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Kinetic modelling of the adsorption of nitrates by ion exchange resin

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Abstract

The capacity of ion exchange resins, Amberlite IRA 400, for removal of nitrates from aqueous solution was investigated under different initial concentrations. The suitability of the Freundlich, Langmuir and Dubinin-Radushkevich adsorption models to the equilibrium data was investigated. The equilibrium data obtained in this study were found to follow Freundlich adsorption isotherm. The maximum sorption capacity was 769.2 mg/g at 25 °C. Reversible-first-order, intraparticle diffusion, film diffusion and Bangham models were used to fit the experimental data. The adsorption of nitrates on Amberlite IRA 400 resin follows reversible-first-order kinetics. The overall rate constants were estimated for different initial concentrations. Results of the intra-particle diffusion and the film diffusion models show that the film diffusion was the main rate-limiting step. The low correlation of data to the Bangham's equation also confirms that diffusion of nitrates into pores of the resin was not the only rate-controlling step. The thermodynamic constants of adsorption phenomena, ΔH° and ΔS° were found to be −26.122 kJ/mol and −68.76 J/mol in the range 298–318 K and +19.205 kJ/mol and +68.76 J/mol in the range 318–343 K, respectively. The negative values of the Gibbs free energy (ΔG) demonstrate the spontaneous nature of adsorption of nitrates onto Amberlite IRA 400.

Keywords: Adsorption; Resin; Nitrates; Kinetics

1. Introduction

Several nitrogenous compounds, including ammonia, nitrite and nitrate are frequently present in drinking water [1]. Nitrates can cause several environmental problems. Nitrates and phosphates can stimule eutrophication where pollution is caused in waterways by heavy algal growth, as they are both rate-limiting nutrients for process. A high concentration of nitrate-nitrogen in drinking water leads to the production of nitrosamine, which is related to cancer, and increases the risks of diseases such as methemoglobinemia in new-born infants [2,3].

Several methods that serve to reduce nitrates in drinking water have been developed. The use of biological reactor seems to be the most promising technique in the treatment of high nitrate concentrations. However, maintaining biological processes at their optimum conditions is difficult, and the problems of contamination by dead-bacteria have to be solved to make such processes satisfactory for a safety use in drinking water treatment. Adsorption is a useful process for in situ treatment of underground and surface water, primarily due to it's easy of use [3].

Adsorbent resins are considered the most promising owing to their chemical stability and ability to control surface chemistry [4].

The characteristics of adsorption behaviour are generally inferred in terms of both adsorption kinetics and equilibrium isotherms. They are also important tools to understand the adsorption mechanism, viz. the theoretical evaluation and interpretation of thermodynamic parameters [5,6].

The objective of this study was to investigate equilibrium and kinetic parameters for the removal of nitrates from aqueous solutions by adsorption onto an ionized adsorbent, Amberlite IRA 400. The Langmuir, Freundlich and Dubinin-Radushkevich (D-R) equations were used to fit the equilibrium isotherms. Thermodynamic parameters were also evaluated through adsorption measurements.

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Nomenclature

b	Langmuir constant (cm^3/mg)
C_0	initial concentration in solution (mg/l)
C_e	equilibrium concentration (mg/l)
C_t	concentration at time t (mg/l)
D_p	pore diffusion coefficient (cm^2/s)
D_f	film diffusion coefficient (cm^2/s)
E	free energy of adsorption (kJ/mol)
ΔG	Gibbs free energy (kJ/mol)
ΔH°	enthalpy of adsorption (kJ/mol)
k	overall rate constant of adsorption (min^{-1})
k_1	forward rate constant (min^{-1})
k_2	backward rate constant (min^{-1})
k_d	distribution constant (l/g)
k_f	Freundlich's constant related to the sorption capacity
k_i	intraparticle diffusion parameter ($mg/g\,min^{0.5}$)
m	mass of adsorbent (g)
n	Freundlich's constant related to the sorption intensity of a sorbent
q	the amount of nitrates adsorbed or transferred (mg/l)
q_o	maximum adsorption capacity (mg/g)
q_e	adsorption capacity in equilibrium (mg/g)
q_t	amount of adsorption at time t (mg/g)
R	ideal gas constant (8.314 J/mol K)
R_p	radius of the adsorbent (cm)
ΔS°	entropy of adsorption (J/mol K)
t	time (min)
$t_{1/2}$	time for half adsorption (min)
T	temperature (K)
v	volume of solution (l)
Greek letter	
ε	film thickness (cm)

