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Adsorption equilibria of formic acid by weakly basic adsorbent Amberlite IRA-67: Equilibrium, kinetics, thermodynamic

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ABSTRACT

Formic acid is an important chemical and biochemical compound used in various industries. It is important to separate this acid from wastewater streams. In this study, adsorption of formic acid was studied from aqueous solution by using weakly basic adsorbent (Amberlite IRA-67) at three different temperatures (298 K, 318 K, and 328 K). Adsorption of formic acid was investigated in terms of equilibrium, kinetics and thermodynamic conditions. Optimal amount of IRA-67 was determined as 1.00 g. The most used isotherms, Freundlich and Langmuir, were applied to experimental data. Langmuir isotherm gave good results with R^2 value over 0.99 at different temperatures. Pseudo-second-order model was fitted for this adsorption system. Thermodynamic parameters, ΔH°_{ads}, ΔS°_{ads} and ΔG°_{ads}, were calculated.

1. Introduction

Recovery of carboxylic acids from wastewater stream or fermentation broth presents a challenging separation problem, because of complex nature of fermentation broth and high affinity to water. Methods of recovery that utilize separating agents, such as solid sorbents, that are selective for carboxylic acids are attractive. This has been reported by Tung and King [1]. Important characteristics of solid sorbents is a high adsorption capacity for the acid, a high selectivity for the acid as opposed to water and substrate, regeneration and process configuration, and the biocompatibility with microorganisms. Adsorption or ion exchange is a reliable technology. Adsorption on ion exchange resin has the advantage that it can be coupled with fermentation process. In recent years, the amount of carboxylic acids obtained by biotechnological methods has increased [2]. Uslu has extensively studied separation of organic acids from wastewater stream by using amine extractant [3–7]. Evangelista and Nikolov [8] recovered other carboxylic acids from fermentation broth by weak base polymer adsorbents. Inci has investigated adsorption equilibria of some carboxylic acids from wastewater streams by activated carbon [9–11]. Aşçı and Hasdemir investigated removal of some carboxylic acid from wastewater by using gel absorbent [12].

Weakly basic ion exchangers are frequently used for recovery of carboxylic acid from aqueous solution or fermentation broth. Liu and Ren [13] studied sorption equilibrium of levulinic acid. Tong et al. [14] reported the purification of lactic acid from fermentation broth with paper sludge as feedstock using Amberlite IRA-92, a weak anion exchanger. Takatsuji and Yoshida [15] found out that DIAION WA30 was a good adsorbent for recovery of organic acids from wine, which contained glucose, ethanol, and various acids. Kanazawa et al. [16,17] investigated sorption equilibria of nine organic acids including monocarboxylic and monosulfonic acids on 16 anion exchangers. Acid separation behavior on a different resin type and basicity [18] and carboxylic acid transport in porous anion exchangers [19,20] were also studied.

The aim of this study is to define separation efficiencies of Amberlite IRA-67 on the adsorption of formic acid from fermentation broth or wastewater stream. Thermodynamic parameters, ΔH°_{ads}, ΔS°_{ads} and ΔG°_{ads}, were calculated. Regeneration was not studied in these experiments.

2. Material and methods

2.1. Material

Formic acid and Amberlite IRA-67 were obtained from Merck Co. Amberlite IRA-67 is a weakly basic gel-type polyacrylic resin with a tertiary amine functional group. It was used without further treatment.

2.2. Equilibrium methods

Five different concentrations of formic acid were prepared for the equilibrium studies. These concentrations

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Table 1
Experimental results of the adsorption of formic acid onto Amberlite IRA-67 at different temperatures (298 K, 318 K, and 328 K).

