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Nitrates removal on PUROLITE A 520E resin: kinetic and thermodynamic studies

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ABSTRACT

Ion-exchange technology was studied to remove nitrates using PUROLITE A 520E. Predicting the rate at which adsorption takes place for a given system is probably the single most important factor for adsorber design, with adsorbate residence time and ultimately the reactor dimensions controlled by the system's kinetics. A fixed volume stirred tank reactor was used to study the kinetics of adsorption in a single-component system. Results of the intraparticle diffusion and the film diffusion models show that the film diffusion was the main rate-limiting step at high concentrations of nitrates. Process parameters including the rate of agitation, pH, and initial concentrations of nitrates were examined and the obtained data were modeled using three kinetic models including the pseudo-first-order equation, second-order equation, and intraparticular diffusion model. The best fit of experimental adsorption data was obtained by means of the pseudo-second-order models. Equilibrium data were fitted to the Freundlich, Langmuir, and Dubinin–Radushkevich isotherm equations, and the equilibrium data were found to be well represented by the Langmuir isotherm equation. The thermodynamic constants of adsorption phenomena, ΔH^0 and ΔS^0 were found to be -14.88 kJ/mol and 1.08 J/mol in the range 300–343 K respectively. The negative values of the Gibbs free energy ΔG^0 demonstrate the spontaneous nature of adsorption of nitrates onto PUROLITE A 520E.

Keywords: Adsorption; Nitrates; Resin; Kinetics

1. Introduction

Several nitrogen compounds including ammonia, nitrites, and nitrates have been frequently present in drinking water and various types of agricultural, domestic, and industrial wastewater [1]. Especially nitrates can cause severe problems, including eutrophication and infectious diseases, such as cyanosis and cancer of the alimentary canal [2].

Several methods that serve to reduce nitrates in drinking water were 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 safe use in drinking water treatment. Adsorption is a useful process for *in situ* treatment of underground and surface water, primarily due to its ease 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 behavior are generally inferred in terms of both

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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, PUROLITE A 520E. The Langmuir, Freundlich, and Dubinin–Radushkevich equations were used to fit the equilibrium isotherms. Thermodynamic parameters were also evaluated through adsorption measurement.

2. Materials

2.1. Pretreatment 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 0.3–1.2 mm.

2.2. Resin characteristics

The main characteristics of the PUROLITE A 520E, 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.

2.4. Sorption experiments

The pH of the aqueous solutions of NO_3^{-1} was 6.7 and did not vary significantly with the dilution. The effect of temperature on the sorption rate of nitrates on PUROLITE A 520E was investigated by equilibrating the sorption mixture (500 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:

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

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

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

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

C_e (mg/L) is the concentration of nitrates at equilibrium. The distribution constant k_d, which is a thermodynamic constant and consequently depends only on the temperature, is calculated using the following equation:

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

The calculated distribution constant is then used to find the thermodynamic parameters of adsorption mechanism.

Table 1
Physico-chemical properties of resin PUROLITE A 520 E

Skeleton	Polystyrene cross-linked with DVB of the macroporous type
Functional groupings	Quaternary ammonium
Physical aspect	Opaque balls, beige color
Granulometry	0.3–1.2 mm
Ionic form	Cl^-
Total exchange capacity	0.9 meq/mL min
Humidity	45–52%
Limit of temperature	100°C
Limits of pH	0–14
Real density	1.06

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 expressed 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 $\ln q_e$ vs. $\ln C_e$ (Fig. 1) shows that the adsorption obeys the Freundlich model. k_f and n were determined from the Freundlich plot and found to be 3.331 and 4.01 (Fig. 1), respectively. n values greater than 1 indicate disfavorable 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:

$$q_e = \frac{q_0 b C_e}{1 + bC_e} \tag{5}$$

The Langmuir constants q_0 and b are related to the adsorption capacity and the energy of adsorption, respectively. The linear plot of $1/q_e$ vs. $1/C_e$ shows that the adsorption obeys the Langmuir model (Fig. 2), and gives the following values for q_0 and b, 66.66 mg/g and 4.3×10^{-5} L/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:

$$\ln q_e = \ln q_0 - \beta \varepsilon^2 \tag{6}$$

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

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

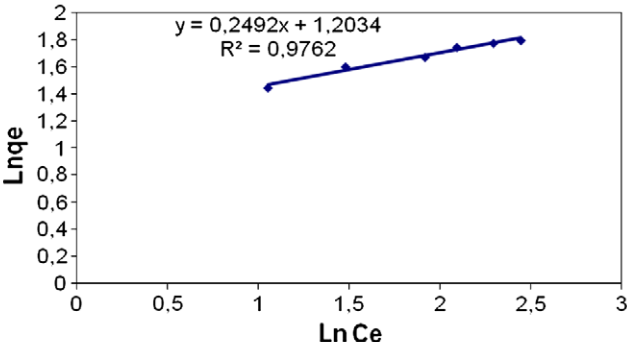

Fig. 1. Linearized Freundlich isotherm (Eq. (4)) for nitrates adsorption by PUROLITE A 520E; $T = 27$°C, pH = 6.7, adsorbent dose 8.4 g/L.