2. Materials

2.1. Pre-treatment of resin

Before use, the resin was washed in distilled water to remove the adhering dirt and then dried at 50 °C. After drying, the resin was screened to obtain a particle size range of 0.3–0.8 mm.

2.2. The resin characteristics

The main characteristics of the Amberlite IRA 400 (Merck, Darmstadt, Germany), a macroporous anion exchange resin, are given in Table 1.

2.3. Nitrate solutions

The stock solution of NO_3^- used in this study was prepared by dissolving an accurate quantity of KNO_3 in distilled water. A range of dilutions, 1–18 mg/l, was prepared from the stock solution.

Table 1
Characteristics of Amberlite IRA 400 ion exchange resin

Polymer matrix	Polystyrene DVB
Functional group	$-N^+R_3$
Ionic form	Cl^-
Exchange capacity	2.6–3 eq kg^{-1} of dry mass
Appearance	Yellow to golden spherical beads, translucent
Effective size	0.3–0.8 mm
Water retention	42–48%
Visual density in wet state	0.66–0.73 g/ml
True density in wet state	1.07–1.10 g/ml

2.4. Sorption experiments

The pH of the aqueous solutions of NO_3^- was approximately 6.8 and did not varied significantly with the dilution. The effect of temperature on the sorption rate of nitrates on Amberlite IRA 400 was investigated by equilibrating the sorption mixture (800 ml) containing dried resin (2 g) and nitrates (15 mg/l) in a temperature range 298–343 K. The solutions were placed in flasks and stirred for 3 h. Experiments were mainly carried out without initial adjustment of the pH. Preliminary tests showed that the adsorption was complete after 1 h.

The concentration of residual nitrate ions was determined spectrophotometrically according to Rodier protocol [7]. The sorption capacity at time t, q_t (mg/g) was obtained as follows:

$$q_t = (C_0 - C_t)\frac{v}{m} \tag{1}$$

where C_0 and C_t (mg/l) were the liquid-phase concentrations of solutes at the initial and a given time t, respectively, v (l) the volume of solution and m the mass resin (g).

The amount of adsorption at equilibrium, q_e was given by:

$$q_e = (C_0 - C_e)\frac{v}{m} \tag{2}$$

C_e (mg/l) was the concentration of nitrates at equilibrium.

The distribution constant k_d was calculated using the following equation:

$$k_d = \frac{\text{Amount of nitrates in adsorbent}}{\text{Amount of nitrates in solution}} \times \frac{v}{m}. \tag{3}$$

3. Results and discussion

3.1. Adsorption isotherms

Sorption equilibrium is usually described by an isotherm equation whose parameters express the surface properties and affinity of the sorbent, at a fixed temperature and pH [8].

An adsorption isotherm describes the relationship between the amount of adsorbate adsorbed on the adsorbent and the concentration of dissolved adsorbate in the liquid at equilibrium. Equations often used to describe the experimental isotherm data are those developed by Freundlich [9], by Langmuir [10] and by Dubinin-Radushkevich [11]. The Freundlich and Langmuir isotherms are the most commonly used to describe the adsorption characteristics of adsorbent used in water and wastewater.

3.1.1. *Freundlich isotherm (1906)*

The empirical model can be applied to non-ideal sorption on heterogeneous surfaces as well as multilayer sorption and is expresses by the following equation:

$$q_e = k_f C_e^{1/n} \tag{4}$$

n and k_f are the Freundlich constants.