Initial conc., C_0 (g L^{-1})	Amount of IRA-67 (g)	Equilibrium conc.			Removal of acid		
		298 K, C (g L^{-1})	318 K, C (g L^{-1})	328 K, C (g L^{-1})	298 K (%)	318 K (%)	328 K (%)
23.01	0.25	12.08	12.52	12.78	47.501	45.588	44.458
23.01	0.50	10.20	10.58	10.76	55.671	54.019	53.237
23.01	0.75	8.43	8.79	9.04	63.363	61.799	60.712
23.01	1.00	7.96	8.36	8.54	65.406	63.667	62.885
23.01	1.25	7.42	7.85	8.06	67.753	65.884	64.971
46.02	0.25	23.79	24.28	24.46	48.305	47.240	46.849
46.02	0.50	20.11	20.57	20.88	56.301	55.302	54.628
46.02	0.75	16.38	16.80	17.21	64.406	63.494	62.603
46.02	1.00	15.72	16.51	16.86	65.840	64.124	63.363
46.02	1.25	14.62	15.27	15.69	68.231	66.818	65.906
69.03	0.25	35.04	35.65	36.06	49.239	48.355	47.761
69.03	0.50	29.20	30.03	30.57	57.699	56.497	55.714
69.03	0.75	23.95	24.74	25.23	65.304	64.160	63.450
69.03	1.00	23.27	23.98	24.51	66.290	65.261	64.493
69.03	1.25	22.18	23.11	23.52	67.869	66.521	65.927
92.04	0.25	45.75	46.84	47.19	50.293	49.109	48.728
92.04	0.50	38.54	39.57	40.08	58.126	57.007	56.453
92.04	0.75	31.44	32.50	33.06	65.840	64.689	64.080
92.04	1.00	29.95	31.04	31.57	67.459	66.275	65.699
92.04	1.25	29.18	30.24	30.92	68.296	67.144	66.405
115.05	0.25	55.27	56.39	57.06	51.960	50.986	50.404
115.05	0.50	47.81	48.92	49.43	58.444	57.479	57.036
115.05	0.75	38.74	39.88	40.42	66.327	65.336	64.867
115.05	1.00	36.89	37.95	38.49	67.935	67.014	66.544
115.05	1.25	35.92	37.10	37.65	68.778	67.753	67.275

were 23.01 g L^{-1}, 46.02 g L^{-1}, 69.03 g L^{-1}, 92.04 g L^{-1}, and 115.05 g L^{-1}.

The mixtures of known amount of adsorbent present in Table 1 and 50 mL formic acid solution was prepared, and equilibration was carried out in a thermostatic shaker. So, the period of equilibrium state was determined as 90 min. The samples were shaken for 120 min, and optimum amount of adsorbent was determined as 1.0 g for IRA-67. After equilibration, aqueous phase sample was titrated to determine amount of formic acid by NaOH (0.1N) with phenolphthalein indicator. Each experiment was carried out in three different temperatures (298 K, 318 K, and 328 K). Adsorption isotherms were applied according to optimum amount of IRA-67.

2.3. Kinetic methods

The kinetic experiments were carried out in a 250 mL stirred cell. The cell was equipped with a fish agitator and was rotated with high speed (1100–1200 rpm) to prevent bulk diffusion as controlling step of adsorption kinetics as suggested by Azizian [21]. The volume of solution was 50 mL and amount of IRA-67 is 1.0 g as like as equilibrium experiments. At appropriate time intervals, 1 mL of solution was taken from the vessel and were analyzed by titration method with 0.1N NaOH in indicator phenolphthalein. The kinetic experiments were carried out at 69.03 g L^{-1} concentration of formic acid; each experiment was repeated two times but the average values were used.

2.4. FTIR analysis

Information on the nature of possible interactions between Amberlite IRA-67 and formic acid has been obtained by FTIR spectroscopy. Fig. 1 shows FTIR spectroscopy of Amberlite IRA-67 after (a) and before (b) adsorption, respectively. The broad and strong band at 3275 cm^{-1} was owing to the overlapping of –OH and NH$_2$ stretching vibration. The peaks at 1635 cm^{-1} were attributed to stretching vibration of carboxyl group –C=O. After the adsorption, The stretching vibration peaks at 3275 cm^{-1} and 1635 cm^{-1} were shifted to 3330 cm^{-1} and 1645 cm^{-1}, respectively The results indicated that the adsorption could be carried out by ion exchange between Amberlite LA-2 and –COOH of formic acid via hydrogen atoms.

