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Adsorption of boron from aqueous solutions by activated carbon impregnated with salicylic acid: equilibrium, kinetic and thermodynamic studies

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ABSTRACT

The adsorption of boron from aqueous solution containing boron by activated carbon impregnated with salicylic acid (ACISA) was studied in a batch system. In order to investigate the effect of initial boron concentration and temperature on boron adsorption capacity of ACISA; the equilibrium, kinetic and thermodynamic parameters were calculated. The adsorption capacity data were obtained by using Langmuir and Freundlich isotherm models and both models fitted well. The pseudo-first-order, pseudo-second-order and the intraparticle diffusion models were used to describe the kinetic parameters and the rate constants were evaluated. The experimental data fitted very well the pseudo-second-order kinetic model. The activation energy (E_a) calculated using the Arhenius equation was found to be 58.25 kJ mol^{-1}. Various thermodynamic parameters such as Gibbs free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) changes were computed and the results showed that the adsorption of boron onto ACISA was spontaneous and endothermic in nature.

Keywords: Boron removal; Adsorption; Activated carbon; Salicylic acid; Kinetics; Thermodynamics

1. Introduction

Boron is found in the Earth's crust at an average of 10 mg kg^{-1} and in the ocean approximately 4.5 mg l^{-1} [1]. Boron enters the environment mainly from the weathering of boron-containing rocks, from seawater in the form of boric acid vapour and from volcanic and other geothermal activity such as geothermal steam. Boron is also released from anthropogenic sources to a lesser extent. Anthropogenic sources include sewage sludge and effluents, coal combustion, glass, cleaning compounds and agrochemicals [2]. Boron wastes released from these plants bring about various pollutions in the land, under the ground water and the surface water. Boron cannot be destroyed in the environment. It can only change its form or become attached or separated from particles in soil, sediment, and water. The waters polluted with more than allowable concentration of boron have negative effects on plants, animals and human life. According to the guidelines for drinking water quality published by World Health Organization (WHO), the concentration of boron is estimated to be between 0.1 and 0.3 mg l^{-1} for most of the world [3].

Boron content in wastewater should not exceed 10 mg l^{-1}. Numerous studies addressed removal of boron from aqueous solution and waste waters. Among

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key techniques they can listed; adsorption on fly ash [4], calcined alunite [5] and activated sludge [6], adsorption by clays and modified clays [7], chitosan resin modified by saccarides [8], solvent extraction [9,10], biosorption onto cotton cellulose [11], use of boron selective resin amberlite IRA 743 [12], ion exchange resin [13], reverse osmosis [14,15], donan dialysis [16,17], electrodialysis [18], coagulation–precipitation [19], adsorption–membrane hybrid process [20–22], electrocoagulation [23], a microwave hydrothermal method [24].

The adsorption method is effective for the removal of low levels of boron from solution. Boron selective adsorbents can be classified into two groups as inorganic and organic. The inorganic adsorbents such as activated carbon, activated alumina, hydrous cerium oxide, hydrous lanthanum oxide and organic adsorbents with polyol groups in arrangement offer a highly selective adsorptivity for boron [25].

At present, activated carbon systems are in use in water treatment throughout the world. Because activated carbon has a high specific surface area and exhibits a strong adsorption capacity [26]. Öztürk and Kavak proposed a model for improving boron removal by adsorption from aqueous solutions using activated carbon [27]. They have reported that the pH and temperature of the solution were effective on boron removal. Both activated carbon and activated carbon impregnated with various compounds have been used in boric acid and borax removal from wastewaters. Boric acid and borax sorption have been investigated by using activated carbon impregnated with citric and tartaric acid [28], glucose, calcium chloride, orthophosphoric (V) acid, mannitol [29].

Boric acid is planer. It dissociates in aqueous media and various borate ions such as $B(OH)_4^-$, $B_3O_3(OH)_4^-$, $B_5O_6(OH)_4^-$ can form in according to medium pH. The OH ends of these ions can make rings with 1,3-diols in aqueous solutions. They also can make rings with salicylic acid group of ACISA [30].

