Removal of direct blue-106 dye from aqueous solution using new activated carbons developed from pomegranate peel: Adsorption equilibrium and kinetics

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ABSTRACT

The use of cheap, high efficiency and ecofriendly adsorbent has been studied as an alternative source of activated carbon for the removal of dyes from wastewater. This study investigates the use of activated carbons prepared from pomegranate peel for the removal of direct blue dye from aqueous solution. A series of experiments were conducted in a batch system to assess the effect of the system variables, i.e. initial pH, temperature, initial dye concentration adsorbent dosage and contact time. The results showed that the adsorption of direct blue dye was maximal at pH 2, as the amount of adsorbent increased, the percentage of dye removal increased accordingly but it decreased with the increase in initial dye concentration and solution temperature. The adsorption kinetics was found to follow pseudo-second-order rate kinetic model, with a good correlation ($R^2 > 0.99$) and intra-particle diffusion as one of the rate determining steps. Langmuir, Freundlich, Temkin, Dubinin–RadushKevich (D–R) and Harkins–Jura isotherms were used to analyze the equilibrium data at different temperatures. In addition, various thermodynamic parameters, such as standard Gibbs free energy (ΔG°), standard enthalpy (ΔH°), standard entropy (ΔS°), and the activation energy (E_a) have been calculated. The adsorption process of direct blue dye onto different activated carbons prepared from pomegranate peel was found to be spontaneous and exothermic process. The findings of this investigation suggest that the physical sorption plays a role in controlling the sorption rate.

1. Introduction

The textile industry plays a part in the economy of several countries around the world. Dyeing is a fundamental operation during textile fiber processing. This operation causes the production of more or less colored wastewater, depending on the degree of fixation of the dyestuffs on the substrates, which varies with the nature of the substances, the desired intensity of coloration, and the application method [1]. Effluents discharged from textile and dyeing industries are of low BOD and high COD. Disposal of this colored water into receiving water can be toxic to aquatic life. The dyes upset the biological activity in water bodies. They also pose a problem because they may be mutagenic and carcinogenic and can cause severe damage to human beings, such as dysfunction of kidney, reproductive system, liver, brain and central nervous system [2,3]. The dye bearing effluents are considered to be a very complex and inconsistent mixture of many pollution substances

ranging from organic-chlorine based pesticides to heavy metals and are considered to be recalcitrant, non-biodegradable and persistent [4]. Treatment of dye-based effluents is considered to be most challenging in the environmental fraternity and the industries; the recent stringent regulations compound the problem further. Various treatment methods including, physical, physico-chemical and chemical processes have been investigated for treating dye-bearing effluents [5–9]. All these methods have different color removal capabilities, capital costs and operating rates. Among these processes, adsorption has been found to be superior to other techniques for wastewater treatment in terms of initial cost, simplicity of design, ease of operation and insensitivity of toxic substances. Activated carbon is the most widely used adsorbent with great success because of its high adsorption capacity, but its use is limited due to its high-cost, has led to a search for cheaper substitutes. Natural materials that are available in large quantities may have potential as inexpensive sorbents. Due to their low-cost, after these materials have been expended, they can be discarded without expensive regeneration. The abundance and availability of agricultural by-products make them good sources of raw materials for activated carbons [10]. Several wastes and residues have been

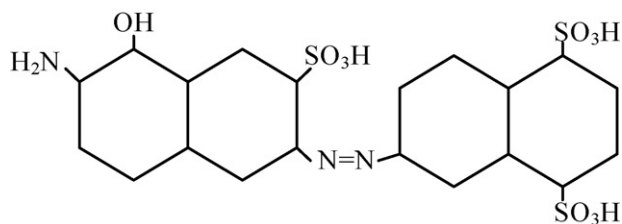*E-mail address:* nkamalamin@yahoo.com.

Fig. 1. Chemical structure of direct blue-106 dye.

investigated for the adsorption of dye bearing effluents with varying success [11–17]. However, new economical, easily available and highly effective adsorbents are still needed.

Pomegranate is an important fruit crop of many tropical and subtropical regions of the world, grown especially in the moderate climates of Mediterranean countries. It is widely consumed fresh and in processed forms as juice, jams and wine. Pomegranate peel, a by-product of the pomegranate juice industry, is therefore inexpensive. Pomegranate peel is a material composed of several constituents, including polyphenols, ellagic tannins and gallic and ellagic acids [18].

In the present study activated carbons were prepared from low-cost adsorbent (pomegranate peel) as a new adsorbent for the removal of direct blue dye from aqueous solutions. While no study has been reported for the adsorption of dye on activated carbons prepared from pomegranate peel, but it has shown high efficiency for the removal of heavy metals [19]. The effect of different parameters such as pH, temperature, contact time and initial dye concentration were investigated. Finally, the isotherm and kinetics as well as the diffusion parameters for the adsorption of direct blue dye onto the activated carbons is evaluated.

2. Materials and methods

2.1. Materials

Direct blue dye-106, a product of ISMA dye Company, Alexandria, Egypt, was used as received without any purification; its color is stable within the pH range of the study. The chemical structure of the direct blue is given in Fig. 1. A stock solution of 1000 mg/L was prepared by dissolving the required amount of dye in double distilled water. Working solutions of the desired concentrations were obtained by successive dilutions of the stock solution. The concentration of the dye was determined at 594 nm, using UV spectrophotometer (Shimadzu Model: UV 1601).

2.2. Preparation of activated carbons

Pomegranate peels were washed with distilled water and dried in a drier for 2 h at 105 °C until a constant weight was reached. It was then ground in a ball mill and sieved to particle sizes ranging from 0.3 to 0.6 mm. The sieved raw material was then divided into three portions. The first portion was physically activated by carbonization in a muffle furnace for an hour at 500 °C in the absence of air by placing the sample in a well-sealed stainless steel tube. The activated carbon prepared by physical activation is termed PC1. The second and third portions were activated by chemical treatment followed by pyrolysis. One of these samples was soaked for 24 h in a solution of phosphoric acid (20 Be') and zinc chloride (50 wt%) at a ratio 1:1 by volume, while the other sample was soaked in a nitric acid solution (10 wt%) for 24 h.

The samples are then decanted, dried in an oven at 105 °C then carbonized in a muffle furnace for 1 h at 500 °C in the absence of

air. The activated carbon treated with $ZnCl_2$ and H_3Po_4 is termed PC2 while that treated with H_3NO_3 is termed PC3.