The fit of data to Freundlich isotherm indicates the heterogeneity of the sorbent surface. The magnitude of the exponent $1/n$ gives an indication of the adequacy and capacity of the adsorbent/adsorbate system [12]. In most cases, an exponent between 1 and 10 shows beneficial adsorption. The linear plot of $\ln q_e$ versus $\ln C_e$ (Fig. 1) shows that the adsorption obeys to the Freundlich model. k_f and n were determined from the Freundlich plot and found to be 0.982 and 1.074 (Fig. 1), respectively. n values above 1 indicate favourable adsorption.

3.1.2. *Langmuir isotherm (1916)*

The Langmuir model is probably the best known and most widely applied sorption isotherm. It may be represented as follows:

$$q_e = \frac{q_o b C_e}{1 + b C_e} \tag{5}$$

The Langmuir constants q_o and b are related to the adsorption capacity and the energy of adsorption, respectively.

The linear plot of $1/q_e$ versus $1/C_e$ shows that the adsorption obeys to the Langmuir model (Fig. 2), and gave the following values for q_o and b, 769.2 mg/g and 1.02 cm^3/mg, respectively.

3.1.3. *Dubinin-Radushkevich (D-R) isotherm*

Radushkevich [13] and Dubinin [14] have reported that the characteristic sorption curve is related to the porous structure of the sorbent. The sorption data were applied to the D-R model in order to distinguish between physical and chemical adsorption [15]. The D-R equation was given by:

$$\ln q_e = \ln q_o - \beta \varepsilon^2 \tag{6}$$

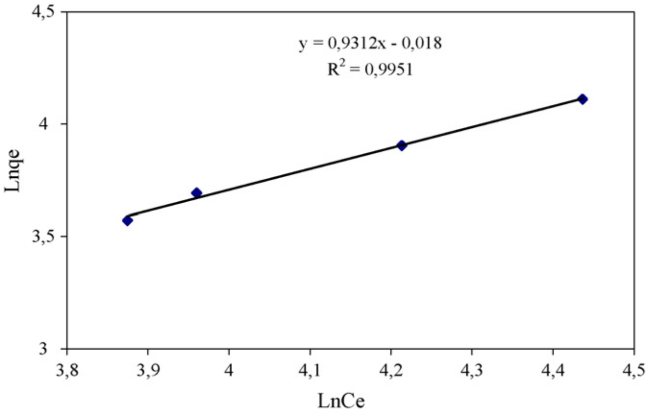

Fig. 1. Linearized Freundlich isotherm (Eq. (4)) for nitrates adsorption by Amberlite IRA 400; T = 25 °C, pH 6.8, adsorbent dose 1.25 g/l.

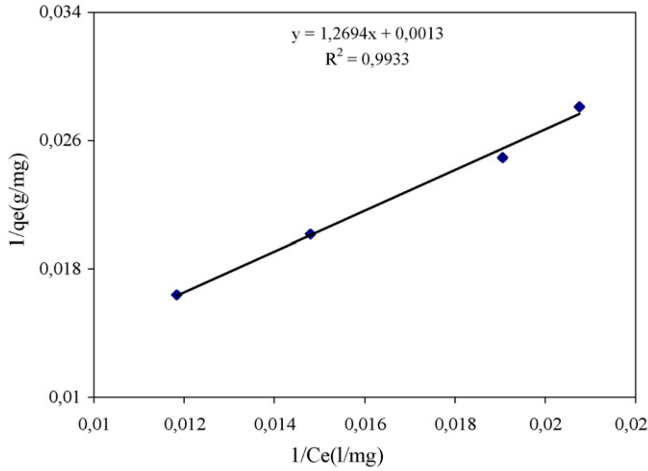

Fig. 2. Linearized Langmuir isotherm (Eq. (5)) for nitrates adsorption by Amberlite IRA 400; T = 25 °C, pH 6.8, adsorbent dose 1.25 g/l.

where β was the activity coefficient related to mean sorption energy and ε the Polanyi potential given by:

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{7}$$

where R was the gas constant (kJ/mol K) and T the temperature (K).