In our former study [30], the effects of parameters such as initial boron concentration, adsorbent dosage, shaking rate, temperature and pH on removal of boron from aqueous solution were studied using activated carbon impregnated with salicylic acid (ACISA) as an adsorbent. This study explores and reports the values of thermodynamic functions and kinetic studies of the system for removing boron from aqueous solution proposed in the study mentioned above.

2. Materials and methods

2.1. Reagents

All reagents employed in this study are analytical grade reagents. Model solutions with a boron concentration ranging from 5 to 50 mg l^{-1} were prepared by adding a suitable amount of standard boron solution to distilled water. The standard solution with a boron concentration of 1 g l^{-1} was prepared by dissolving the appropriate amount of boric acid in distilled water. Powdered activated carbon was supplied from J.T.Baker and other chemicals from Acros. Activated carbon has an apparent density of 150 kg m^{-3}, surface area of 609 m^2 g^{-1}, particle size of –125 μm and specific pore volume of 0.4543 m^3 g^{-1}.

2.2. Activated carbon impregnation

Activated carbon impregnated with salicylic acid (ACISA) was used as an adsorbent in adsorption of boric acid and/or borate ion. ACISA and adsorbate solutions were prepared using a method proposed by Çelik et al. [30]. Both impregnation experiments and adsorption experiments were carried out in a 250 ml erlenmayer shaked by a shaker marked Julabo. In impregnation experiments, a gravimetric analysis was designated to find saturation value by salicylic acid of activated carbon. For this purpose, after 2 g SA was dissolved in 100 ml of diethyl ether, 10 g AC was added to this solution and mixture was shaked for 24 h. Then, 25 ml of clear part of erlenmayer content was taken to a 50 ml-beherglass, diethyl ether content was evaporated. The amount of salicylic acid obtained was determined by weighting. Amount of salicylic acid impregnated on activated carbon is obtained by computing the difference in the amount of salicylic acid before and after impregnation at the diethylether phase. Experiments revealed that 0.0895 g of salicylic acid is kept by 1 g of activated carbon.

2.3. Batch adsorption studies

Adsorption experiments have been carried out in 250 ml erlenmayer flask shaked using a Julabo shaker. Brims of erlenmayer flasks were covered to prevent evaporation of the solutions. In experiments where ACISA was used as an adsorbent, 100 ml boron solutions with concentrations of (5, 10, 25, 50 mg l^{-1}) and pH (4.68) were added to a series of 250 ml erlenmayer flasks in shaker. Two gram of ACISA was added to these solutions. The shaker was shaking rate of 175 rpm and adjusted to a predetermined temperature of (298, 303, 313, 323 K) . After each mixture was shaked for a duration of 2.5, 5, 7.5, 10, 20 and 30 min, they were filtered by blue band filter paper (Schleicher Schuell). The amount of boron removal was calculated from the ratio of boron taken and remaining in the solution. The analytical determination of boron was done spectrophotometrically by Carmine method [31]. For this purpose, a 8500 II Biochrom Model spectrophotometer was used at 585 nm of wavelength. Each of adsorption experiments was replicated twice at least and averaged.

2.4. Calculation

The adsorption capacity of boron adsorbed per gram adsorbent (mg g^{-1}) was calculated as follows:

$$q_e = \frac{V(C_o - C_e)}{W} \tag{1}$$

where C_o and C_e is the initial and equilibrium concentrations (mg l^{-1}) of boron solution at time t respectively; V is the volume (l); and W is the mass (g) of the adsorbent.

3. Results and discussion

3.1. Adsorption isotherms

Adsorption isotherms express the mathematical relationship between the quantity of adsorbate and equilibrium concentration of adsorbate remaining in the solution at a constant temperature. The adsorption data have been analysed with two adsorption models, which are Langmuir and Freundlich isotherm equations [8]. In this study, both models are used to describe the relationship between the adsorbed amount of boron and its equilibrium concentration in solution.

