25	Durian peel	63.3	[37]
Acid red 114	Egyptian bagasse pith	20	[38]
Acid blue	Egyptian bagasse pith	17.5	[38]
Acid violet	Orange peel	19.88	[39]
Acid blue 25	Egyptian bagasse pith	14.40	[40]
Acid violet	Coir pith	7.34	[41]
		Basic dye	
Basic brown 4	Pomegranate peel	444.00	Present work
Basic green 4	Pine saw dust-based activated carbon	370.37	[43]
Basic green 4	Coconut shell	322.6	[44]
Basic green 4	Durian peel	312.5	[44]
Methylene blue	Palm fibre	277.78	[12]
Basic green 4	Bamboo-based activated carbon	263.60	[45]
Basic blue 3	Hevea brasiliensis seed coat	227.27	[46]
Basic green 4	Lignite-based activated carbon	200.00	[47]
Basic red 46	Sewage sludge-based activated carbon	188.00	[48]
Basic green 4	Bagasse fly ash	170.33	[27]
Basic green 4	Waste apricot-based activated carbon	116.30	[49]
Basic green 4	Rice bran-based activated carbon	69.0	[50]
Basic yellow	Coffee grounds	10.00	[42, 50]

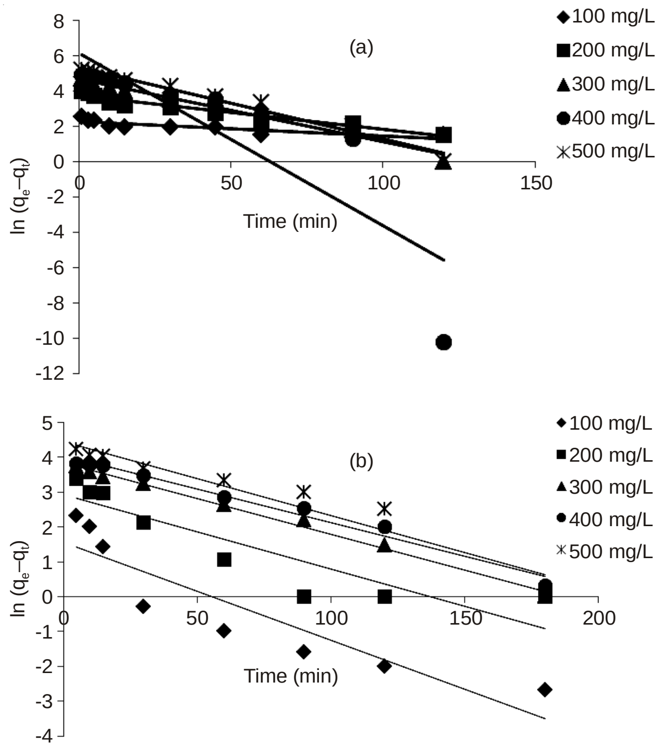

Fig. 8. Pseudo first order kinetics (a) basic brown 4 on pomegranate peel activated carbon (b) acid violet 12 on pomegranate peel activated carbon

that the adsorption of lower concentration 100 mg/L for both acid violet 12 and basic brown 4 on pomegranate peel activated carbon takes place much faster than that of higher concentration of acid violet 12 and basic brown 4.

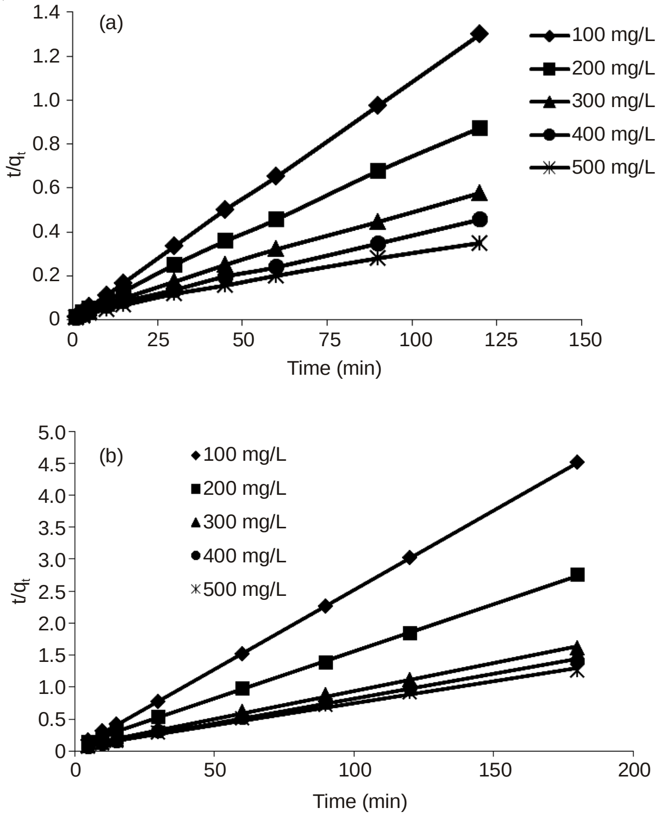

Fig. 9. Pseudo Second order kinetics (a) basic brown 4 on pomegranate peel activated carbon (b) acid violet 12 on pomegranate peel activated carbon

