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Statistical analysis of equilibrium and kinetic data for ascorbic acid removal from aqueous solution by activated carbon

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ABSTRACT

The adsorption of ascorbic acid from aqueous solution onto activated carbon was investigated at different concentrations and temperatures. Equilibrium data were analysed using Langmuir, Freundlich, Dubinin–Radushkevich (D–R), Temkin and Frumkin isotherms. All of the isotherm parameters were calculated and showed that they were well explained by the Langmuir, Temkin and Frumkin isotherms models, as compared with the D–R and Freundlich isotherms. Maximum adsorption capacity was determined to be 520.80 mg g^{-1} according to the Langmuir isotherm. The mean free energy values (E) according to the D–R isotherm were estimated to be 12.50 kJ mol^{-1}. In order to clarify the adsorption kinetics, the fits of pseudo-first-order kinetics second-order kinetics, and Elovich models were compared. It was determined that the ascorbic acid adsorption process followed pseudo-second-order rate kinetics. Kinetic and equilibrium data were evaluated according to standard deviation and correlation coefficients. The external mass transfer coefficient, as well as the film and pore diffusion coefficients were also evaluated at various temperatures.

Keywords: Ascorbic acid; Adsorption; Activated carbon; Mass transfer

1. Introduction

Several methods, including oxidation, chemical preparation, biological processes, ion exchange membrane filtration and adsorption have been used in water treatment schemes. In addition to these mentioned methods, the adsorption process has been widely used [1,2]. The term adsorption refers to a process wherein a material is concentrated at a solid surface from solution. Among various adsorption technologies, activated carbon is commonly used [3]. Activated carbon is a highly porous form of solid carbon produced from carbonaceous raw materials using chemical or physical activation methods. Activated carbon has to be regenerated for further use in purifying water [4].

In the body, the redox balance is, in part, maintained by enzymatic generation of small molecules, such as ascorbic acid, that function to quench reactive oxygen species [5]. Ascorbic acid is distributed widely in both the plant and the animal kingdoms. In vegetable cells, it can be found in free form [6]. Potentially, in cells, the antioxidant potential of ascorbic acid hangs in a tenuous balance with other cellular and medium constituents such as free metal ions. It is generally accepted that oxidation of ascorbic acid in cells is mediated by the reduction of Fe^{3+} to Fe^{2+}

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(or similarly with other transition metals) [7]. Ascorbic acid leads to production of H_2O_2, which is involved in the redox control of several physiological processes.

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH^{\cdot} + OH^{-} \text{ (Fenton reaction)}$$

Radicals of $OH^{\cdot}$ result from the reaction. High doses of ascorbic acid cause excessive $OH^{\cdot}$ formation and contribute to causing kidney stones [8–11].

In this study, activated carbon was used as an adsorbent to remove ascorbic acid from aqueous solutions. The parameters of equilibrium and kinetics involved in this process were investigated herein.

2. Materials and methods

2.1. Materials

The solute selected for this work was ascorbic acid (chemical formula: $C_6H_8O_6$, MW: 176.12 g mol^{-1}) A stock solution of 1,000 mg L^{-1}was prepared by dissolving the required amount of ascorbic acid (AA) in distilled water; various concentrations of the ascorbic acid solution were then investigated by UV–vis spectrophotometry.

In this study, the activated carbon was prepared from waste using a chemical activation process carried out in the presence of KOH and the absence of N_2 at 800°C. The raw material was first mixed with KOH at the KOH/starting material weight ratio of 1:1 and the mixture was kneaded by adding distilled water. The mixture was then dried at 110°C in order to prepare an impregnated sample. The impregnated sample was placed on a quartz dish, which was then inserted in a quartz tube (i.d. = 60 mm). It was heated up to an activation temperature of 800°C under an N_2 flow and held at the same activation temperature for 1 h. Following activation, the sample was cooled under an N_2 flow. The sample was sequentially washed several times with hot distilled water to remove any residual chemicals until a pH of 7 was reached. The BET surface area of the activated carbon was determined to be 1,685 m^2 g^{-1}.