2.3. Batch adsorption experiments

To study the effect of important parameters like the pH, contact time, initial dye concentration and temperature on the adsorptive removal of direct blue dye, batch experiments were conducted. For each experimental run, 100 mL of dye solution of known concentration, known pH and a known amount of the adsorbent were taken in a 200 mL stoppered conical flask. This mixture was agitated in a temperature controlled shaking water bath at a constant speed of 150 rpm. Samples were withdrawn at different time intervals (0–120 min), filtrated and analyzed for remaining dye concentration. Experiments were carried out at pH 2. Effect of pH on dye removal was studied over a pH range of 1.5–9.4. The initial pH of the solution was adjusted by addition of dilute aqueous solutions of HCl or NaOH (0.1 M). The percentage removal of dye was calculated using the following relationship

$$\% \text{ color removal} = \frac{C_o - C_t}{C_o} \times 100 \tag{1}$$

where C_o and C_t (mg L^{-1}) are the initial dye concentration and concentration at time t, respectively.

Kinetics of adsorption were determined by analyzing adsorptive uptake of the dye from aqueous solution at different time intervals. For adsorption isotherms, dye solutions of different concentrations (20–100 mg L^{-1}) and at different temperatures (25–80 °C) were agitated with known amounts of adsorbents until the equilibrium was achieved. Batch tests were carried out to compare the adsorptive capacity and intensity of different adsorbents. Equilibrium adsorption capacity was calculated from the relationship

$$q_e = \frac{(C_o - C_e)V}{W} \tag{2}$$

where q_e (mg g^{-1}) is the equilibrium adsorption capacity, C_e is the dye concentration at equilibrium, V (L) is the volume of solution and W (g) is the weight of adsorbent.

3. Results and discussion

3.1. Characterization of adsorbents

Physico-chemical characterization of PC1, PC2 and PC3 are given in Table 1. Bulk density, porosity, moisture content and ash content were determined for each sample of activated carbon. A scanning electron microscope (SEM), Philips XL 30, has been a primary tool for characterizing the surface morphology and fundamental physical properties of the adsorbent. It is useful to determine the particle shape, porosity and appropriate size distribution of the adsorbent. Scanning electron microscope of activated carbons prepared from pomegranate peel is shown in Fig. 2. It is clear that, activated carbons appears to have numbers of pores where, there is a good possibility for dye to be trapped and adsorbed into these pores.

Table 1
Physical properties of various types of activated carbon.

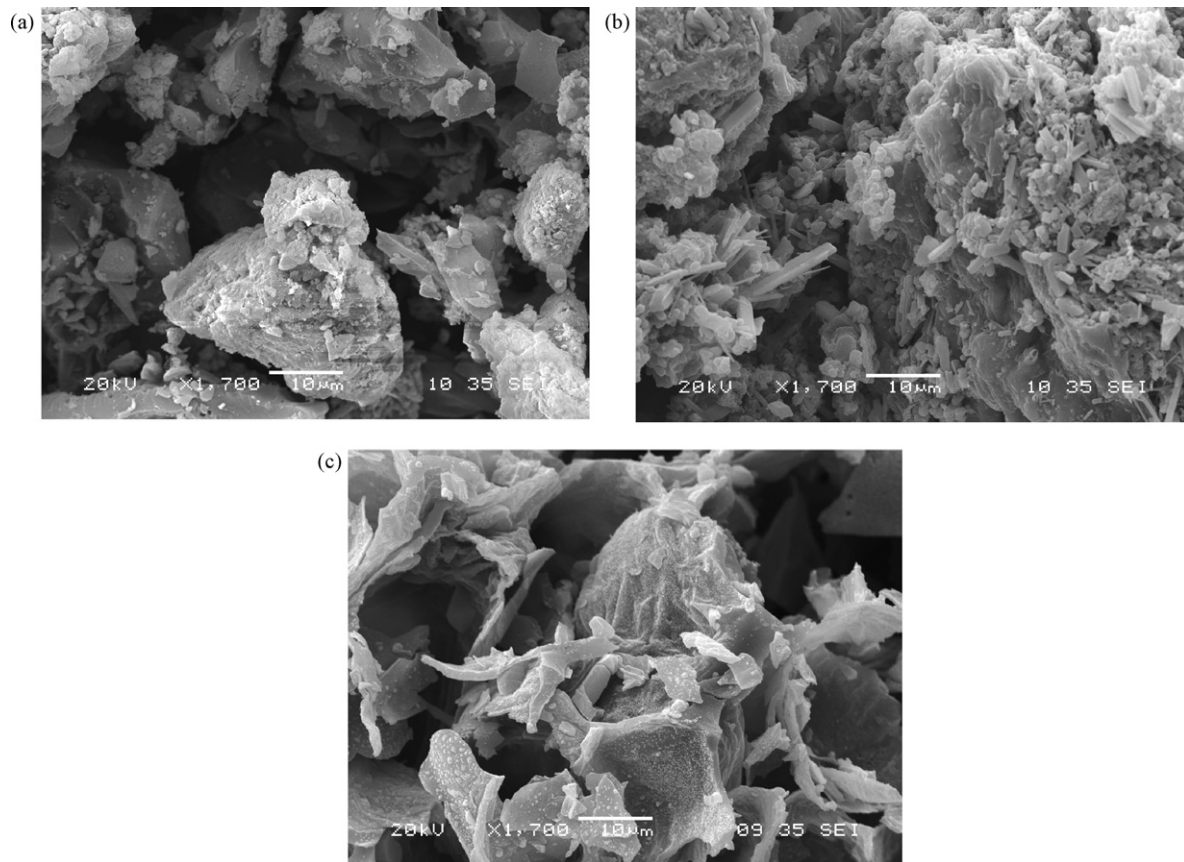| Property	Type of activated carbon		
	PC1	PC2	PC3
Moisture (wt%)	6.79	9.7	1.59
Ash (wt%)	9.98	32.14	58.8
Density (g cm^{-3})	0.585	0.275	0.275
Porosity (%)	60	66	80

Fig. 2. Scanning electron micrograph of activated carbon prepared from pomegranate peel. (a) PC1. (b) PC2. (c) PC3.

3.2. Effect of pH

The pH value of the solution is an important controlling parameter in the adsorption process, and the initial pH of the solution has more influence than the final pH. Effect of pH on the removal of direct blue dye is shown in Fig. 3. The percent color removal decreased when the pH increased from 2 to 9.4 for all activated carbons. Two possible mechanism of adsorption of dye on the adsorbent may be considered: (a) electrostatic interaction between the adsorbent and the dye molecule, (b) a chemical reaction between the dye and the adsorbent. At pH 2 the H^+ ion concentration in the system increased and the surface of the activated carbons acquires positive charge by absorbing H^+ ions. As the carbon surface is positively charged at low pH a significantly high electrostatic attraction exists between the positively charged surface of the carbons and direct blue, an anionic dye molecule, leading to maximum dye adsorption. As the pH of the system increases, the number of negatively charged sites increases and the number of positively charged sites decreases. Negatively charged surface sites on the pomegranate peel carbons do not favor the adsorption of dye anions due to the electrostatic repulsion. Also lower adsorption of direct blue at alkaline pH is due to the presence of excess OH ions, which destabilize anionic dyes and compete with the dye anions for the adsorption sites.