Elovich kinetics model: This model expressed by the following simple equation[35].

$$\frac{dq_t}{dt} = \alpha e^{(-\beta q_t)} \tag{15}$$

which on integration with the boundary conditions 1) at t = 0, $q_t = 0$ and 2) at t = t, $q_t = q_t$ gives the following equation:

$$q_t = \left(\frac{1}{\beta}\right)\ln(\sigma\beta) + \left(\frac{1}{\beta}\right)\ln t \tag{16}$$

where σ is the initial adsorption rate in mg g^{-1} min^{-1}, β is the desorption constant in g mg^{-1}. The Elovich model kinetics can be explained by plotting logarithmic time (ln t) against the amount adsorbed (q_t) as shown in the Fig. 10(a) and (b). The intercept and slope of the plot gives the initial adsorption rate σ and desorption constant β respectively. The regression values and Elovich model constants are tabulated in Tables 3 and 4. It is evident from the regression values that the process of adsorption of higher concentration (200 to 500 mg/L) of acid violet 12 and basic brown 4 on pomegranate peel activated carbon fits the Elovich model well compared to lower concentration (100 mg/L) of both acid violet 12 and basic brown 4. The initial adsorption rate constants were found to be much higher for the adsorption of basic brown 4 on pomegranate peel activated carbon than that on acid violet 12 on pomegranate peel activated carbon. The desorption constant decreases with increase in concentration of the adsorbate indicating that the desorption was significant at lower adsorbate concentrations. It was also found that the initial adsorption rate constant was high for lower adsorbate concentration in the adsorption of both basic brown 4 and acid violet 12 on pomegranate peel activated carbon.

Intra particle diffusion kinetic model: This model can be expressed as follows[35]:

$$q_t = K_{id} t^{0.5} + C \tag{17}$$

where K_{id} is the intra particle diffusion rate constant [mg (g $min^{0.5})^{-1}$] and C is the thickness of the boundary layer. The intra particle diffusion kinetics can be studied by plotting the amount adsorbed (q_t) against square root of time of adsorption ($t^{0.5}$) as shown in the Fig. 11(a) and (b). The intra particle diffusion rate constants were calculated and given in Tables 4 and 5. The mechanism of adsorption involves three stages which is clearly visible from the plot of the intra particle diffusion model. The first stage is external mass transfer followed by the intra particle diffusion which is the rate limiting step which determines the process mechanism.The final stage shows the attainment of equlibrium. There are various stages was found the intra particle diffusion for all concentrations for adsorption of both acid violet 12 and basic brown 4 on pomegranate peel activated carbon. The higher concentration of adsorbate the intra particle diffusion step shows significant effect compared to lower concentration of adsorbate for both the case of acid violet 12 and basic brown 4. The slope of the portion of intra particle diffusion stage gives the rate constant K_{id}. It is evident from Tables 3 and 4 that the intra particle diffusion model fits well for the adsorption of acid violet 12 and basic brown 4 on pomegranate peel activated carbon. It was clearly shown by respective regression values. Also the intra particle diffusion rate constant increases with increase in the concentration of the adsorbate and the thickness of the