2.2. Adsorption experiments

The ascorbic acid solutions were prepared in distilled water at the desired concentrations. Adsorption experiments were carried out by agitating 0.1 g of activated carbon with 50 mL solutions of the desired concentration (200–1,000 mg L^{-1}) at different temperatures (25, 37 and 50°C) in a thermostatic bath operating at 400 rpm. The amount of ascorbic acid adsorbed onto the activated carbon, q_t (mg g^{-1}), was calculated according to the mass balance relationship represented in Eq. (1) as follows:

$$q_t = (C_0 - C_t)\frac{V}{W} \tag{1}$$

where C_0 and C_t are the initial and final (at time t) liquid-phase concentrations of the ascorbic acid (mg L^{-1}), respectively, V is the volume of the solution (L), and W is the weight of the dry activated carbon used (g).

3. Results and discussion

3.1. Investigation of adsorption parameters

3.1.1. Effect of initial concentration of ascorbic acid

The effect of the initial concentration of ascorbic acid (AA) on its removal from aqueous solutions by activated carbon was studied as shown in Fig. 1. The percentage of the AA removed was found to decrease with increasing initial AA concentration. This suggests that higher initial concentrations of the acid decrease its adsorption onto activated carbon owing to a lack of available active sites on the surfaces of the activated carbon. Fig. 1 shows that almost 90% of the AA was adsorbed at a concentration of 1,000 mg L^{-1}. Therefore a concentration of 1,000 mg L^{-1} AA was selected in this study to investigate the effect of temperature.

3.1.2. Effect of temperature

The effect of temperature on the removal of AA by activated carbon is shown in Fig. 1. The percentage of

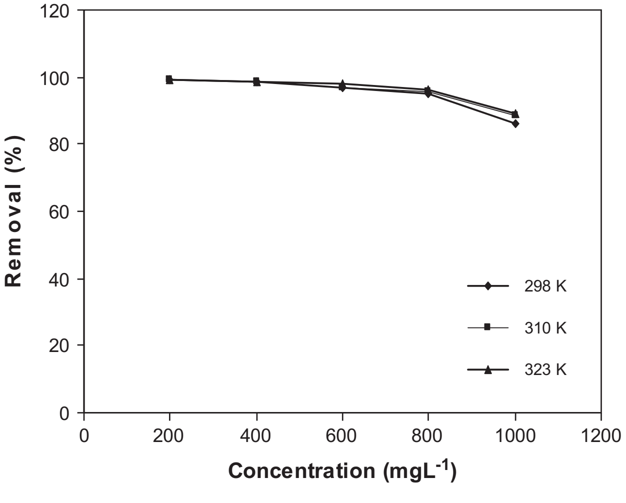

Fig. 1. Removal ascorbic acid relation with concentration.

the 1,000 $\mathrm{mg\,L^{-1}}$ AA removed increased from 88.9 to 90.2 as the adsorption temperature was increased from 25 to 50°C. The increase in the rate of adsorption may be due to the increase in the rate of mobility and diffusion of the adsorbate species induced by the increase in the temperature. An increasing number of molecules may also acquire sufficient energy to interact with the active sites on the surface of the activated carbon [12].

3.2. Adsorption isotherms

Equilibrium adsorption isotherms are important for the design of adsorption systems. Some of these isotherms were originally proposed for the treatment of gas mixtures, but their use in the present context is supported by both theoretical and practical reasons, such as simple isotherm models for homogeneous surfaces without lateral interactions. The isotherm equations used in this study to analyse adsorption equilibrium data were the Langmuir, Freundlich, Dubinin–Redushkevich (D–R), Temkin and Frumkin isotherms [13–18].

3.2.1. Langmuir isotherms

The Langmuir adsorption isotherm posits that when an adsorbate occupies a site, further adsorption cannot take place at that site. Every adsorption site is equivalent, and there is no interaction between molecules adsorbed on neighboring sites. The linear form of the Langmuir model [13] is given by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \tag{2}$$

where C_e is the equilibrium concentration ($\mathrm{mg\,L^{-1}}$), q_e is the amount adsorbed at equilibrium ($\mathrm{mg\,g^{-1}}$), Q_0 is the Langmuir constant related to adsorption capacity ($\mathrm{mg\,g^{-1}}$) and b is the Langmuir constant related to the energy of adsorption ($\mathrm{L\,mg^{-1}}$).