3.1.1. Langmuir adsorption isotherm

The Langmuir isotherm is based on the assumption that adsorption takes place at specific homogeneous sites within the adsorbent and there is no significant interaction among adsorbed species. The adsorbent is saturated after one layer of adsorbate molecules formed on the adsorbent surface [32]. Langmuir isotherm is represented by the following equation:

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

where C_e is the boron concentration at equilibrium (mg l^{-1}) (equilibrium state within 10 min, $t = 10$); q_e is the amount of boron adsorbed at equilibrium (mg g^{-1}); q_m is the monolayer adsorption capacity of the adsorbent (mg g^{-1}) and the constant b is the Langmuir adsorption constant related to the energy of adsorption (l mg^{-1}). When C_e/q_e is plotted against C_e and the data are regressed linearly, q_m and b constants can be calculated from the slope and the intercept as 1.777 mg $g^{-1}$and 0.0072 l mg^{-1}, respectively as shown in Fig. 1.

For various initial boron concentrations (5, 10, 25 and 50 mg l^{-1}) at adsorbent dosage of 20 g l^{-1} (solid/liquid ratio is 2 g/100 ml) and temperature of 303 K, boron amounts adsorbed per unit adsorbent at equilibrium (q_e) have been found as 0.052, 0.100, 0.224, 0.415 mg g^{-1} and C_e values from analysis of adsorption solutions were found as 3.962, 8.003, 20.520 and 41.521 mg l^{-1} respectively from the experiments.

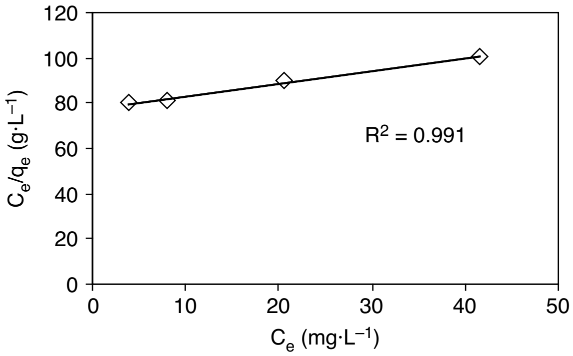


Fig. 1. Langmuir isotherm plot for the adsorption of boron on ACISA (2 g ACISA, pH = 4.68, t = 10 min, T = 303 K).

In our experiments the boron adsorption coefficients obtained on activated carbon impregnated with salicylic acid was in agreement with to the ones obtained by Kluczka et al. [29]. The effectiveness of boron adsorption depends on the type of activated carbon and impregnant. The activated carbon used in these studies had a surface area of 900–1100 m^2 g^{-1}. In our study, the surface area of activated carbon is 609 m^2 g^{-1}, and the monolayer adsorption capacity of ACISA was calculated to be 1.777 mg g^{-1}. If surface areas of activated carbon in both studies are compared, the result obtained in this study will be close to that of activated carbon impregnated with tartaric acid. Therefore, activated carbon impregnated with salicylic acid creates a great possibility to be used in the boron wastewater treatment.

Langmuir isotherm can be expressed by a dimensionless constant separation factor or equilibrium parameter R_L which is defined as:

$$R_L = \frac{1}{1 + bC_o} \tag{3}$$

where b is the Langmuir constant. The value of R_L indicates the shape of isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$) [33]. Accordingly, the R_L values obtained as 0.965, 0.933, 0.847 and 0.735 for initial boron concentrations of 5, 10, 25, 50 mg l^{-1} at a temperature of 303 K and pH 4.68. The results indicate that adsorption of boron on ACISA was favourable.

3.1.2. Freundlich adsorption isotherm

The Freundlich isotherm model takes multilayer and heterogeneous adsorption into account [32]. Freundlich isotherm model is given by the following equation:

$$\ln q_e = \ln K_f + \left(\frac{1}{n}\right) \ln C_e \tag{4}$$

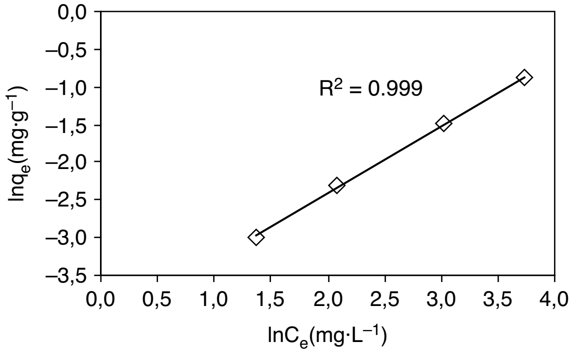


Fig. 2. Freundlich isotherm plot for the adsorption of boron on ACISA (2 g ACISA, pH = 4.68, t = 10 min, T = 303 K).