3. Results and discussion

3.1. Equilibrium studies

In this study, firstly the period of the equilibrium state of the adsorbents was determined; the effect of amount of adsorbent on adsorption was investigated. Secondly, the effect of initial acid concentrations on adsorption was determined. At last, Langmuir and Freundlich isotherms were applied.

3.2. Effect of amount of adsorbent

The effect of adsorbent dose on the extent of solute adsorption was investigated by varying dose from 0.25 g to 1.25 g IRA-67 for each initial formic acid concentration from 23.01 g L^{-1} to 115.05 g L^{-1} at different temperatures (298 K, 318 K, and 328 K). It was observed from Table 1 that as the dose increases the amount of solute adsorbed increases for each initial acid concentration. The maximum adsorption capacity was reached in 1.25 g of IRA-67.

3.3. Effect of initial acid concentration

Different initial formic acid concentrations (23.01 g L^{-1}, 46.02 g L^{-1}, 69.03 g L^{-1}, 92.04 g L^{-1}, and 115.05 g L^{-1}) were studied for IRA-67 adsorbent. It was observed from Table 1 and Fig. 2 that when increasing initial acid concentration from 23.01 g L^{-1} to 115.05 g L^{-1} adsorbed acid concentrations decreased in the efficiency by IRA-67. Efficiency of removal decreased from 67.275% to 44.458% with the increased initial acid concentration of formic acid. This may be explained by the saturation of accessible exchangeable sites of these adsorbents.