In order to quantitatively compare the applicability of different isotherm models in fitting their predictions to the actual data, a standard deviation Δq (%) was calculated:

$$\Delta q = \sqrt{\frac{\sum[(q_{t\,exp} - q_{t\,cal})/q_{t\,exp}]^2}{n-1}} \times 100 \tag{3}$$

where n is the number of data points; $q_{t\mathrm{exp}}$ is the experimental value; and $q_{t\mathrm{cal}}$ is the value calculated by the isotherm.

A plot of C_e/q_e vs. C_e was employed to generate the intercept value of $1/bQ_o$ and the slope of $1/Q_o$. The results are shown in Table 1. The adsorption capacity of the adsorbent increases at increasing temperature. It seems that the isotherm obtained from Langmuir expression for adsorption of AA onto activated carbon provides a better fit to the experimental data because of the higher correlation coefficients ($R^2 > 0.998$) and relatively low values of the standard deviation ($\Delta q < 6.90$). The adsorption is limited, with monolayer coverage, and the surface is relatively homogeneous.

3.2.2. Freundlich isotherms

The Freundlich isotherm model takes multi-layer and heterogeneous adsorption into account. Its linearized form can be represented as [14] follows:

Table 1
Equilibrium constants of ascorbic acid adsorption

Isotherms	Temperatures (K)		
	298	310	323
Langmuir			
Q_0 ($\mathrm{mg\,g^{-1}}$)	500	507.61	520.80
b ($\mathrm{L\,mg^{-1}}$)	0.108	0.109	0.135
R^2	0.999	0.998	0.998
Δq (%)	6.90	6.46	6.05
Freundlich			
k_f ($\mathrm{L\,g^{-1}}$)	7.02	7.03	7.33
n	2.81	2.70	2.75
R^2	0.931	0.932	0.922
Δq (%)	17.26	16.10	16.11
D–R			
q_m ($\mathrm{mol\,g^{-1}}$) 10^3	7.67	8.41	8.58
K ($\mathrm{mol^2\,kJ^{-2}}$) 10^3	3.29	3.00	2.70
E ($\mathrm{kJ\,mol^{-1}}$)	12.50	12.91	13.60
R^2	0.961	0.962	0.955
Δq (%)	11.82	12.42	12.65
Temkin			
B	83.20	87.56	88.96
K_T ($\mathrm{L\,mg^{-1}}$)	1.65	1.58	1.99
R^2	0.983	0.985	0.983
Δq (%)	5.23	5.04	5.30
Frumkin			
a	−4.44	−4.56	−4.74
ln k	9.48	9.59	9.70
$-\Delta G$ (kJ mol−^{1})	23.51	24.74	26.05
R^2	0.921	0.921	0.912
Δq (%)	2.50	2.02	1.90

$$\ln q_e = \ln k_f + \frac{1}{n}\ln C_e \tag{4}$$

where k_f is the Freundlich constant for the system related to the bonding energy. The $1/n$ value indicates the relative distribution of high-energy sites and depends on the nature and strength of the adsorption process. The parameters of k_f ($L\,g^{-1}$) and n can be estimated from the intercept and slope of the plot between $\ln q_e$ against $\ln C_{e,}$ respectively. The calculated parameters are listed in Table 1. Based on R^2 and Δq values, it can be said that the Langmuir isotherm model fit the data slightly better than the Freundlich model. The Freundlich constant $1/n$ is higher than 1. This reflects the favourable adsorption.