where K_f and n is the Freundlich adsorption isotherm constants, being indicative of the saturation capacity and intensity of adsorption. Values of K_f and n are obtained as 0.0147 mg g^{-1} and 1.1102 from the intercept and slope of the plots of ln (q_e) versus ln (C_e) respectively (Fig. 2). It has been analytically shown that (n) will vary between 1 and 10 representing beneficial adsorption [8]. Hence, ACISA adsorbent used in the study provide beneficial adsorption at 303 K and pH 4.68.

The coefficient of determination (R^2) was used to specify the relationship between the experimental data and the isotherm. A high correlation coefficient ($R^2 >$ 0.99) with both Freundlich (0.999) and Langmuir (0.991) isotherms was obtained, as reflected by correlation coefficients are shown in Table 1.

3.2. Kinetic studies

In order to investigate the mechanism of adsorption, the pseudo-first-order kinetics model (Lagergreen model), the pseudo-second-order kinetics model and intraparticular diffusion model were used to test dynamical experimental data. The rate constant for boron adsorption on ACISA was determined using the model given by Lagergreen for the adsorption in liquid/solid system. It was pointed out that Lagergreen model was known as first order kinetic model and based on the solid capacity [34]. This model is generally expressed as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{5}$$

where q_e and q_t is the amounts of boron adsorbed (mg g^{-1}) at equilibrium and at time t (min), respectively, and k_1 is the pseudo-first-order rate constant for the adsorption process (min^{-1}). First-order adsorption correlation coefficients R_1^2 and rate constant k_1 were determined from the slopes and intercepts of the plots (Fig. 3. Lagergreen graph for temperature) in our former study [30]. The values of these parameters are presented in Table 2.

Table 1
Langmuir and Freundlich constants for the adsorption of boron on ACISA (T = 303 K and pH = 4.68)

Langmuir isotherm			Freundlich isotherm		
q_m (mg·g^{-1})	b (l mg^{-1})	R^2	K_f (mg g^{-1})	N	R^2
1.7771	0.0072	0.991	0.0147	1.1102	0.999

For the second-order adsorption kinetics, the rate equation is expressed as:

$$\frac{d q_t}{d t} = k_2 (q_e - q_t)^2 \tag{6}$$

where k_2 is the rate constant of pseudo-second-order adsorption (g mg^{-1} min^{-1}). For boundary conditions (t = 0 to $t = t$ and q_t =0 to $q_t = q_t$), pseudo-second-order kinetic model of Ho and McKay [35] is given as:

$$\frac{1}{q_t} = \frac{1}{k_2 q_2^{\,2}} + \frac{t}{q_2} \tag{7}$$

Second-order adsorption correlation coefficients (R_2^2), rate constant (k_2) and q_e values were determined from the slopes and intercepts of the plots (Fig. 3). The values of these parameters are presented in Table 2.

The correlation coefficients (R_1^2) for the pseudo first-order-kinetic model are obtained between 0.843 and 0.999 and the correlation coefficients (R_2^2) for the pseudo-second-order-kinetic model are observed to be between 0.998 and 0.999 (Fig. 3). Moreover, the q values ($q_{e,cal(2)}$) calculated from pseudo second-order model were more consistent with the experimental q values ($q_{e,exp}$) than those calculated from the pseudo first-order model. Hence, we can suggest that the pseudo second-order model better represents the adsorption kinetics.