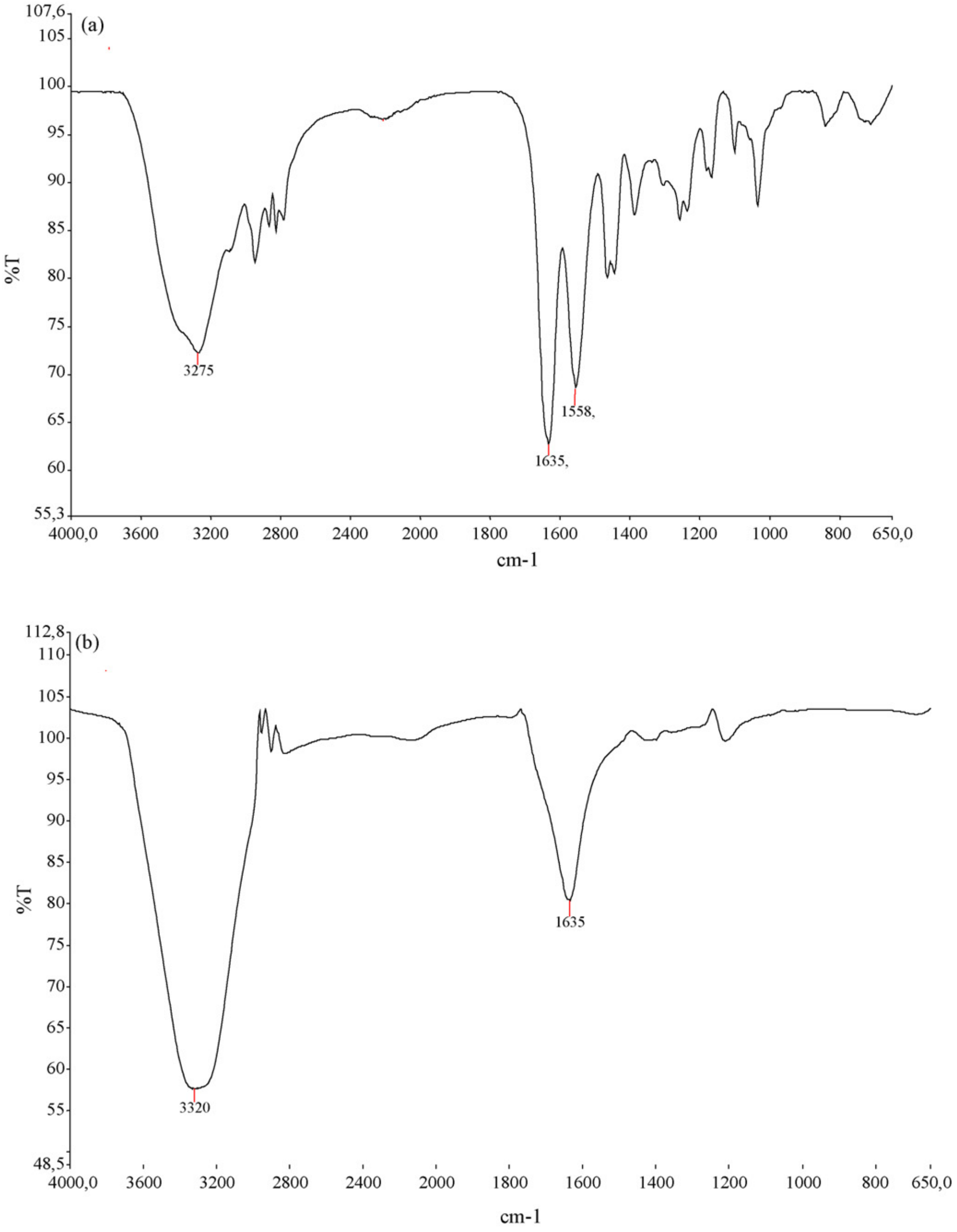

Fig. 1. FTIR spectroscopes of Amberlite LA-2 after (a) and before (b) adsorption.

3.4. *Adsorption isotherms*

Langmuir isotherm and Freundlich isotherm were studied to find equilibrium characteristics of adsorption.

The Langmuir equation [21–23]:

$$q_A = \frac{K_A Q_0 C_e}{1 + K_A C_e} \quad (1)$$

where q_A and Q_0 denote the adsorbent-phase concentrations of formic acid and saturation capacity.

The values of K_A and Q_0 are determined by the following equation to which Eq. (2) is transformed.

$$C_e = -K_L + C_e \frac{Q_0}{q_A}, \quad K_L = \frac{1}{K_A} \quad (2)$$

The values of K_L and Q_0 are determined from the intercept and slope of the straight line in Fig. 3. And calculated parameters of Langmuir equation was presented in Table 2.

Freundlich isotherm was used in this study as second isotherm [24–26].

$$q_A = K_f C_e^{1/n} \quad (3)$$

Table 2
Freundlich and Langmuir isotherm parameters of formic acid onto Amberlite IRA-67.

Temperature (K)	Freundlich parameters				Langmuir parameters			
	log K_f (mg g^{-1})	K_f	n	R^2	$1/Q_0$	Q_0	K_L	R^2
298	2.67	473.47	1.28	0.9649	0.0179	55.866	0.0313	0.996
318	2.38	241.26	1.59	0.9818	0.0180	55.555	0.0110	0.998
328	2.34	218.62	1.57	0.9892	0.0182	54.945	0.0066	0.997