3.2.3. Dubinin–Radushkevich (D–R) isotherms

In order to derive the possibility of interactions occurring between adsorbate particles, and estimate the type of adsorption reaction, the energy entailed in the present case was verified through the D–R Eq. (5)[15]:

$$q_e = q'_m \exp(K'\varepsilon^2) \tag{5}$$

where ε (Polony potential) is equal to $RT\ln(1+1/C_e)$. Q_e is the amount of AA adsorbed per unit of activated carbon ($mol\,L^{-1}$), q_m is the theoretical monolayer saturation capacity ($mol\,g^{-1}$), C_e is the equilibrium concentration of the solution ($mol\,L^{-1}$), K' the constant of the adsorption energy ($mol^2\,kJ^{-2}$), R the gas constant ($kJ\,mol^{-1}\,K^{-1}$), and T is the temperature (K). The linear form of the D–R isotherm is given as follows:

$$\ln q_e = \ln q_m - K'\varepsilon^2 \tag{6}$$

The value of K' is related to the mean adsorption energy produced (E, $kJ\,mol^{-1}$), given as follows:

$$E = \frac{1}{\sqrt{2K'}} \tag{7}$$

By plotting $\ln q_e$ vs. ε^2, it is possible to determine the value of K' from the slope and the value of q'_m from the intercept [16].

The parameters for the D–R isotherm are shown in Table 1. Values for adsorption capacity increased with an increase in temperature from 298 to 323 K. The magnitude of E is useful for estimating the type of adsorption process; the value of E was found to range between 12.50 and 13.60 $kJ\,mol^{-1}$ in this study. These values are within the energy range of adsorption reactions (8–16 $kJ\,mol^{-1}$). If the interval of (8–16 $kJ\,mol^{-1}$) is taken into consideration, AA adsorption by activated carbon may be classified as chemical adsorption.

3.2.4. Temkin isotherms

The Temkin isotherm takes into account the effect of indirect adsorbate–adsorbate interactions on adsorption, and suggests that the heat of adsorption for all molecules in the adsorbent surface layer should decrease linearly with coverage [17]. The Temkin isotherm equation is given as. follows:

$$q_e = \frac{RT}{b} \times \ln(K_T \times C_e) \tag{8}$$

Eq. (8) can be linearized as

$$q_e = B_1 \times \ln K_T + B_1 \times \ln C_e \tag{9}$$

where $B_1 = RT/b$, T is the absolute temperature in K, R is the universal gas constant, 8.314 $J\,mol^{-1}\,K^{-1}$, K_T is the equilibrium binding constant ($L\,mg^{-1}$) and the value of B_1 is related to the heat of adsorption. A plot of q_e vs. $\ln C_e$ was employed to generate the intercept value of $B_1\ln K_T$ and slope of B_1. The parameters are shown in Table 1; further, it also revealed that the heat of adsorption (B_1) increased with an increase in the temperature, indicating the occurrence of an endothermic adsorption process.

3.2.5. Frumkin isotherms

The Frumkin equation, which takes into account the interaction that occurs between the adsorbed spaces can be expressed as [18] follows:

$$\frac{\theta}{(1-\theta)} \times e^{-2a\theta} = k \times C_e \tag{10}$$

where θ is the fractional occupation ($\theta = q_e/q_m$, q_e is the adsorption capacity at equilibrium ($mg\,g^{-1}$), q_m is the theoretical monolayer saturation capacity ($mg\,g^{-1}$) as determined by the D–R isotherm equation), and C_e is the concentration of the AA on the activated carbon at equilibrium ($mol\,L^{-1}$). In its linearized form:

$$\ln\left[\left(\frac{\theta}{(1-\theta)}\right) \times \frac{1}{C_e}\right] = \ln k + 2a\theta \tag{11}$$

The parameters a and k are obtained from the slope and intercept of the plot of $\ln\left[\left(\frac{\theta}{(1-\theta)}\right)\frac{1}{C_e}\right]$ vs. θ. The constant k is the related to the adsorption equilibrium [18]:

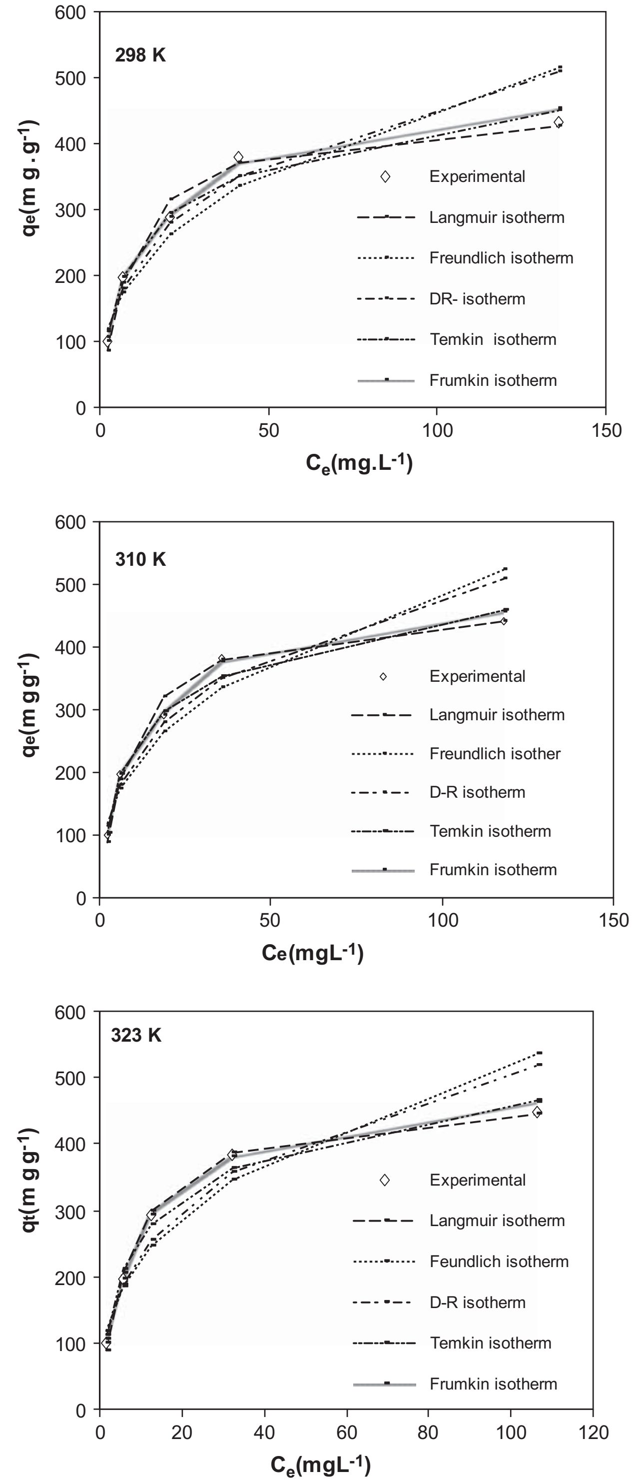

Fig. 2. Comparison of the various adsorption isotherms for ascorbic acid removal.

$$\ln k = \frac{-\Delta G}{RT} \tag{12}$$

The Frumkin equation has been specifically developed to take into account lateral interactions occuring at the surface. The term $e^{-2a\theta}$ in Eq. (10) reflects the extent of the lateral interaction; values of $a > 0$ indicate attraction while $a < 0$ means repulsion. The Frumkin isotherm constants are summarized in Table 1. The different values are attributable to differences arising in the orientation of the AA molecules. The negative values of the free energy of ΔG indicate the feasibility of the adsorption process, and its spontaneous nature.

Comparisons of the experimentally determined isotherms with the adsorption isotherm models are shown in Fig. 2 for all temperatures. The results show that the equilibrium data of the adsorption system were better explained by the Langmuir, Temkin and Frumkin isotherm models, compared with the D–R and Freundlich isotherms.

3.3. Kinetics of adsorption

Three kinetic models were applied to the adsorption kinetic data in order to investigate the behaviour of the adsorption process of AA onto activated carbon. These models were the pseudo-first-order, pseudo-second-order and Elovich models [19–22].