The slope of the plot $\ln q_e$ versus ε gives β (mol^2/J^2) and the ordinate intercept yields the sorption capacity q_o (mg/g). The mean sorption energy (E) is given by $E = 1/\sqrt{-2\beta}$; for a magnitude of E between 8 and 16 kJ/mol, the adsorption process follows chemical ion-exchange [6,16], while values of E below 8 kJ/mol characterize a physical adsorption process [17].

The plot of $\ln q_e$ against ε^2 for nitrate ions sorption on resin is shown in Fig. 3. The E value was 40.8 J/mol, which corresponds to a physical adsorption.

The linear correlation coefficients for Freundlich, Langmuir and D-R are shown in Table 2, and are always greater than 0.980. The Freundlich equation represents a better fit of experimental data than Langmuir and D-R equations.

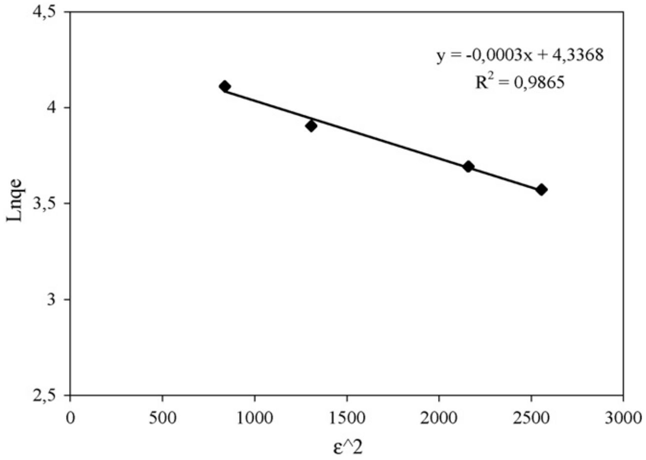

Fig. 3. Radushkevich-Dubinin isotherm (Eq. (6)) for nitrates adsorption by Amberlite IRA 400; T = 25 °C, pH 6.8, adsorbent dose 1.25 g/l.

Table 2
Isotherm parameters collected for removal of nitrates by Amberlite IRA 400

Freundlich constants	
k_f	0.982
n	1.074
R^2	0.9951
Langmuir constants	
q_o (mg/g)	769.2
b (cm^3/mg)	1.02
R^2	0.9933
D-R constants	
q_o (mg/g)	76.5
E (J/mol)	40.8
R^2	0.987

3.2. Adsorption kinetics

3.2.1. Effect of initial concentrations

Predicting the adsorption rate, in addition to the adsorbate residence time and the reactor dimensions, controlled by the system's kinetics, are probably the most important factors in adsorption system design [18].

Preliminary experiments showed high initial rates of adsorption of nitrates followed by lower rates near equilibrium. Kinetics of nitrates removal at 298 K showed high rates during the initial 15 min, and decreased thereafter until nearly constant values after 40 min of adsorption (Fig. 4).

In batch adsorption processes the adsorbate molecules diffuse in porous adsorbent and the rate process usually depends upon $t^{1/2}$ rather than the contact time, t [19,20]:

$$q_t = k_i t^{0.5} \tag{8}$$

The plot of q_t, the amount of adsorbate adsorbed per unit weight of adsorbent versus square root of time has been commonly used to describe an adsorption process controlled by diffusion in the adsorbent particle and consecutive diffusion in the bulk of the solution [21]. Therefore, as can be observed in Fig. 5, adsorption was linear and charaterized by extremely fast uptake. During this phase, nitrates were adsorbed within a $t^{1/2}$ value of about 10 min; this behaviour can be attributed to the rapid use of the most readily available adsorbing sites on the adsorbent surface. After this phase, adsorption became negligible. It may be attributed to a very slow diffusion of adsorbed nitrates from the film surface into the micropores, which are the less accessible sites of adsorption [20,22,23]. Fig. 5 shows two consecutive linear steps during the adsorption of nitrates on Amberlite IRA 400, and the deviation from the straight line indicates that the pore diffusion is not the only rate-limiting step.