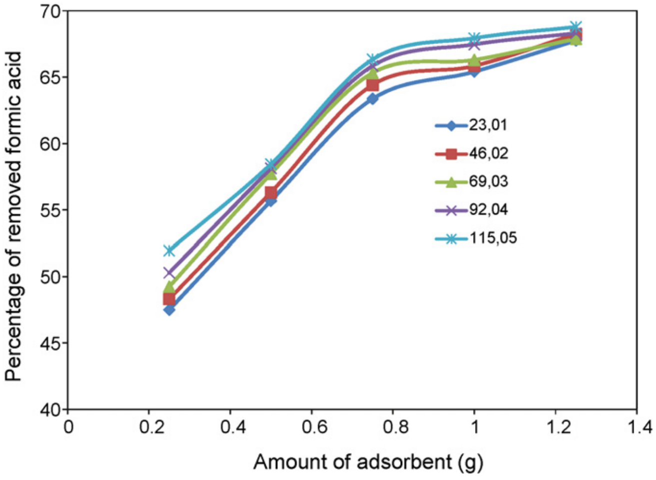

Fig. 2. A plot of effect of initial acid concentration on the adsorption of formic acid at 298 K.

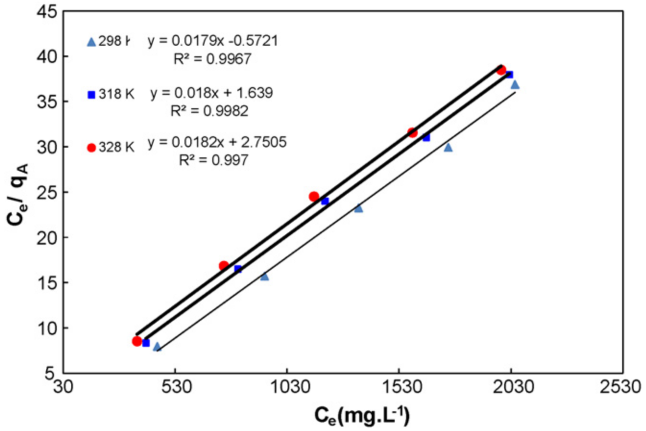

Fig. 3. Langmuir isotherm for amount of 1.00 g IRA-67 at different temperatures.

A logarithmic plot linearizes the equation enabling the exponent n and the constant K_f to be determined.

$$\log q_A = \log K_f + (1/n) \log C_e \quad (4)$$

The values of K_f and $1/n$ at different concentrations were determined from the slope and intercept of the linear plots of $\log q_A$ and $\log C_e$. Fig. 4 shows plot of Freundlich equation isotherm for formic acid adsorption. The results of Freundlich equation were presented in Table 2.

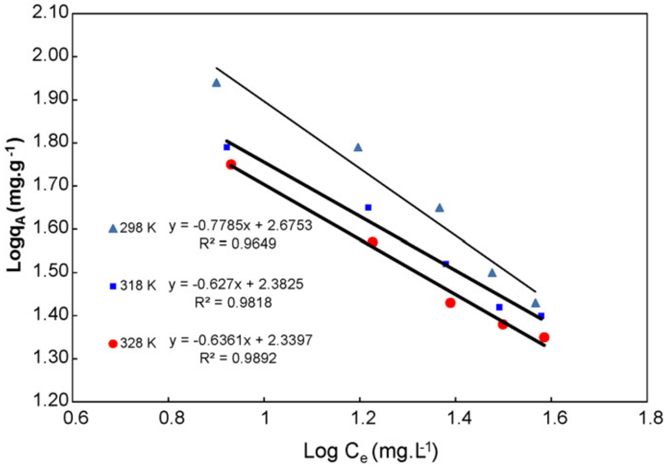

Fig. 4. Freundlich isotherm for amount of 1.00 g IRA-67 at different temperatures.

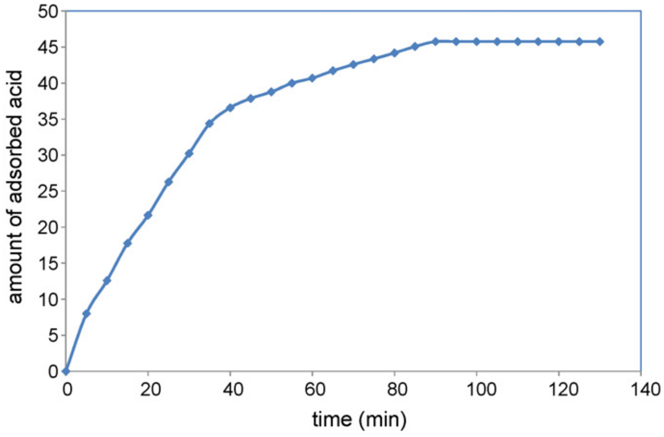

Fig. 5. A plot of effect of contact time on the adsorption of formic acid at 298 K.