3.3.1. Pseudo-first-order model

A widely used Lagergren model was employed to study pseudo-first-order kinetics [19]:

$$\ln(q_e - q_t) = \ln q_e - kt \tag{13}$$

where q_e and q_t are the amounts of AA (mg g^{-1}) adsorbed at the equilibrium time and time (min), respectively, and k (min^{-1}) is the pseudo-first-order rate constant of AA. The values of k at different temperatures were calculated from the slopes of the respective linear plots of $\ln(q_e - q_t)$ vs. time and are shown in Table 2. The calculated $q_{e,cal}$ values did not agree with the experimental data. These results indicate that adsorption of AA onto activated carbon does not follow pseudo-first-order kinetics.

3.3.2. Pseudo-second-order model

The differential equation for the pseudo-second-order model takes the following form [20]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{14}$$

where q_e is the maximum adsorption capacity (mg g^{-1}), k_2 is the rate constant of the pseudo-second-order

Table 2
Kinetics and diffusion constants of ascorbic acid adsorption

	Temperatures (K)		
	298	310	323
$q_{e[experimental]}$ (mg g^{-1})	497.55	499.36	499.41
The pseudo-first-order			
q_e (mg g^{-1})	421.21	435.11	359.50
k_1 (min^{-1}) × 10^2	4.28	4.51	4.55
R^2	0.789	0.935	0.938
Δq (%)	22.90	21.72	20.11
The pseudo-second-order			
q_e (mg g^{-1})	513.13	516.31	516.31
k_2 (g mg^{-1} min^{-1}) × 10^3	16.48	19.40	23.29
h (mg g^{-1}min^{-1})	45.66	53.76	64.51
R^2	0.986	0.992	0.994
Δq (%)	14.19	13.02	12.23
E_a (kJ mol^{-1})	11.10		
Elovich			
β (g mg^{-1})	0.015	0.014	0.013
α (mg g min^{-1})	448.47	508.21	511.91
R^2	0.870	0.905	0.892
Δq (%)	15.61	14.89	13.17
Diffusion coefficients			
D_1 (cm^2 min^{-1}) 10^{10}	3.69	4.10	4.18
D_2 (cm^2 min^{-1}) 10^{11}	5.56	7.00	8.95
External mass transfer coefficient			
k_L (cm min^{-1}) 10^2	1.98	2.33	2.81

equation (g mg^{-1} min^{-1}), and q_t is the amount of AA adsorbed per unit mass of the adsorbent (mg g^{-1}).

A straight line when t/q_t vs. t is plotted indicates the applicability of the second-order model. The values of $q_{2,}$ and the maximum adsorption capacities, q_e, of the AA solutions were calculated from these plots at different temperatures (Table 2). The values of q_e calculated from the equation agree with the experimental values, demonstrating that the process follows a pseudo-second-order kinetics.

3.3.3. Elovich model

The Elovich equation is expressed as follows [21,22]:

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

where α is the initial adsorption rate (mg g^{-1} min^{-1}) and β is the desorption constant (g mg^{-1}). $q_t = 0$ at $t = 0$, and $q_t = q_t$ at $t = t_t$, at which point Eq. (15) becomes:

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

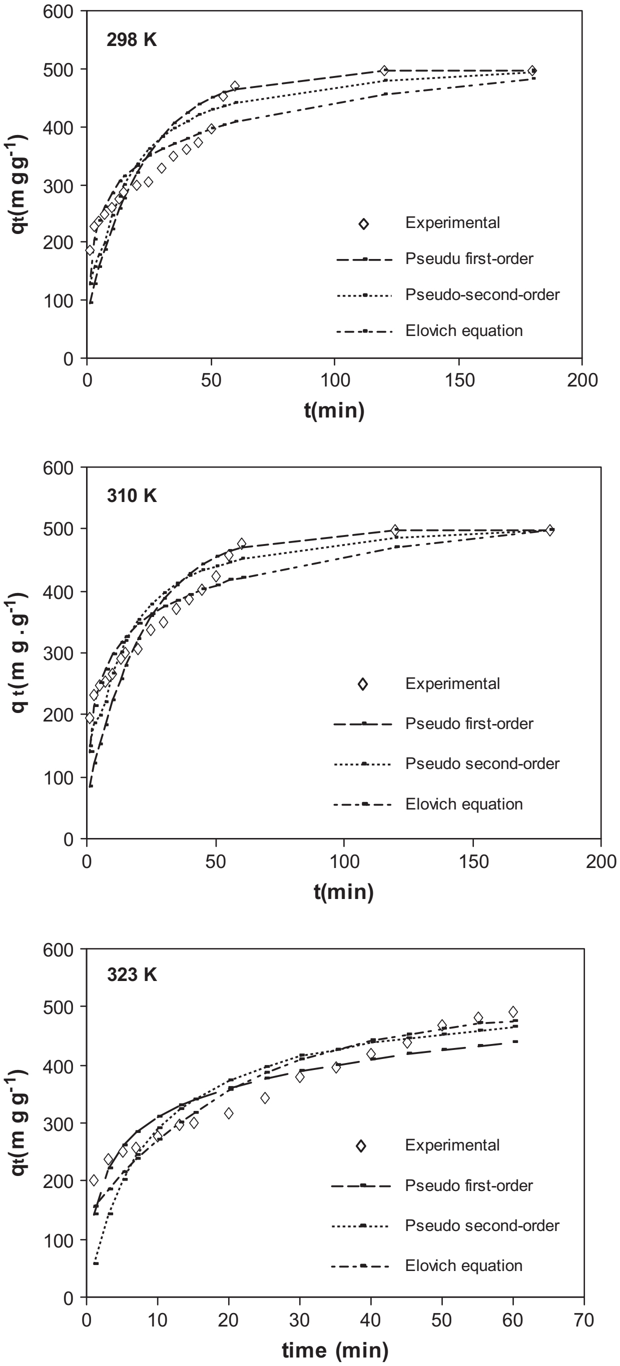

Fig. 3. Comparison of the various kinetic models for ascorbic acid removal.

A plot of q_t vs. $\ln t$ was used to obtain the rate parameters. The initial adsorption rate (α) increased with increasing temperature (Table 2).

The results obtained from the application of pseudo-first-order and pseudo-second-order models and the Elovich model were used to predict the variation in adsorbed AA ions with time. The resulting curves and kinetic parameters were compared with the experimental data for all temperatures in Fig. 3 (a)–(c) and Table 2, respectively. It was observed that the ranking of Δq values was pseudo-second > elovich > pseudo-first model for AA. As shown, values of Δq for the pseudo-second-order model were less than those for the other two models, and the correlation coefficients (R^2) for the pseudo-second-order model were higher.

3.4. Diffusion

Transport of adsorbate ions to the external surface of the adsorbent (film diffusion), transport of adsorbate particles within the pores of the adsorbent and adsorption of adsorbate ions on the interior surfaces of the adsorbent; these three parameters explain how adsorption was confirmed with diffusion [23–26].

The rates of film diffusion (D_1, $\mathrm{cm^2\,sn^{-1}}$) and diffusion within the adsorbent (D_2, $\mathrm{cm^2\,sn^{-1}}$), control the intraparticle diffusion proces. Assuming the adsorbent particle is a sphere of radius "a" and the diffusion follows Fick's law, the relationship between uptake and time is given by [27]:

$$\frac{q_t}{q_e} = 6\left(\frac{Dt}{a^2}\right)^{1/2}\left\{\pi^{-1/2} + 2\sum_{n=1}^{\infty} ierfc\frac{na}{Dt^{1/2}}\right\} - 3\frac{Dt}{a^2} \quad (17)$$

At short times, D is replaced by D_1 and Eq. (17) reduces to:

$$\frac{q_t}{q_e} = 6\left(\frac{D_1}{\pi a^2}\right)^{1/2} t^{1/2} \quad (18)$$

Using the slopes of the plots of q_t/q_e vs. $t^{1/2}$, values of the film diffusion coefficient (D_1) of activated carbon at different temperatures could be calculated. At long times, the relation between weight uptake and the diffusion equation is as follows:

$$\frac{q_t}{q_e} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(\frac{-Dn^2\pi^2 t}{a^2}\right) \quad (19)$$