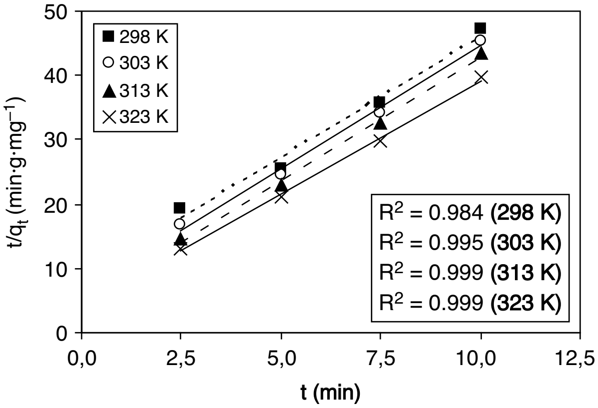


Fig. 3. Pseudo-second-order kinetic plots for the adsorption of boron at different temperatures. (Conditions: 2 g ACISA, initial boron concentration = 25 mg l^{-1}, pH = 4.68, contact times = 2.5, 5, 7.5, 10 min).

Table 2
Kinetic parameters for the adsorption of boron at various temperatures

Models	Parameters	Temperatures (K)			
		298	303	313	323
Pseudo first order	k_1 (min^{-1})	0.459	0.561	1.697	2.229
	$q_{e,exp}$ (mg g^{-1})	0.212	0.224	0.230	0.252
	$q_{e,cal(1)}$ (mg g^{-1})	0.220	0.308	9.680	63.04
	R_1^2	0.942	0.999	0.884	0.843
	E_a (kJ mol^{-1})	54.85			
Pseudo second order	k_2 (g mg^{-1} min^{-1})	1.676	2.130	4.047	9.926
	$q_{e,exp}$ (mg g^{-1})	0.212	0.224	0.230	0.252
	$q_{e,cal(2)}$ (mg g^{-1})	0.266	0.267	0.268	0.270
	R_2^2	0.998	0.999	0.999	0.999
	E_a (kJ mol^{-1})	58.25			
Intraparticle diffusion	K_d (mg g^{-1}·min$^{-0.5}$)	0.052	0.047	0.037	0.039
	C (mg g^{-1})	0.061	0.085	0.124	0.140
	R_3^2	0.833	0.874	0.837	0.860

Neither the pseudo first-order nor the second-order model can identify the diffusion mechanism. Typically, the adsorption kinetics are controlled by various diffusion mechanisms; including external diffusion, boundary layer diffusion and intraparticle diffusion. The kinetic results were analysed by the intraparticle diffusion model given in Eq. (8) to elucidate the diffusion mechanism:

$$q_t = K_d t^{1/2} \tag{8}$$

where q_t (mg g^{-1}) is the adsorbate uptake at time t (min), K_d (mg g^{-1}·min$^{-0.5}$) is the rate constant of intraparticle transport. Intraparticle diffusion correlation coefficients R_3^2 values and rate constant K_d were determined from the plots of q_t versus $t^{1/2}$ given in Fig. 4 [36]. The intraparticle diffusion model was utilized to determine the rate-limiting step of the adsorption process. If the regression of q_t versus $t^{1/2}$ is linear and passes through the origin, then intraparticle diffusion is the sole rate-limiting step [37]. In our experiments regression was observed to be linear, but the plot did not pass through the origin (Fig. 4), suggesting that adsorption involved intraparticle diffusion. However it was not the only rate-controlling step.

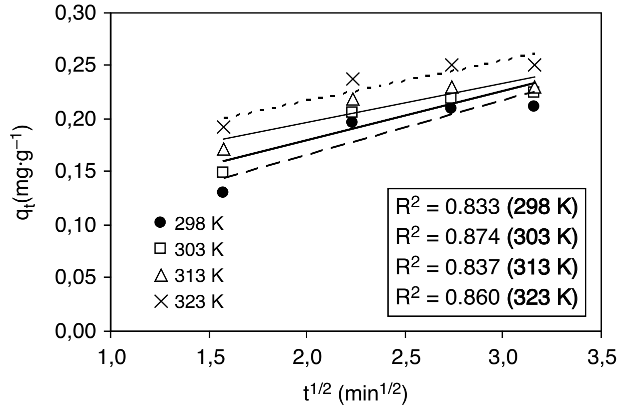


Fig. 4. Intraparticle diffusion plots for the adsorption of boron at different temperatures. (Conditions: 2 g ACISA, initial boron concentration = 25 mg l^{-1}, pH = 4.68, contact times = 2.5, 5, 7.5, 10 min).