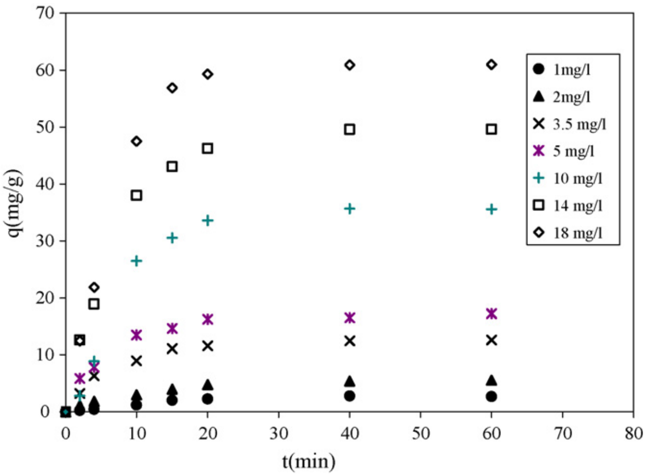

Fig. 4. Time-courses of nitrates adsorption for different initial concentrations of nitric nitrogen.

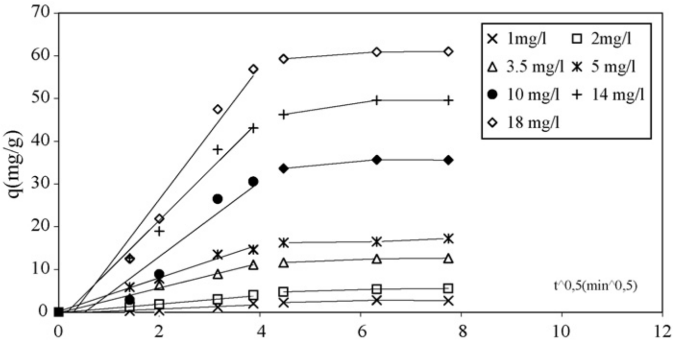

Fig. 5. Effect of $t^{1/2}$ on adsorption of nitrates by Amberlite IRA 400 (Eq. (8)), adsorbent dose 1.25 g/l, pH 6.8.

The slope of the linear portion from Fig. 5 was used to derive values for the rate parameter, k_i, for the intra-particle diffusion (Eq. (8)). The results show that intraparticle diffusion model was valid for the considered system. Kinetic parameters and correlation coefficients obtained by the intra-particle model are given in Table 3. The values of k_i increased for increasing initial concentrations.

Kinetic data can further be used to check whether pore-diffusion was the only rate-controlling step or not in the adsorption system using Bangham's equation [24–26]:

$$\log \log \left(\frac{C_0}{C_0 - qm} \right) = \log \left(\frac{k_B m}{2.303 v} \right) + a \log t \tag{9}$$

As observed, the model did not match experimental data (Fig. 6), showing that the diffusion in the pores of the sorbent was

Table 3
Intraparticle diffusion (Eq. (8)) kinetic parameters for adsorption of nitrates on Amberlite IRA 400 resin at different concentrations

Concentration of nitric nitrogen (mg/l)	Intraparticle diffusion	
	Correlation coefficient R^2	Kinetic parameters, k_i (mg/g min$^{0.5}$)
1	0.874	0.51
2	0.990	1.2
3.5	0.987	2.91
5	0.990	3.93
10	0.903	8.75
14	0.982	11.7
18	0.966	15.5