The obtained linear plot with a good correlation coefficient confirms that the Langmuir isotherm is a suitable isotherm for adsorption of formic acid onto Amberlite IRA-67. Their R^2 value is over 0.99 for each studied temperature in this work. However, the Freundlich isotherm does not obey the results of adsorption in each temperature. Especially, at 298 K some deviations were observed with Freundlich isotherm.

3.5. *Kinetic studies*

3.5.1. *Effect of contact time*

The effect of contact time for the adsorption of formic acid by activated carbon and Amberlite IRA-67 was studied for a period of 120 min for initial formic acid concentrations of 69.03 g L^{-1} at 298 K. IRA-67 dosage was 1.00 g which is under the selected optimal amount. The effect of contact time on removal of formic acid is shown in Fig. 5. The uptake of adsorbate species is fast at the initial stages of the contact period, and thereafter, it becomes slower near the equilibrium. In between these two stages of the uptake, the rate of adsorption is found to be nearly constant. This is obvious from the fact that a large number of vacant surface sites are available for adsorption during the initial stage, and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases [27].

3.6. *Adsorption rate*

Various models can be used to analyze the kinetics of sorption process. Lagergren [28] suggested a rate equation for the sorption of solutes from a liquid solution. This pseudo-first-order rate equation is

$$\frac{dq}{dt} = k_1(q_A - q) \quad (5)$$

Integrating Eq. (5) for the boundary conditions $t = 0$ to $t = t$ and $q = 0$ to $q = q$ gives

$$\ln\left(\frac{q_A - q}{q_A}\right) = -k_1 t \quad (6)$$

where q and q_A are the grams of solute absorbed per gram of sorbent at any time and at equilibrium, respectively, and k_1 is the rate constant of first-order sorption. The pseudo-first-order equation was used extensively to describe the sorption kinetics [29,30].

If the adsorption kinetics obey pseudo-first-order model, then the plot of $\ln(q_A - q)$ versus t should be linear. Fig. 6 shows the plot

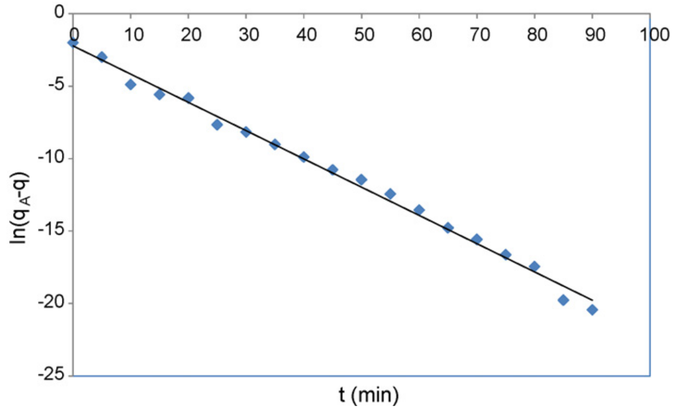

Fig. 6. The linear plot of pseudo-first-order kinetic model at 69.03 g L^{-1} initial formic acid concentration and 1.00 g IRA-67.