3.3. Thermodynamic studies

In any adsorption process, both energy and entropy considerations must be taken into account in order to determine which process will occur spontaneously. Values of thermodynamic parameters are the actual indicators for practical application of a process [38]. The amount of boron adsorbed at equilibrium at temperatures of 298, 303, 313 and 323 K, have been examined to obtain thermodynamic parameters of the adsorption system. The pseudo-second-order rate constant of boron adsorption is expressed as a function of temperature by the following Arrhenius type relationship:

$$k_2 = Ae^{-E_a/RT} \tag{9}$$

$$\ln k_2 = \ln A - \frac{E_a}{RT} \tag{10}$$

where E_a is the activation energy of adsorption; A is the Arrhenius factor; R is the gas constant and is equal to 8.314 J K^{-1} mol^{-1} and T is the temperature (K). When $\ln k_2$ is plotted against $1/T$ (Fig. 5), a straight line with slope $-E_a/R$ is obtained. The magnitude of activation energy gives an idea about the type of adsorption which

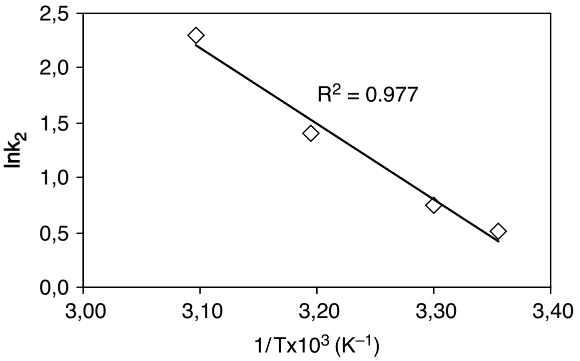


Fig. 5. Arrhenius plot for the adsorption of boron on ACISA.

is mainly physical or chemical. Low activation energies (5–40 kJ mol^{-1}) are characteristics for physical adsorption, while higher activation energies (40–800 kJ mol^{-1}) suggest chemisorption [39]. The forces involved in physical adsorption are weak. On the other hand, chemical adsorption is specific and involves forces much stronger than in physical adsorption. The activation energy obtained in this study is 58.25 kJ·mol^{-1} for the adsorption of boron onto ACISA, indicating that the type of adsorption can be described as chemisorption.

In order to evaluate the feasibility and the effect of temperature better, for boron adsorption onto ACISA, thermodynamic parameters such as standard free energy change ΔG^o, standard entalpy change (ΔH^o) and standard entropy change (ΔS^o) were also obtained. The free energy change of adsorption process was calculated by using the following equation [40]:

$$K_c = \frac{C_A}{C_S} \tag{11}$$

$$\Delta G^o = -RT \ln K_c \tag{12}$$

where K_c is the the equilibrium constant; C_A is the amount of boron adsorbed on the adsorbent from the solution at equilibrium (mg l^{-1}); C_S is the equilibrium concentration of the boron in the solution (mg l^{-1}). The q_2 of the pseudo-second-order model given in Table 3 was used to obtain C_A and C_S. In Eq. (12), T is the solution temperature and R is the gas constant (8.314 J K^{-1} mol^{-1}). ΔH^o and ΔS^o values of adsorption are determined by using the following equation [38]:

$$\ln K_c = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \tag{13}$$

The values of $\Delta H^o$and ΔS^o were estimated from the slope and intercept of ln K_c against $1/T$ (Fig. 6).

When temperature increased from 298 to 323 K, ΔG^o is decreased from 3.690 to 3.630 kJ mol^{-1}. As presented in Table 3, the positive values of ΔG^o values at given temperatures indicates the non-spontaneous nature of the adsorption. The positive value of standard enthalpy change corresponds to the endothermic nature of the adsorption process. Positive ΔS^omeans increase of desorders at the solid–solution interface during the adsorption of boron.