The most effective pH was 2 and it was used in further studies. A similar trend was observed for the adsorption of direct dye [20–23].
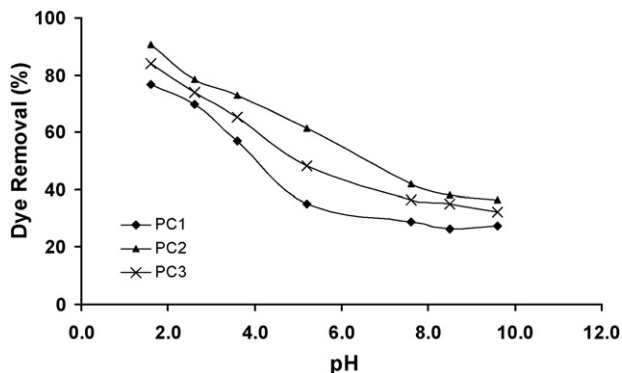

Fig. 3. Effect of pH on direct blue dye removal by pomegranate peel activated carbons (contact time = 2 h, dose of activated carbon = 2.5 g L^{-1}, dye concentration = 20 mg L^{-1}, temperature = 25 °C).
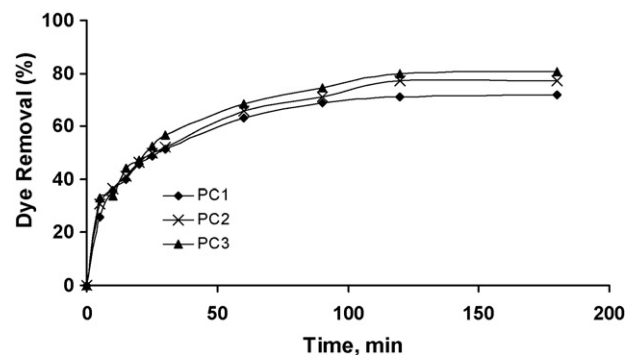

Fig. 4. Effect of contact time on direct blue dye removal by pomegranate peel activated carbons (pH 2, temperature = 25 °C, dye concentration = 20 mg L^{-1}, dose of activated carbon = 2.5 g L^{-1}).
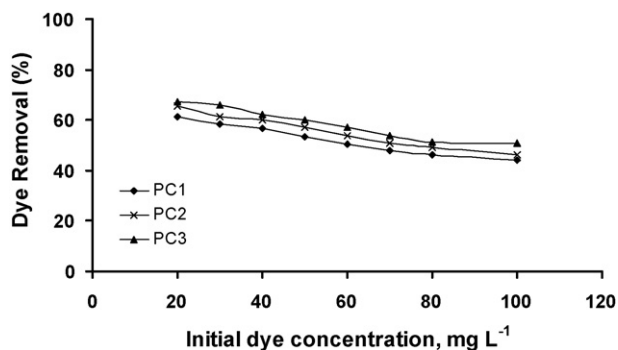
Fig. 5. Effect of initial dye concentration on dye removal at room temperature (pH 2, dose of activated carbon = 2.5 g L^{-1}).
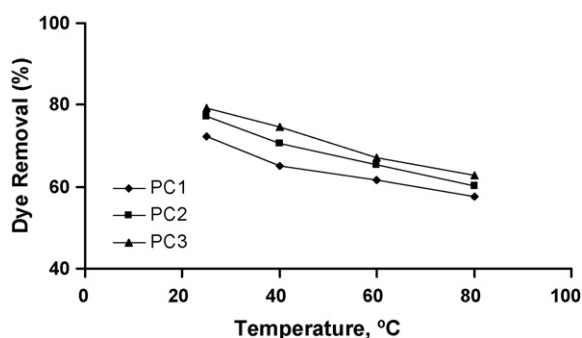

Fig. 6. Effect of temperature on direct blue dye removal by pomegranate peel activated carbons (pH 2, dye concentration = 20 mg L^{-1}, contact time = 2 h, dose of activated carbon = 2.5 g L^{-1}).

3.3. Effect of contact time

The effect of contact time for the removal of direct dye by adsorbent is shown in Fig. 4. The dye was rapidly adsorbed in the first 20–25 min, and then the adsorption rate decreased gradually and reached equilibrium in about 2 h. At the beginning the adsorption rate was fast as the dye ions were adsorbed by the exterior surface of the activated carbons. When the adsorptions of the exterior surface reached saturation, the dye ions extered onto the pores of the adsorbent particles and were adsorbed by the interior surface of the particle. This phenomenon takes a relatively long contact time [14,24].

3.4. Effect of initial dye concentration and temperature on adsorption of direct blue dye

Effect of initial dye concentration on adsorption was investigated at concentration ranging from 20 to 100 mg/L as shown in Fig. 5. By increasing the initial dye concentration the percentage of dye removal decreased, although the actual amount of dye adsorbed per unit mass of activated carbon increased with the increase in initial concentration. This increase is due to the decrease in resistance to the uptake of solute from dye solution. As the ini-

tial concentration provides an important driving force to overcome the mass transfer resistance of dye between the aqueous and solid phases.

Fig. 6 illustrates the effect of temperature on adsorption for different activated carbons. It is shown that the adsorption of direct blue dye on activated carbon decreases as the solution temperature increases. Similar results were obtained by various authors for the adsorption of dyes on various adsorbents [25–28]. This can be explained by the exothermic spontaneity of the adsorption process and by the weakening of bonds between dye molecules and active sites of adsorbents at high temperatures.

3.5. Adsorption kinetic study

The adsorption of a solute by a solid in aqueous solution is a phenomenon with often complex kinetics. The adsorption rate is strongly influenced by several parameters related to the state of the solid, generally having very heterogeneous reactive surface, and to the physico-chemical conditions under which adsorption is carried out. In order to investigate the adsorption processes of direct blue on the adsorbents, pseudo-first-order, pseudo-second-order, Elovich and intra-particle diffusion kinetic models were studied.

3.5.1. Pseudo-first-order model

The pseudo-first-order model was described by Lagergren [29]

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \tag{3}$$

where q_e and q_t refer to the amount of dye adsorbed (mg g^{-1}) at equilibrium and at any time, t (min), respectively and K_1 is the equilibrium rate constant of pseudo-first-order adsorption (min^{-1}). Integration of Eq. (3) for the boundary conditions $t = 0$ to t and $q_t = 0$ to q gives:

$$\log(q_e - q) = \log(q_e) - \frac{K_1}{2.303}t \tag{4}$$

The values of $\log(q_e - q)$ were linearly correlated with t. The plot of $\log(q_e - q)$ vs. t should give a linear relationship from which the values of K_1 were determined from the slope of the plot (Table 2). In many cases, the first-order equation of Lagergren does not fit well with the whole range of contact time and is generally applicable over the initial stage of the adsorption processes [30].