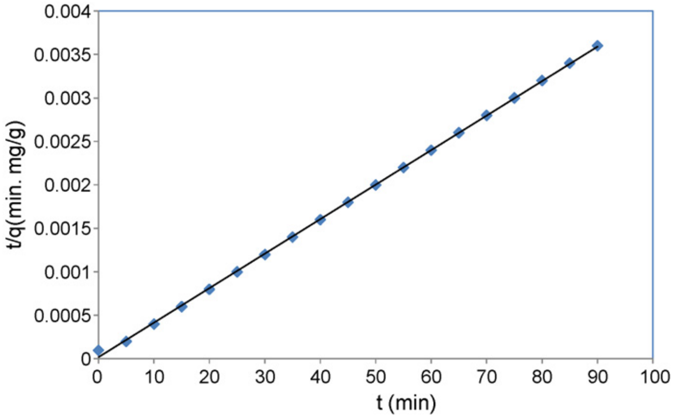

Fig. 7. The linear plot of pseudo-second-order kinetic model at 69.03 g L^{-1} initial formic acid concentration and 1.00 g IRA-67.

for adsorption of formic acid on Amberlite IRA-67. The constants of Eq. (7) were obtained from Fig. 6 at different concentrations and were listed in Table 3 including the correlation coefficients, r^2. As it is clear from Fig. 6 and Table 3, the fitting of experimental data to the pseudo-first-order model is not so good. Although the correlation coefficients are good but as it can be seen in Fig. 6 there is a deviation from this model especially for high times (when t is more than 80 min).

Another model for the analysis of sorption kinetics is pseudo-second-order. The rate law for this system is expressed as

$$\frac{dq}{dt} = k_2(q_A - q)^2 \tag{7}$$

Integrating Eq. (7), for the boundary conditions $t = 0$ to $t = t$ and $q = 0$ to $q = q$, gives

$$\frac{1}{q_A - q} = \frac{1}{q_A} + k_2 t \tag{8}$$

where k_2 is the pseudo-second-order rate constant of sorption. Eq. (8) can be rearranged to obtain a linear form.

$$\frac{t}{q} = \frac{1}{k_2 q_A^2} + \frac{1}{q_A} t \tag{9}$$

The plot of t/q versus t gives a straight line with slope of $1/(k_2 q_A^2)$ and intercept of $1/q_A$. So the gram of solute sorbed per gram of sorbent at equilibrium (q_A) and sorption rate constant (k_2) could be evaluated from the slope and intercept, respectively. The pseudo-second-order model was recently applied for analysis of sorption kinetics from liquid solutions by Ho and McKay [31–33].

The values of q_A and k_2 were obtained from the slopes and intercepts of plots in Fig. 7. These constants and also the correlation coefficients were listed in Table 3. As it can be seen in Fig. 7 this model was fitted to these experimental results very well.

3.7. Thermodynamics studies

3.7.1. Effect of temperature

The effect of temperature on the adsorption of formic acid onto the Amberlite IRA-67 was studied at 298 K, 318 K, and 328 K. Table 1 shows results of adsorption efficiency in different temperatures. It can be seen from the experimental results in Table 1 that the adsorption capacity of the IRA-67 decreases with increasing temperature.

Table 4
Thermodynamic parameters for adsorption of formic acid onto Amberlite IRA-67 at different temperatures (298 K, 318 K, and 328 K).

Temperature (K)	ΔG°_{ads} (kJ mol^{-1})	K_0 (kg^{-1})	ΔS°_{ads} (J mol^{-1} K^{-1})	ΔH°_{ads} (J mol^{-1})
298	−17.721	4521.716	45.628	−43.760
318	−15.472	3663.529		
328	−11.608	3351.833		

As related to temperature effect, the thermodynamic parameters have been calculated for this adsorption system. The free energy change of adsorption ΔG°_{ads} was calculated by using the equation:

$$\Delta G^\circ_{ads} = -RT \ln K_0 \tag{10}$$

where R is the universal gas constant and T is the Kelvin temperature. K_0 is the thermodynamic equilibrium constant for the adsorption process. It was determined by plotting $\ln(C_e/q_A)$ versus C_e and extrapolating to zero C_e as suggested by Khan and Singh [34].