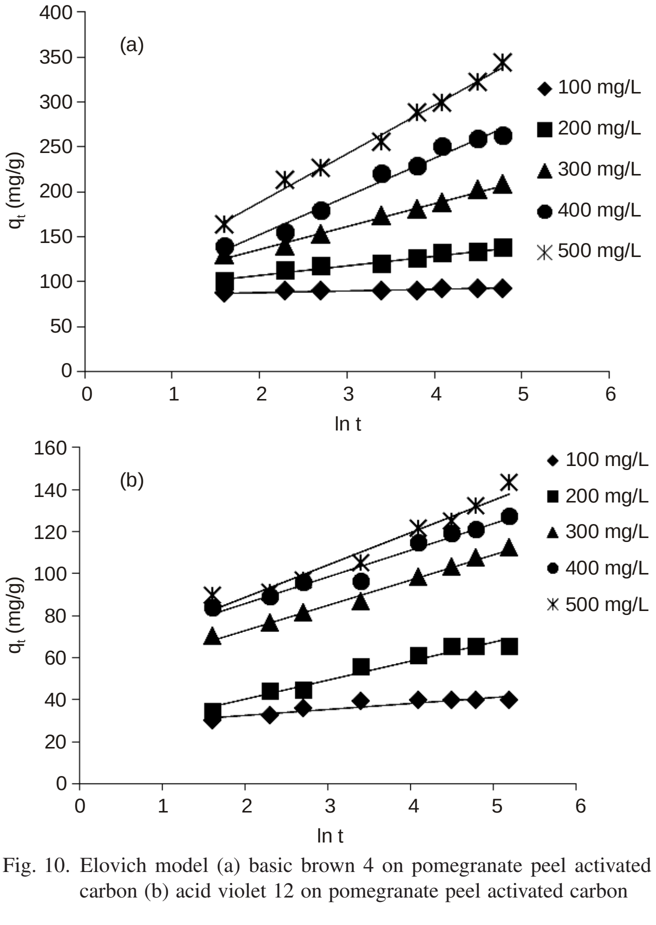

Fig. 10. Elovich model (a) basic brown 4 on pomegranate peel activated carbon (b) acid violet 12 on pomegranate peel activated carbon

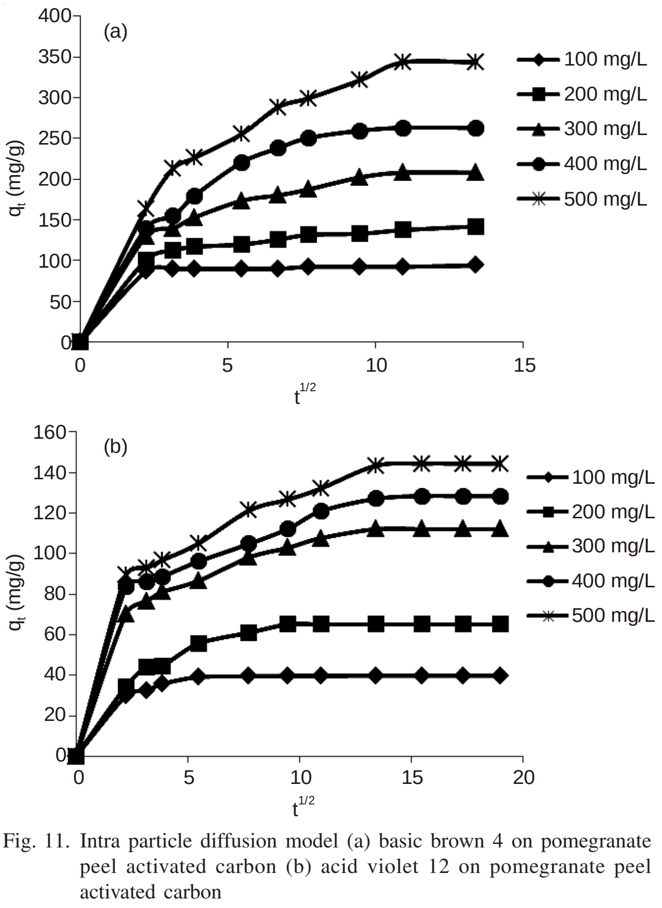

Fig. 11. Intra particle diffusion model (a) basic brown 4 on pomegranate peel activated carbon (b) acid violet 12 on pomegranate peel activated carbon

boundary layer was found to be more in case of adsorption of basic brown 4 on pomegranate peel activated carbon than that of acid violet 12 on pomegranate peel activated carbon.

Conclusion

The present investigation determines that the activated carbon prepared from pomegranate peel was effectively employed for the removal of acid violet 12 and basic brown 4 dyes. The adsorption studies suggest that a time of 180 min and 120 min required to attained equlibrium for acid violet 12 on pomegranate peel activated carbon and basic brown 4 on pomegranate peel activated carbon respectively. At higher pH values showed higher adsorption capacity for basic brown 4 and lower pH values showed higher adsorption capacity for acid violet 12 on pomegranate peel activated carbon. Temperature has adverse effect on the percentage of dye removal due to the increased surface activity suggesting that adsorption between acid violet 12 and basic brown 4 on pomegranate peel activated carbon was an endothermic process. The equilibrium data have been analyzed using Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms. The equilibrium sorption data of basic brown 4 on pomegranate peel activated carbon are satisfactorily fitted in the order: Langmuir > Dubinin-Radushkevich > Freundlich > Temkin. In case of acid violet 12 on pomegranate peel activated carbon was Langmuir > Dubinin-Radushkevich > Temkin > Freundlich. The kinetic study of acid violet 12 and basic brown 4 on pomegranate peel activated carbon was investigated based on pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion equations. The adsorption data could be well represented by the pseudo second order model. These results indicated that the agricultural soild waste of pomegrante peel activated carbon could be employed as a low cost alternative to commerical activated carbon in the removal of acid violet 12 and basic brown 4 dyes from wastewater.

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