3.5.2. Pseudo-second-order model

The pseudo-second-order model [31] is represented by the following differential equation

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \tag{5}$$

where K_2 is the equilibrium rate constant of pseudo-second-order adsorption (g mg^{-1} min^{-1}). Integrating Eq. (5) for the boundary condition $t = 0$ to t and $q_t = 0$ to q, gives:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \tag{6}$$

The slope and intercept of plot of t/q vs. t were used to calculate the second-order rate constant K_2 (Fig. 7). The values of

Table 2
Kinetic constants for different kinetic models.

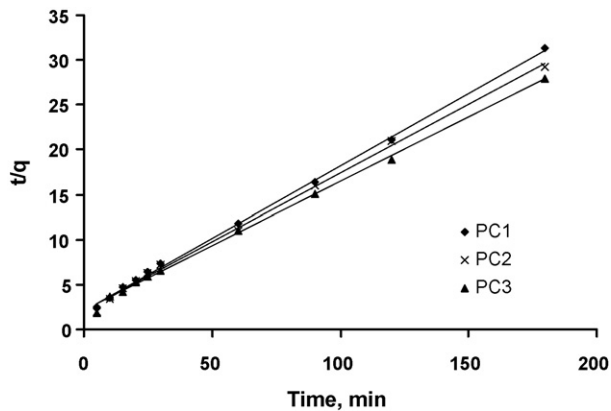| Type of adsorbent	Pseudo-first-order		Pseudo-second-order		Elovich equation			Intra-particle diffusion		
	K_1	R^2	K_2	R^2	a	b	R^2	K_i	I	R^2
PC1	0.035	0.9943	0.015	0.999	0.2974	1.114	0.9859	0.3314	1.993	0.8967
PC2	0.016	0.9665	0.011	0.9819	0.4931	1.074	0.9382	0.3556	2.040	0.9387
PC3	0.026	0.9958	0.012	0.9977	0.2766	1.233	0.9734	0.3745	2.103	0.9226

Fig. 7. Pseudo-second-order kinetics for direct blue dye adsorption onto different activated carbons (pH 2, temperature = 25 °C, dye concentration = 20 mg L^{-1}, dose of activated carbon = 2.5 g L^{-1}).
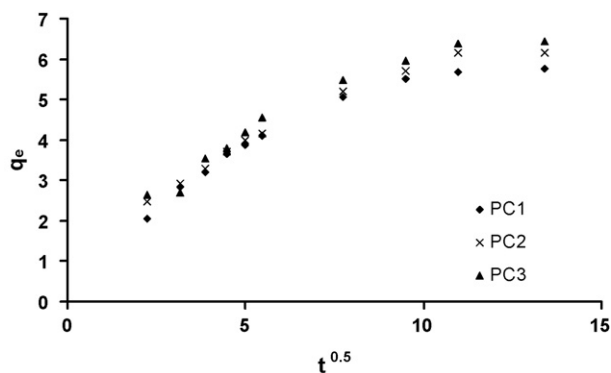

Fig. 8. Intra-particle diffusion plot for direct blue dye adsorption onto activated carbons (pH 2, temperature = 25 °C, contact time = 2 h, dye concentration = 20 mg L^{-1}, dose of activated carbon = 25 g L^{-1}).

equilibrium rate constant (K_2) are presented in Table 2. The correlation coefficients of all examined data were found very high ($R^2 \geq 0.99$). This shows that the model can be applied for the entire adsorption process and confirms that the sorption of direct blue dye on activated carbons prepared from pomegranate peel follows the pseudo-second-order kinetic model. Similar phenomenon was observed for the adsorption of direct dyes onto activated carbon prepared from saw dust [32], palm ash [30] and Fe (III)/Cr (III) hydroxide [22].

3.5.3. Elovich equation

The simple Elovich model equation is generally expressed by the following equation [33]

$$q_1 = a + b \ln t \tag{7}$$

The slope and intercept of plot of q vs. $\ln(t)$ were used to calculate the values of the constants a and b as shown in Table 2.

3.5.4. Intra-particle diffusion model

The adsorption mechanism of adsorbate onto adsorbent follows three steps: film diffusion, pore diffusion and intra-particle transport. The slowest of three steps controls the overall rate of the process. Generally, intra-particle diffusion is often rate-limiting in a batch reactor, while for a continuous flow system film diffusion is more likely the rate-limiting step. In order to investigate the possibility of intra-particle diffusion resistance affecting the adsorption intra-particle diffusion model [34] was explored

$$q_t = K_i t^{0.5} + I \tag{8}$$

where K_i is the intra-particle diffusion rate constant. Fig. 8 represents a plot of q_t vs. $t^{0.5}$ for all adsorbents; it shows two separate regions the initial part is attributed to the bulk diffusion while the final part to the intra-particle diffusion. Values of I give an idea about the thickness of boundary layer (Table 2), i.e. the larger the intercept the greater is the boundary layer effect [35]. The data indicate that intra-particle diffusion controls the adsorption rate. Simultaneously, external mass transfer resistance cannot be
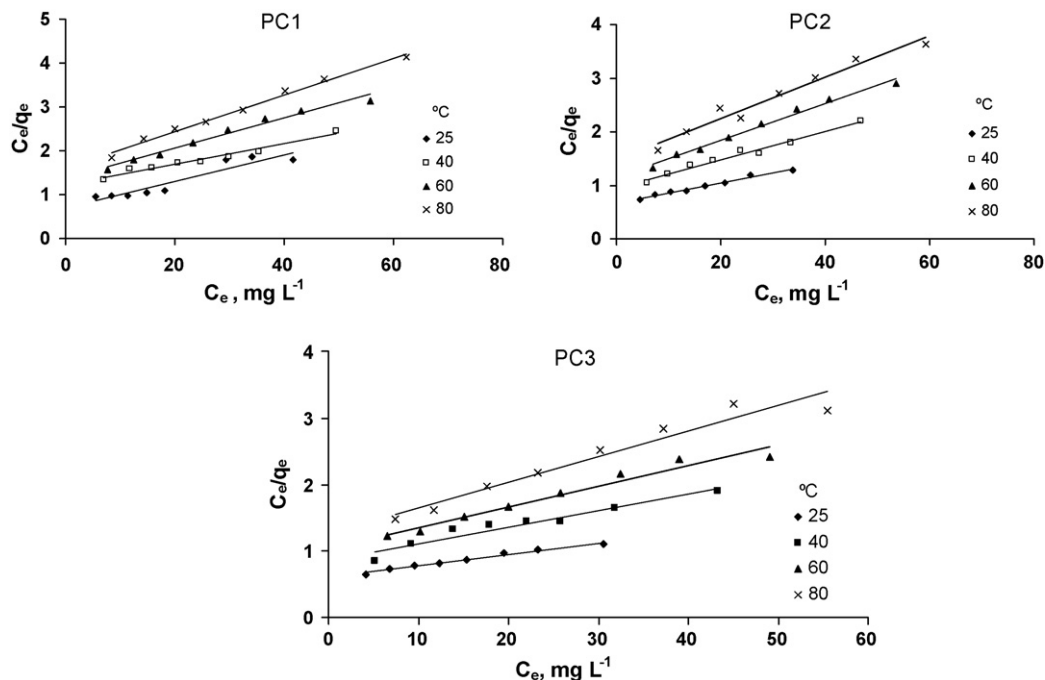

Fig. 9. Langmuir isotherm plots for adsorption of direct blue dye onto PC1, PC2 and PC3 at different temperatures (pH 2, contact time = 2 h, dose of activated carbon = 2.5 g L^{-1}).