As t tends to longer times, Eq. (19) can be written in the form:

$$\left(1 - \frac{q_t}{q_e}\right) = \frac{6}{\pi^2}\exp\left(\frac{-D_2\pi^2}{a^2}t\right) \quad (20)$$

If $B = (D_2\pi^2/a^2)$, Eq. (20) can be simplified as:

$$\left(1 - \frac{q_t}{q_e}\right) = \frac{6}{\pi^2}\exp(-Bt) \quad (21)$$

$$Bt = -0.4977 - \ln\left(1 - \frac{q_t}{q_e}\right) \quad (22)$$

The plots of Bt vs. t are shown in Fig. 4. The B values were calculated from the slopes of these plots. These plots can be used to identify whether external transport or intraparticle transport control the rate of adsorption. If the plot of Bt vs. t is a straight line passing through the origin, and then, the adsorption rate is governed by a particle diffusion mechanism; otherwise, it is governed by film diffusion. In Fig. 4, the plots obtained were linear but did not pass through the origin, indicating film diffusion is the rate determining mechanism for adsorption of AA onto activated carbon. The film diffusion (D_1) and pore diffusion (D_2) coefficient values are given in Table 2 that D_1 and D_2 increased with increasing temperature.

External diffusion across the boundary layer surrounding each adsorbent particle and internal diffusion into the porous particle are two main mass transfer resistances. The external mass transfer coefficient is [28]:

$$k_L = \frac{mk_2q_e^2}{C_0A} \quad (23)$$

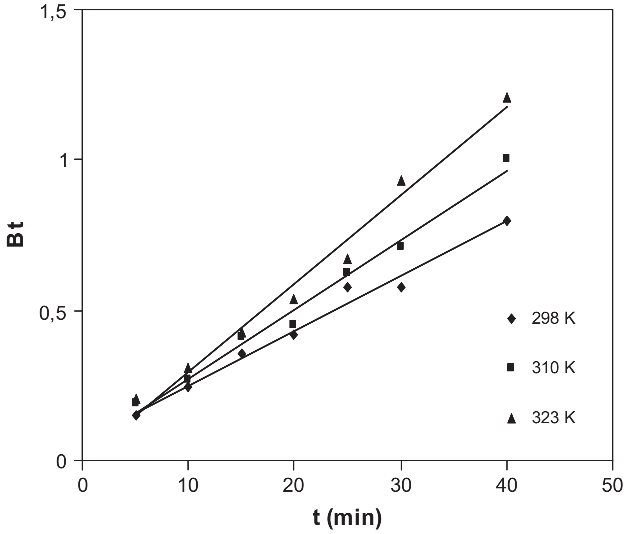

Fig. 4. Figures of *Bt-t*.

where m is the mass of adsorbent (g), k_2 is the second-order-rate constant ($\text{g}\,\text{mg}^{-1}\,\text{min}^{-1}$) q_e is the ascorbic acid adsorbed ($\text{mg}\,\text{g}^{-1}$), C_0 is the initial ascorbic acid concentration ($\text{mg}\,\text{m}^{-3}$) and A is the external surface area of activated carbon. The k_L values, shown in Table 2, increased with increasing adsorption temperature. This shows that the surface of activated carbon adsorbed from solution with ascorbic acid concentration with temperature increases.

4. Conclusion

The results obtained from this study show that activated carbon is an effective adsorbent for the removal of ascorbic acid from aqueous solution. The studies performed show that ascorbic acid adsorption on activated carbon increased with increases in the initial ascorbic acid concentration and the temperature. The maximum adsorption capacity for ascorbic acid onto activated carbon was $520.80\,\text{mg}\,\text{g}^{-1}$. The equilibrium data for the adsorption system were better explained by the Langmuir, Temkin and Frumkin isotherm models, compared with the D–R and Freundlich isotherms. The Langmuir model was successfully applied to show that the adsorption was localized to a monolayer. The ΔG^{o} values for ascorbic acid were negative according to the Frumkin isotherm; therefore, the adsorption was spontaneous. From these kinetic studies, we conclude that the adsorption tends to follow a pseudo-second-order kinetic model.

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