Table 3
Thermodynamic parameters for the adsorption of boron on ACISA at different temperatures

Temperature (K)	K_c	ΔG^o (kJ mol^{-1})	ΔH^o (kJ mol^{-1})	ΔS^o (kJ K^{-1} mol^{-1})
298	0.225	3.690	4.337	0.0022
303	0.234	3.660		
313	0.246	3.647		
323	0.259	3.630		

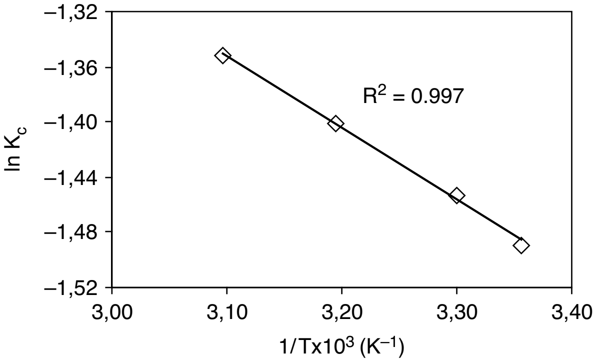


Fig. 6. Thermodynamic parameters for the adsorption of boron on ACISA.

4. Conclusions

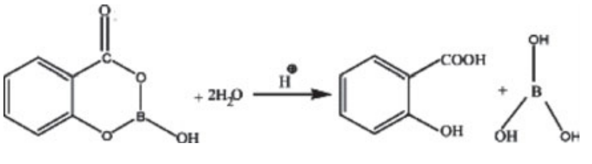
In this study, removal of boron from aqueous solution containing boron was investigated by using activated carbon impregnated with salicylic acid (ACISA). Experiments revealed that the adsorption reached the equilibrium state within 10 min. The boron adsorption was found to be dependent on initial boron concentration and temperature. The adsorption capacity of ACISA increased with increasing initial boron concentration and temperature. The adsorption of boron onto ACISA was endothermic in nature with the boron adsorption capacity increasing temperature due to increasing mobility of boron molecules.

The equilibrium sorption isotherm is very important in design of sorption systems. Therefore for finding out the sorption isotherm, the experimental results were analyzed by using Freundlich and Langmuir equations. A high correlation coefficient ($R^2 > 0.99$) with both isotherms was obtained so both models fitted well. The monolayer adsorption capacity (q_m) and saturation capacity (K_f) of ACISA were calculated as 1.777 and 0.0147 mg g^{-1} respectively. R_L values ($0 < R_L < 1$) reveal that adsorption of boron on ACISA is favourable and n (Freundlich adsorption isotherm constant) was found to be between 1 and 10 represents a beneficial adsorption. Freundlich model represents principally the case of physical adsorption wheras the Langmuir model represents the case of chemical adsorption. The pseudo second-order kinetic model indicated an activation energy of 58.25 kJ mol^{-1}. It is hinted that the overall rate of boron adsorption is likely to be controlled by the chemical process. Therefore we conclude that the Langmuir isotherm is more suitable than the Freundlich isotherm for this process.

In order to investigate kinetics of adsorption of boron onto ACISA, pseudo-first-order, and intraparticle diffusion models were tested. The pseudo-second-order kinetic model agreed very well with the dynamic behavior for the adsorption of boron onto ACISA under different temperatures. The adsorption of boron onto ACISA is a complex process, so the whole process can not be sufficiently described by a single kinetic model. For example intraparticle diffusion (up to 10 min) played a significant role, but it was not the main rate determining step during the adsorption.

The enthalpy change (ΔH^o) and entropy change (ΔS^o) were calculated as 4.337 and 0.0022 kJ K^{-1} mol^{-1} for the process. The positive value of standard enthalpy change ΔH^o confirms the endothermic nature of the process, the positive entropy of adsorption ΔS^o reflects the affinity of the adsorbent material toward boron. The positive values of ΔG^o at given temperatures indicate that the adsorption process is non-spontaneous.

On the other hand, lacton structure forming between ACISA and boric acid or borates can be easily hydrolized in acidic medium in accorging to the following reaction and ACISA can be reused in the process [30].



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These results indicate that the adsorption process proposed in this paper is promising for the removal of boron from aqueous solutions containing boron.

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