Table 3
Constant parameters and correlation coefficients calculated for various adsorption models at different temperatures for PC1, PC2 and PC3.

Isotherm parameters	Isotherm equation	Temperature, K											
		PC1				PC2				PC3			
		298	313	333	353	298	313	333	353	298	313	333	353
Langmuir													
K_L (L/mg)		0.019	0.021	0.025	0.026	0.027	0.028	0.030	0.026	0.028	0.029	0.030	0.031
Q_m (mg/g)	$\dfrac{C_e}{q_e} = \dfrac{1}{K_L Q_m} + \dfrac{C_e}{Q_m}$	42.59	35.92	28.90	23.87	54.05	37.59	29.07	25.91	58.14	40.16	31.95	25.84
R^2		0.918	0.964	0.979	0.991	0.989	0.979	0.986	0.965	0.983	0.940	0.960	0.943
X^2		1.048	0.505	0.247	0.119	0.491	0.324	0.233	0.251	0.057	0.291	0.204	0.297
Freundlich													
$1/n$		0.63	0.73	0.61	0.61	0.73	0.66	0.67	0.61	0.73	0.65	0.62	0.58
K_F (L/mg)		2.270	1.270	1.688	1.396	2.116	1.799	1.688	1.396	2.301	2.008	1.791	1.668
R^2	$\log q_e = \log K_F + \dfrac{1}{n} \log C_e$	0.934	0.989	0.993	0.981	0.995	0.992	0.993	0.987	0.997	0.993	0.988	0.985
X^2		1.683	0.294	1.222	0.953	0.157	0.200	5.612	0.170	0.101	0.136	0.167	0.194
Tempkin													
B_1		7.62	6.51	6.22	5.29	10.11	7.81	6.36	5.65	10.54	8.03	6.90	5.72
K_T (L/mg)		0.39	0.23	0.26	0.25	0.37	0.30	0.29	0.26	0.37	0.33	0.30	0.29
R^2	$q_e = B_1 \ln K_T + B_1 \ln(C_e)$	0.931	0.977	0.978	0.986	0.976	0.975	0.983	0.970	0.970	0.951	0.968	0.954
X^2		0.860	0.565	0.256	0.180	0.680	0.535	0.230	0.367	0.872	1.480	0.354	0.386
D–R													
Q_S (mg/g)		17.78	15.50	13.46	11.82	19.11	16.12	14.15	12.43	19.69	16.12	15.18	13.20
$B \times 10^6$		5.11	7.74	7.60	7.82	3.45	5.01	5.97	6.88	2.76	3.5	5.53	5.96
E (kJ/mol)	$\ln q_e = \ln Q_S - B\varepsilon^2, \quad \varepsilon = RT \ln(1 - \dfrac{1}{C_e})$	3.12	2.54	2.56	2.53	3.80	3.16	2.89	2.70	4.26	3.78	3.01	2.90
R^2		0.867	0.780	0.811	0.792	0.783	0.773	0.798	0.773	0.772	0.700	0.823	0.810
X^2		2.674	4.088	2.580	2.237	5.519	4.306	2.874	2.739	6.157	6.019	2.933	2.448
H–J													
A		39.06	25.45	25	21.37	40.16	36.1	31.06	27.40	38.17	32.57	28.82	23.47
B_2		1.55	1.60	1.71	1.75	1.33	1.56	1.64	1.72	1.43	1.58	1.67	1.73
R^2	$\dfrac{1}{q_e} = \left(\dfrac{B_2}{A}\right) - \left(\dfrac{1}{A}\right) \log C_e$	0.713	0.842	0.837	0.867	0.893	0.893	0.813	0.835	0.815	0.846	0.840	0.869
X^2		37.07	57.13	22.60	11.63	23.37	2.981	3.080	2.628	29.85	2.583	6.338	3.620

neglected although this resistance is only significant for the initial period of time [36].

3.6. Adsorption equilibrium study

Equilibrium data, commonly known as adsorption isotherms, are basic requirements for the design of adsorption systems. In order to discover the adsorption capacity of activated carbons prepared from pomegranate peel, the experimental data points were fitted to the Langmuir, Freundlich, Temkin, D–R and Harkins–Jura isotherm equations and the constant parameters of the isotherm equations were calculated. For each isotherm, the temperature of solution was varied while the dye concentration and adsorbent weight in each sample were held constant.

The Langmuir equation, which is valid for monolayer adsorption onto a completely homogenous surface with a finite number of identical sites and with negligible interaction between adsorbed molecules, is represented in the linear form as follows [37]

$$\frac{C_e}{q_e} = \frac{1}{k_L Q_m} + \frac{C_e}{Q_m} \tag{9}$$

where K_L is the Langmuir adsorption constant ($\mathrm{L\,mg^{-1}}$) and Q_m is the theoretical maximum adsorption capacity ($\mathrm{mg\,g^{-1}}$). Fig. 9 shows the Langmuir (C_e/q_e vs. C_e) plots for adsorption of direct blue at different temperatures. The value of Q_m and K_L constants and the correlation coefficients for Langmuir isotherm are presented in Table 3. The isotherms of all activated carbons were found to be linear over the whole concentration range studies and the correlation coefficients were extremely high ($R^2 > 0.99$) as shown in Table 3. The values of Q_m decrease with temperature increase, thereby confirming that the process is exothermic [38].

The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of sorption over the surface. It can be expressed in the linear form as follows [39]:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{10}$$

where K_F ($\mathrm{L\,mg^{-1}}$) and n are isotherm constants indicate the capacity and intensity of the adsorption, respectively. The linear plot of $\log q_e$ vs. $\log C_e$ at each temperature indicates that adsorption of direct blue dye also follows Freundlich isotherm (Fig. 10). Table 3 shows the Freundlich adsorption isotherm constant and correlation coefficients. The value of $1/n$ for Freundlich isotherm was found to lie between zero and one, indicating that direct blue dye is favorably adsorbed by activated carbon prepared from pomegranate peel at all temperatures studied.