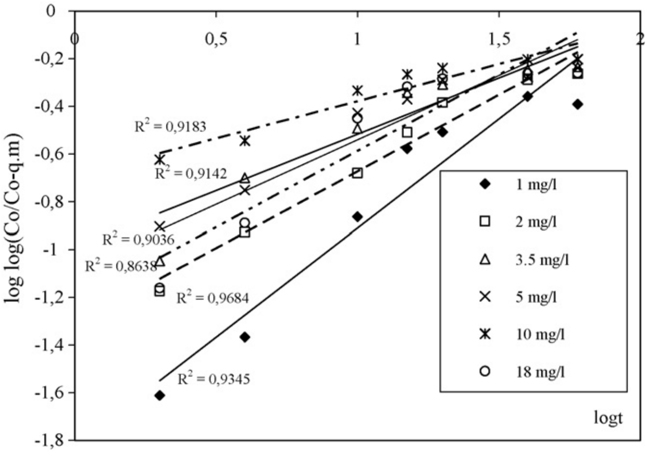

Fig. 6. Fit of adsorption kinetics at different initial concentrations of nitric nitrogen by means of the Bangham's model (Eq. (9)).

not the only rate-controlling step. The correlation coefficients given by the Bangham's equation (Fig. 6) confirmed that the model did not fit satisfactory experimental data. Similar results were previously reported for 4-CP adsorption by macroreticular resins [27] and for adsorption of 4-chlorophenol by XAD-4 [12].

3.2.2. First-order reversible model

When a single species is considered to adsorb on a heterogeneous surface, the adsorption of a solute from an aqueous solution follows reversible-first-order kinetics [28,29]. The heterogeneous equilibrium between the solute in solution and the ion exchange resin may be expressed as:

$$A \underset{k_2}{\overset{k_1}{\rightleftarrows}} B, \tag{10}$$

With k_1 the forward reaction rate and k_2 the backward reaction rate constant. If C_0 (mg/l) was the initial concentration of nitrates and q (mg/l) the amount transferred from the liquid phase to the solid phase at a given time t, then the rate was:

$$\frac{\mathrm{d}q}{\mathrm{d}t} = \frac{-\mathrm{d}(C_0 - q)}{\mathrm{d}t} = k(C_0 - q) \tag{11}$$

where k (min^{-1}) is the overall reaction rate constant. Since k_1 (min^{-1}) and k_2 (min^{-1}) are the rate constants for the forward and the reverse processes, the rate can be expressed as:

$$\frac{\mathrm{d}q}{\mathrm{d}t} = k_1(C_0 - q) - k_2 q \tag{12}$$

If X_e (mg/l) represents the concentration of nitrates adsorbed at equilibrium, then at equilibrium:

$$k_1(C_0 - X_e) - k_2 X_e = 0, \qquad \frac{\mathrm{d}q}{\mathrm{d}t} = (k_1 + k_2)(X_e - q) \tag{13}$$

after integration,The above equation can be rearranged:

$$\ln(1 - U_t) = -(k_1 + k_2)t = -kt \tag{14}$$

where $U_t = q/X_e$ and k was the overall rate constant; U_t, called the fractional attainment of equilibrium of nitrates, is given by the following expression:

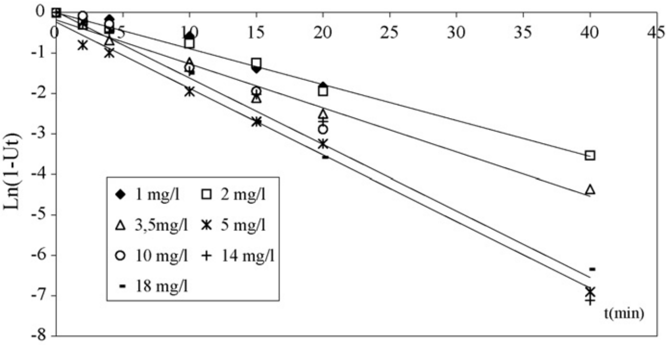

Fig. 7. Fit of adsorption kinetics at different initial concentrations of nitric nitrogen by means of the reversible-first-order model (Eq. (14)).