The other thermodynamic parameters, the enthalpy change ΔH°_{ads} and the entropy change ΔS°_{ads} were calculated from the slope and intercept of the plot of $\ln K_0$ against $1/T$ according to the equation:

$$\ln K_0 = \frac{\Delta S^\circ_{ads}}{R} - \frac{\Delta H^\circ_{ads}}{RT} \tag{11}$$

ΔH°_{ads} was obtained from the slope of the straight line and ΔS°_{ads} was determined from the intercept of the graph [35,36]. In order to evaluate the thermodynamic equilibrium constant K_0, the C_e/q_A values were plotted versus C_e values at 298 K, 318 K, and 328 K as seen in Fig. 3. The linear graphs were obtained for all the temperatures. The obtained K_0 parameters were used to calculate ΔG°_{ads} function [37]. The calculated thermodynamic parameters (ΔH°_{ads}, ΔS°_{ads} and ΔG°_{ads}) at different temperatures are given in Table 4. ΔH°_{ads} and ΔS°_{ads} were obtained plotting a graph between $\ln K_0$ and $1/T$ as shown in Fig. 8.

Table 3
Obtained constant for pseudo-first-order and pseudo-second-order kinetic models at 69.03 g L^{-1} initial formic acid concentration.

C_0 (g L^{-1})	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
	q_A (g/g)	k_1 (min^{-1})	R^2	q_A (g/g)	k_2 (g/(g min))	R^2
69.03	2.31×10^{-3}	0.037	0.9934	4.48×10^{-3}	57.92	0.9996

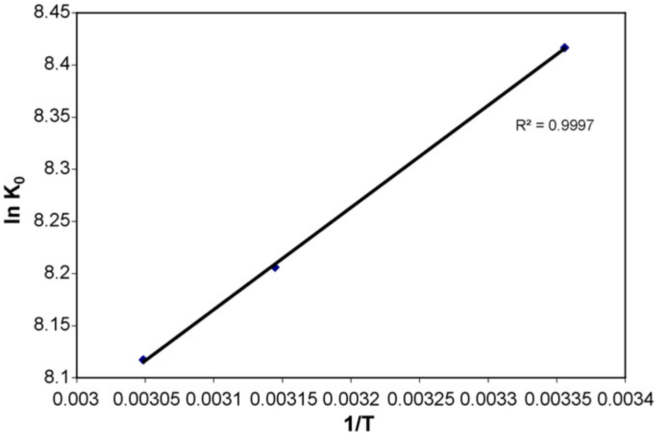

Fig. 8. Plot of $\ln K_0$ against $1/T$.

4. Conclusions

The objectives of this study were to investigate the adsorption data of formic acid removal from wastewater stream using Amberlite IRA-67 in a temperature controlled batch shaker. In light of experimental and calculated results, following conclusions can be presented:

(1) The present study shows that the weakly basic absorbent Amberlite IRA-67 is an effective adsorbent for the removal of formic acid from aqueous solution. The reason of this result: formic acid adsorption on Amberlite IRA-67 is a neutralization reaction shown by the equation: $n(\text{R–N}) + \text{AH}_n \leftrightarrow \text{R–(NH}^+)_n\text{A}^{n-}$ ($n = 1$ for formic acid) and acid-amine complex formed. R–N denotes tertiary amine; [AH] represents formic acid occurs and acid-amine complex $(\text{R–(NH}^+)_n\text{A}^{n-})$ formed.
(2) Adsorption of formic acid by Amberlite IRA-67 was decreased with increasing temperature.
(3) Pseudo-first and second-order models were tried to fit experimental kinetic results. Pseudo-second-order model showed good result with R^2 value over than 0.999.
(4) Freundlich and Langmuir isotherms were applied to equilibrium data at the optimum amount of adsorbent (1.00 g). Langmuir isotherm was fitted more than Freundlich isotherm at all temperatures.
(5) Thermodynamics parameters indicate that adsorption of formic acid onto Amberlite IRA-67 was an endothermic process controlled by ion-exchange mechanism.

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