Heat of adsorption and the adsorbent–adsorbate interaction on adsorption isotherms were studied by Temkin and Pyzhev [40]. The Temkin isotherm equation is given as

$$q_e = \frac{RT}{b} \ln(K_T C_e) \tag{11}$$

Eq. (11) can be linearized as

$$q_e = B_1 \ln K_T + B_1 \ln C_e \tag{12}$$

where $B_1 = RT/b$, T is the absolute temperature in K, R the universal gas constant, $8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}$, K_T the equilibrium binding constant ($\mathrm{L\,mg^{-1}}$) and B_1 is related to the heat of adsorption. A plot of q_e vs. $\ln C_e$ at studied temperature is given in Fig. 11. The constants obtained for Temkin isotherm are shown in Table 3. The Temkin constant, B_1, shows that the heat of adsorption decreases with the increase in temperature, indicating exothermic adsorption.

The linear form of Dubinin and RadushKevich isotherm equation can be expressed as [41]
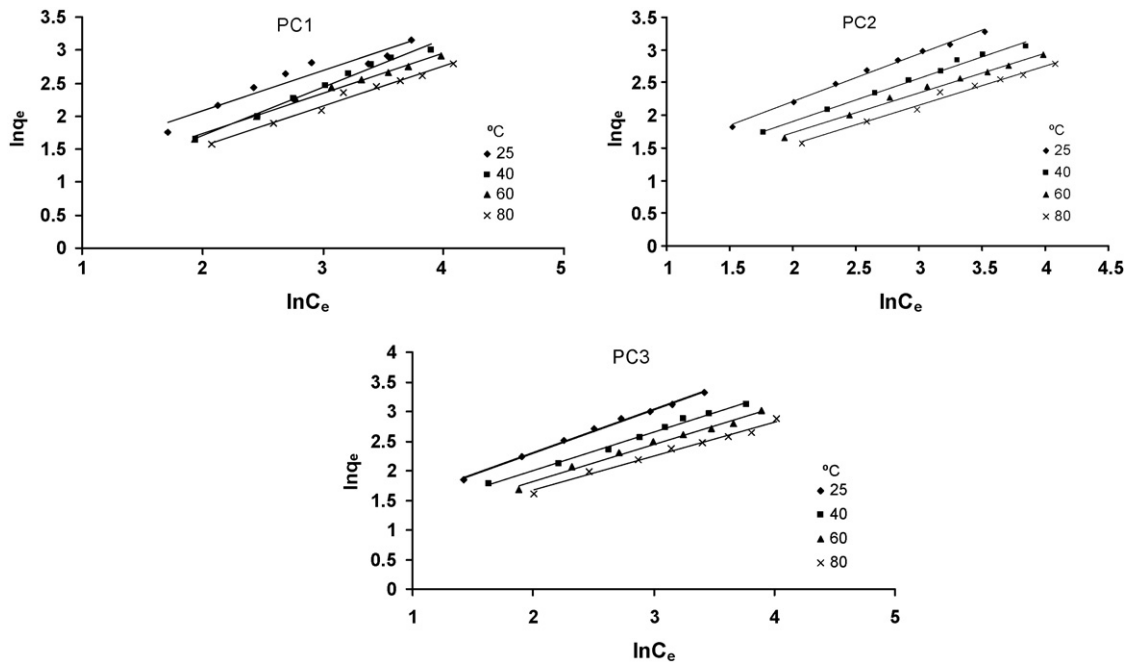
$$\ln q_e = \ln Q_s - B\varepsilon^2 \tag{13}$$

Fig. 10. Freundlich isotherm for adsorption of direct blue dye onto PC1, PC2 and PC3 at different temperatures (pH 2, contact time = 2 h, dose of activated carbon = 2.5 g L^{-1}).

where Q_s is the theoretical monolayer saturation capacity (mg g^{-1}), B is the Dubinin–Radushkevich model constant (mol^2 kJ^{-2}). ε, is the polanyi potential and is equal to

$$\varepsilon = RT \ln \left[1 + \frac{1}{C_e} \right] \tag{14}$$

The mean energy of sorption, E (kJ mol^{-1}), is related to B as [42]

$$E = \frac{1}{\sqrt{2B}} \tag{15}$$

The plot of $\ln q_e$ vs. ε^2 at different temperatures for PC1, PC2 and PC3 is presented in Fig. 12. The constant obtained for D–R isotherms are shown in Table 3. The mean adsorption energy (E) gives infor-

mation about chemical and physical nature of adsorption [43]. It was found to be in the range of 2.54–3.8 kJ mol^{-1}, which is in the range of physical adsorption reactions [38].

The Harkins–Jura adsorption isotherm can be expressed as [17]:

$$\frac{1}{q_e^2} = \left(\frac{B_2}{A} \right) - \left(\frac{1}{A} \right) \log C_e \tag{16}$$

where B_2 and A are the isotherm constants. The Harkins–Jura adsorption isotherm accounts to multilayer adsorption and can be explained with the existence of a heterogeneous pore distribution. $1/q_e^2$ was plotted vs. $\log C_e$ (Fig. 13). Isotherm constants and correlation coefficients are summarized in Table 3.
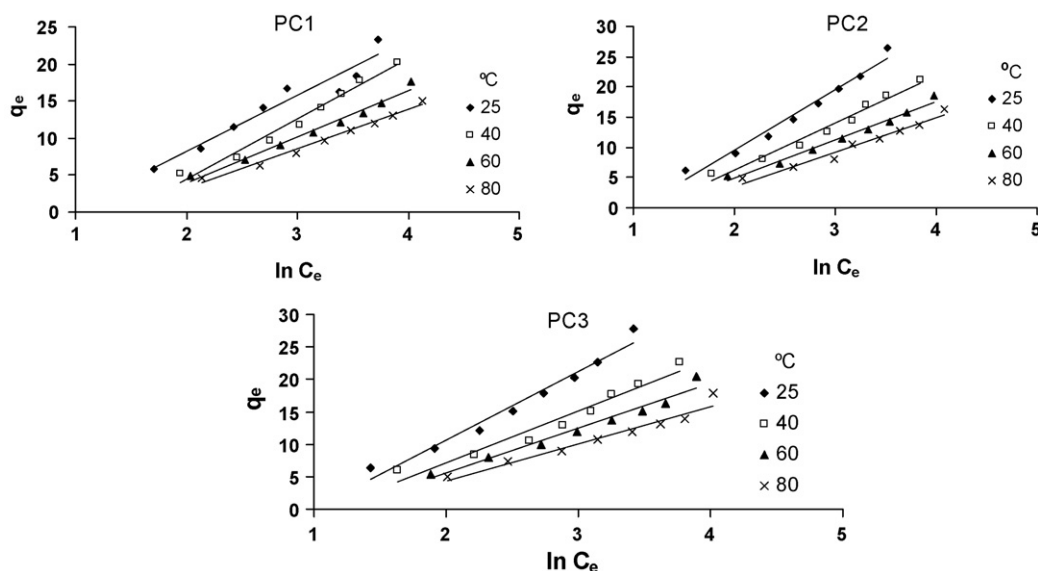