$$U_t = \frac{C_0 - C_t}{C_0 - C_e} \tag{15}$$

where C_0, C_t and C_e were the initial nitrates concentration, its concentration at a given time t and at equilibrium, respectively. The overall constant rate k for a given concentration corresponded to the slope of the straight line of the plot $\ln(1 - U_t)$ versus t (Fig. 7). The equilibrium constant and the forward and backward constant rates k_1 and k_2 were calculated using Eq. (14) and are collected in Table 4. The high correlation coefficient values, if compared to that given in the available literature [30], confirm the applicability of the model. It could be seen that the forward rate constants for the removal of nitrates were much higher than the backward rate constants for the desorption process (Table 4). The constant rates depend on the adsorption capacity, the diffusion coefficient, the effective mass transfer area, the hydrodynamic of the system and other physicochemical parameters. Our finding agreed with previous results [12].

3.2.3. Diffusion process

In order to assess the nature of the diffusion process responsible for adsorption of nitrates on Amberlite IRA 400, attempts were made to calculate the coefficients of the process. If film diffusion was to be the rate-determining step in the adsorption of nitrates on the surface of the resin, the value of the film diffusion coefficient (D_f) should be in the range 10^{-6} to 10^{-8} cm^2/s. If pore diffusion was to be rate limiting, the pore diffusion coefficient (D_p) should be in the range 10^{-11} to 10^{-13} cm^2/s [31,32]. Assuming spherical geometry for the sorbent, the overall rate constant of the process can be correlated with the pore diffusion coefficient and the film diffusion coefficient independently according to [29]:

Pore diffusion coefficient:

$$D_p = 0.03\frac{R_p^2}{t_{1/2}}, \tag{16}$$

and film diffusion coefficient:

$$D_f = 0.23\frac{R_p \varepsilon}{t_{1/2}}\frac{q}{C_0} \tag{17}$$

Table 4
Constant rates for the removal of nitrates with Amberlite IRA 400 resin using reversible-first-order model (Eq. (14))

C_0 (mg/l)	Correlation coefficients, R^2	Overall rate constant, $k = k_1 + k_2$ (min^{-1})	Forward rate constant, k_1 (min^{-1})	Backward rate constant, k_2 (min^{-1})
1	0.954	0.086	0.068	0.018
2	0.994	0.089	0.077	0.012
3.5	0.978	0.116	0.107	0.009
5	0.985	0.141	0.129	0.011
10	0.980	0.137	0.128	0.008
14	0.975	0.165	0.151	0.013
18	0.992	0.163	0.146	0.017

where R_p was the radius of the adsorbent ($R_p = 0.045$ cm), ε the film thickness (10^{-3} cm) [19], q (mg/l) the amount of nitrates adsorbed and C_0 the initial concentration. By considering the appropriate data and the respective overall rate constants, pore and film diffusion coefficients for various concentrations of nitrates were determined (Table 5). It clearly appeared that nitrates removal on Amberlite IRA 400 resin was controlled by film diffusion since coefficient values were in the range 10^{-6} to 10^{-8} cm^2/s.

3.3. Thermodynamic studies

The amounts of sorption of nitrates ions by Amberlite IRA 400 were measured in the range temperature 298–343 K. Thermodynamic parameters were determined using the following relation [15,33–36]:

$$\ln k_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{18}$$

where k_d was the distribution coefficient, ΔH, ΔS, and T the enthalpy, entropy and temperature (in Kelvin), respectively, and R was the gas constant. The values of enthalpy (ΔH) and entropy (ΔS) were obtained from the slope and intercept of $\ln(k_d)$ versus *1/T* plot. Fig. 8 shows two linear parts in the temperature range explored. A first decreasing part for a temperature range from 318 to 343 K, and a second and increasing linear part for a temperature range from 298 to 318 K. Gibbs free energy (ΔG) was calculated using the well-known equation:

$$\Delta G = \Delta H - T\,\Delta S \tag{19}$$

The slope was positive in the temperature range 298–318 K and negative in a second step, from 318 to 343 K (Fig. 8). The thermodynamic parameters are collected in Table 6.