Fig. 11. Temkin isotherm for adsorption of direct blue dye onto PC1, PC2 and PC3 at different temperatures (pH 2, contact time = 2 h, dose of activated carbon = 2.5 g L^{-1}).
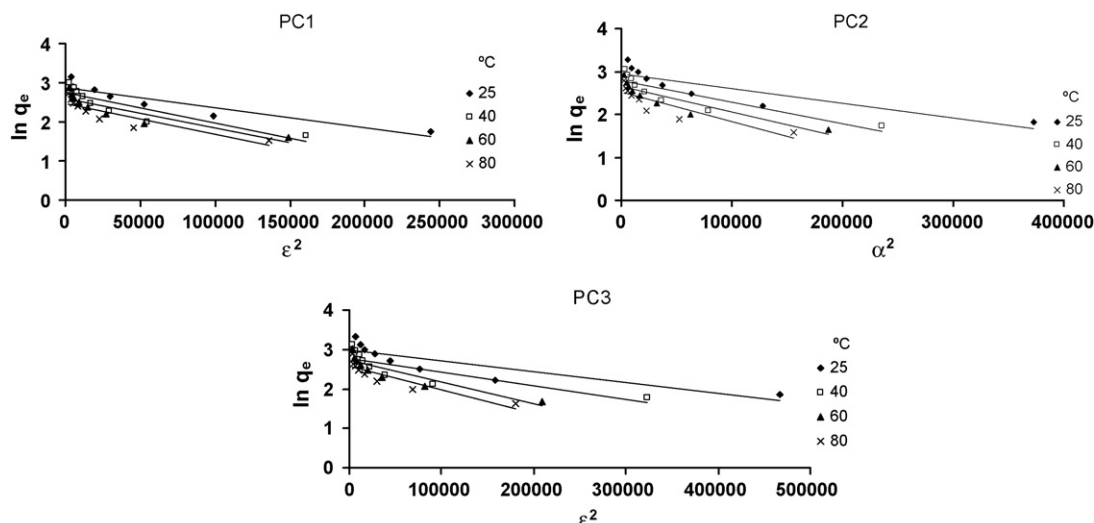
Fig. 12. D–R isotherm for adsorption of direct blue dye onto PC1, PC2 and PC3 at different temperatures (pH 2, contact time = 2 h, dose of activated carbon = 2.5 g L^{-1}).

3.7. Error analysis

In the single-component isotherm studies, the optimization procedure requires an error function to be defined in order to be able to evaluate the fit of the isotherm to the experimental equilibrium data. However, the use of R^2 is limited to solve linear forms of isotherm equation, but not the errors in isotherm curves. In this study, a Chi-square test was used.

The Chi-square test statistic is basically the sum of the squares of the differences between the experimental data and data obtained by calculation from models, with each squared difference divided by the corresponding data obtained by calculation from models. The equivalent mathematical statement is

$$X^2 = \sum_{i=1}^{m} \frac{(q_{e,\exp} - q_{e,calc})^2}{q_{e,\exp}} \tag{17}$$

where $q_{e,\exp}$ is experimental data of the equilibrium capacity (mg g^{-1}), $q_{e,calc}$ is the equilibrium capacity obtained by calculating

from the model (mg g^{-1}). If the data from the model are similar to the experimental data, X^2 will be a small number, if they are different, X^2 will be a large number. Therefore, it is necessary to analyze the data set using Chi-square test to confirm the best-fit isotherm for the adsorption of direct blue dye on activated carbons prepared from pomegranate peel.

The values of X^2 for all isotherms at different temperatures were presented in Table 2. By comparing the values of X^2 for different isotherms, it was found that Longmuir, Freundlich and Temkin models best-fit the adsorption of direct blue on the three adsorbents.

3.8. Thermodynamic study

Thermodynamic parameters were evaluated to confirm the adsorption nature of the present study. The thermodynamic constants, free energy change, enthalpy change and entropy change were calculated to evaluate the thermodynamic feasibility and the spontaneous nature of the process. Therefore, the
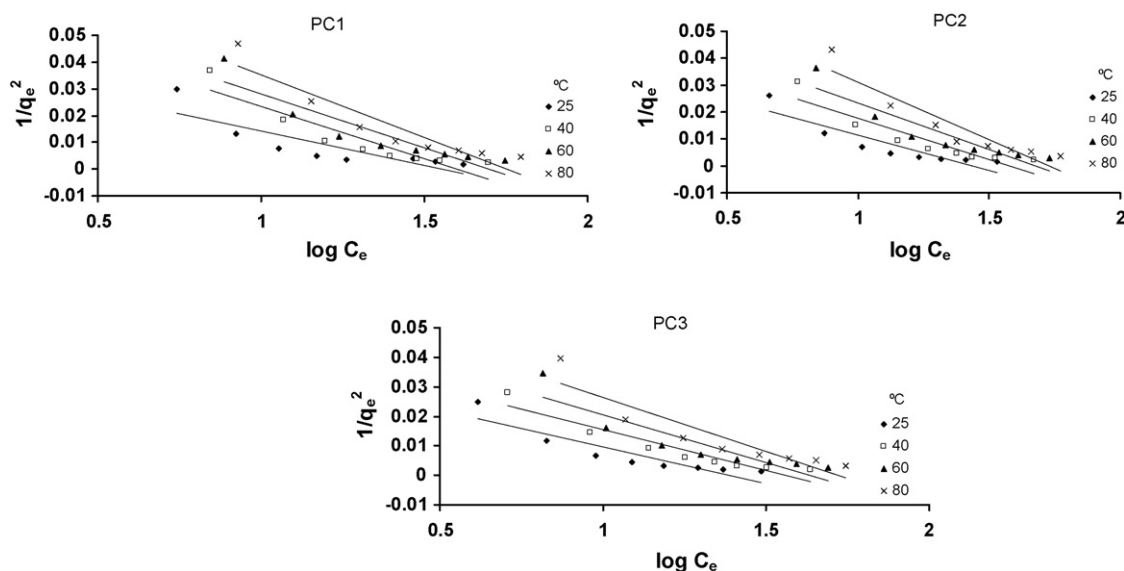

Fig. 13. Harkins–Jura isotherm for adsorption of direct blue dye onto PC1, PC2 and PC3 at different temperatures (pH 2, contact time = 2 h, dose of activated carbon = 2.5 g L^{-1}).

thermodynamic constants can be obtained from the following equations:

$$\Delta G^\circ = -RT \ln K_o \tag{18}$$

where ΔG° is the free energy change (kJ mol^{-1}), R is the universal gas constant (8.314 J mol^{-1} K^{-1}), K_o the thermodynamic equilibrium constant and T is the absolute temperature (K). Values of K_o may be calculated from the relation $\ln q_e/C_e$ vs. q_e at different temperatures and extrapolating to zero [44,45]. The thermodynamic parameters are listed in Table 4. The negative ΔG° values confirm the spontaneous nature and feasibility of the adsorption process. The ΔG° values were decreased as the temperature was increased from 298 to 353 K, which is an indication of the physical adsorption nature of the process. The values of other parameters such as enthalpy change (ΔH°), and entropy change (ΔS°), may be determined from Van't Hoff equation

$$\ln K^\circ = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{19}$$

ΔH° and ΔG° can be obtained form the slope and intercept of Van't Hoff plot of $\ln K^\circ$ vs. $1/T$. The data are presented in Fig. 14 and Table 4. The negative values of ΔH° further confirm the exothermic nature of the adsorption process, while the negative ΔS° values suggest the decrease in adsorbate concentration in solid–liquid interface indicating thereby the increase in adsorbate concentration onto the solid phase. It also confirms the decreased randomness at the solid–liquid interface during adsorption. This is the normal consequence of the physical adsorption phenomenon, which takes place through electrostatic interactions.

In order to further support the assertion that physical adsorption is the predominant mechanism, the values of activation energy (E_a) and sticking probability (S^*) were estimated from the experimental data.

They were calculated using a modified Arrhenius type equation related to surface coverage (θ) as follows [35,45]

$$S^* = (1 - \theta)e^{-(E_a/RT)} \tag{20}$$

The sticking probability, S^*, is a function of the adsorbate/adsorbent system under investigation, its value lies in the range $0 < S^* < 1$ and is dependent on the temperature of the system. The parameter S^* indicates the measure of the potential of an adsorbate to remain on the adsorbent indefinite. The surface coverage, θ, can be calculated from the following equation:

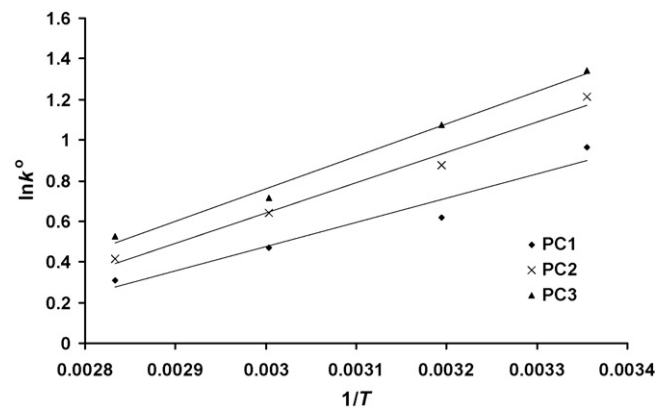$$\theta = \left[1 - \frac{C_e}{C_o}\right] \tag{21}$$

Fig. 14. Plot of Van't Hoff equation for adsorption of direct blue dye onto PC1, PC2 and PC3.

Table 4
Thermodynamic parameters for the adsorption of direct blue dye onto PC1, PC2 and PC3.

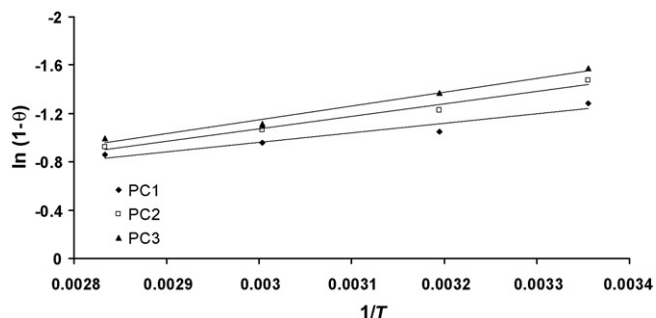| Temperature, K	PC1					PC2					PC3				
	ΔG°, kJ/mol	ΔS°, J/mol K	ΔH°, kJ/mol	E_a, kJ/mol	S^*	ΔG°, kJ/mol	ΔS°, J/mol K	ΔH°, kJ/mol	E_a, kJ/mol	S^*	ΔG°, kJ/mol	ΔS°, J/mol K	ΔH°, kJ/mol	E_a, kJ/mol	S^*
298	−2.383	−25.7	−9.90	−6.44	0.256	−3.007	−31.823	−1.24	−8.54	0.134	−3.320	−33.395	−13.24	−9.45	0.104
313	−1.610					−2.279					−2.789				
333	−1.302					−1.768					−1.979				
353	−0.905					−1.220					−1.543				

Fig. 15. Plot of $\ln(1-\theta)$ vs. reciprocal temperature for adsorption of direct blue onto PC1, PC2 and PC3.

The activation energy and sticking probability were estimated from a plot of $\ln(1-\theta)$ vs. $1/T$ (Fig. 15).

The activation energy, E_a, calculated from the slope of the plot was found to be -6.442, -8.543 and -9.453 kJ/mol for adsorption of direct blue onto PC1, PC2 and PC3 respectively. The negative values of E_a indicate the exothermic nature of the adsorption process. Interestingly, the values of activation energy obtained from Eq. (20) are in the same order of values of activation energy obtained from D–R isotherm. Table 4 indicates that the probability of direct blue dye ions to stick on surface of activated carbon is very high as $S^* \ll 1$ (Table 2) these values confirm that, the sorption process is physisorption.

4. Conclusion

The present investigation showed that activated carbon prepared from chemically treated pomegranate peel is an effective adsorbent for removal of direct blue dye from aqueous solution. Removal of direct blue dye is pH dependent and the maximum removal was attained at pH 2. The equilibrium adsorption is practically achieved in 120 min. It was also a function of adsorbate concentration and temperature of the solution. Adsorption equilibrium data follows Langmuir, Freundlich and Temkin isotherm models and the correlation coefficients for them were fitted better than D–R and H–J isotherm model. The kinetic study of direct blue dye on activated carbons was performed based on pseudo-first-order, pseudo-second-order, Elovich and intra-particle diffusion equations. The data indicate that the adsorption kinetics follow the pseudo-second-order rate with intra-particle diffusion as one of the rate determining steps. The determination of the thermodynamic parameters (ΔG°, ΔH° and ΔS°) indicates the spontaneous and exothermic nature of the adsorption process. The negative sign of ΔS° indicates that the adsorption process takes place through electrostatic interaction between adsorbent surface and adsorbate species in solution. The activation energy of adsorption of direct blue-106 dye was found to be -6.442, -8.543 and -9.453 kJ mol^{-1} for PC1, PC2 and PC3 respectively, indicating that the adsorption process is exothermic with a physical nature. The present study concludes that the activated carbons prepared from pomegranate peel could be employed as low-cost adsorbents as alternatives to commercial activated carbon for the removal of direct blue dye from aqueous solution in particular and for the removal of color and dye from wastewater, in general.

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