Table 5
Diffusion coefficients for the removal of nitrates by Amberlite IRA 400 resin

C_0 (mg/l)	Pore diffusion coefficient, Eq. (16) ($\times 10^{-7}$ cm^2/s)	Film diffusion coefficient, Eq. (17) ($\times 10^{-8}$ cm^2/s)
1	0.67	0.73
2	0.78	0.92
3.5	0.84	1.06
5	0.92	1.15
10	1.01	1.29
14	1.26	1.58
18	1.69	2.06

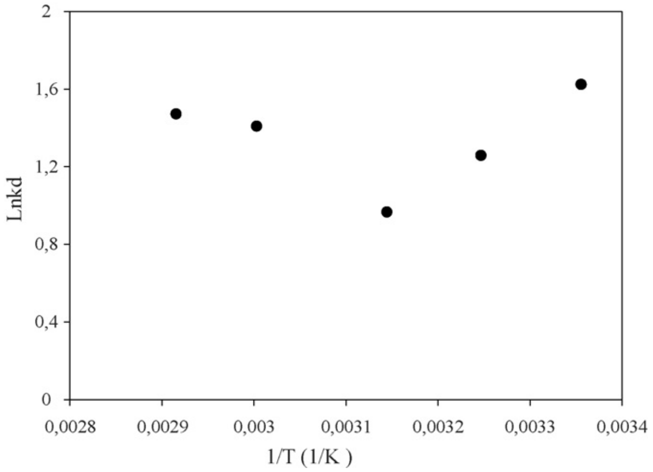

Fig. 8. Estimation of thermodynamic parameters (Eq. (18)) for the adsorption of nitrates onto Amberlite IRA 400.

Table 6
Thermodynamic parameters for the adsorption of nitrates on Amberlite IRA 400

	298 K	308 K	318 K	318 K	333 K	343 K
ΔG (kJ/mol)	−5.631	−4.944	−4.256	−2.66	−3.692	−4.38
ΔH° (kJ/mol)		−26.122			+19.205	
ΔS° (J/mol K)		−68.76			+68.76	

For the first range from 298 to 318 K, the negative value of enthalpy showed that the adsorption of nitrates was exothermic. The negative values of adsorption entropy indicated that the adsorption process was reversible and demonstrated the spontaneous nature of adsorption (Table 6).

In the range 318–343 K, Gibbs free energy (ΔG) decreased for increasing temperatures, indicating that the reaction was spontaneous and favoured by higher temperatures. The positive value of enthalpy indicated that the adsorption was endothermic. The positive value of adsorption entropy showed the irreversibility of the adsorption process and favoured complexation and stability of sorption. The resultant effect of complex bonding and steric hindrance of the sorbed species probably increased the enthalpy and the entropy of the system.

4. Conclusions

These results show that Amberlite IRA 400 is an effective adsorbent for the removal of nitrates from aqueous solution. The equilibrium between nitrates and resin was achieved in approximately 60 min, leading to 96% removal of nitrates. The correlation coefficient showed that Freundlich model gave a better fit of experimental data than Langmuir and Dubinin-Radushkevich models.

Adsorption kinetics was found to follow first order reversible model expression. The film diffusion was the main rate-limiting step. Temperature variations were used to evaluate enthalpy ΔH, entropy ΔS and Gibbs free energy ΔG values. The negative value of ΔG showed the spontaneous nature of adsorption. In the temperature range 298–318 K, ΔH and ΔS were negative, and the reaction was exothermic and reversible. From 318 to 343 K, ΔH and ΔS were positive, and the reaction was endothermic and irreversible. In addition, positive ΔS values favoured complexation and stability of sorption.

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