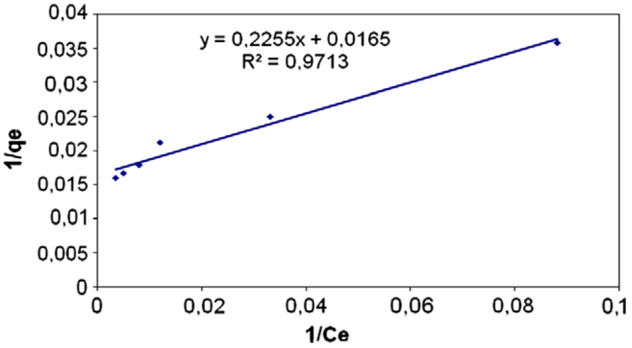

Fig. 2. Linearized Langmuir isotherm (Eq. (5)) for nitrates adsorption by PUROLITE A 520E; $T = 27$°C, pH = 6.7, adsorbent dose 8.4 g/L.

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

The slope of the plot $\ln q_e$ vs. ε^2 gives β (mol^2/J^2) and the ordinate intercept yields the sorption capacity q_0 (mg/g). The free energy E (kJ/mol) of adsorption per molecule of adsorbate is given by $E = 1/\sqrt{1-2\beta}$; for a magnitude of E between 8 and 16 kJ/mol, the adsorption process follows chemical ion exchange [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 126.8 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 0.970 for Freundlich and Langmuir but more less for D–R. The Langmuir equation represents a better fit of experimental data than Freundlich and D–R equations.

3.2. Adsorption kinetics

In order to study the controlling mechanisms of the adsorption process, pseudo-first-order and pseudo-second-order kinetic models and an intra-particle diffusion model were used to test the experimental data. A simple kinetic analysis of adsorption is Lagergren's pseudo-first-order differential equation [18,19].

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{8}$$

where q_e and q_t are the amounts of nitrate adsorbed (mg/g) at equilibrium and at time t (min), respectively, and k_1 (L/min) is the rate constant of first-order adsorption. The pseudo-second-order model can be expressed in the form [18,19].

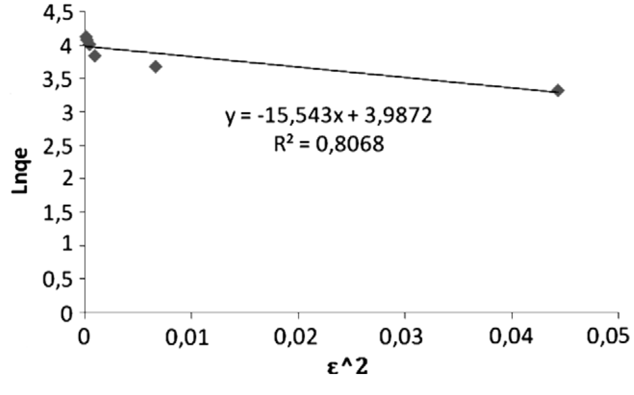

Fig. 3. Radushkevich–Dubinin isotherm (Eq. (6)) for nitrates adsorption by PUROLITE A 520E; $T = 27\,°\mathrm{C}$, pH 6.7, adsorbent dose 8.4 g/L.

Table 2
Isotherms parameters collected for removal of nitrates by PUROLITE A 520E

Freundlich constants	
k_f	3.331
n	4.01
R^2	0.9762
Langmuir constants	
q_o (mg/g)	66.6
b (cm3/mg)	0.043
R^2	0.9959
D–R constants	
q_o (mg/g)	53.9
E (J/mol)	126.8
R^2	0.8068

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{9}$$

where k_2 is the pseudo-second-order rate constant (g/mg min), q_e and q_t are the amounts of nitrate adsorbed (mg/g) at equilibrium and at time t (min), respectively. Adsorption is a multistep process involving transport of the solute molecules from the aqueous phase to the surface of the solid particles followed by diffusion into the interior of the pores. The intra-particle diffusion rate equation is expressed by the following equation [20,21]:

$$q_t = k_p t^{1/2} \tag{10}$$

where k_p is the intra-particle rate constant (g/mg min$^{-1/2}$).

The plot of q_t, the amount of adsorbate adsorbed per unit weight of adsorbent vs. 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.

The fit of these models was checked by each linear plot of $\log(q_e - q_t)$ vs. t (Fig. 4), $(\frac{t}{q_t})$ vs. t (Fig. 5) and q_t vs. $t^{1/2}$ (Fig. 6), respectively, and by comparing to the regression coefficients for each expression. The rate constants, calculated equilibrium uptakes and the corresponding correlation coefficients are given in Table 3. The correlation coefficient is closer to unity (0.9936) and the calculated q_e value is in good agreement with the experimental results for second-order kinetic model. Therefore, the adsorption kinetic could well be approximated more favorably by second-order kinetic model for nitrate.

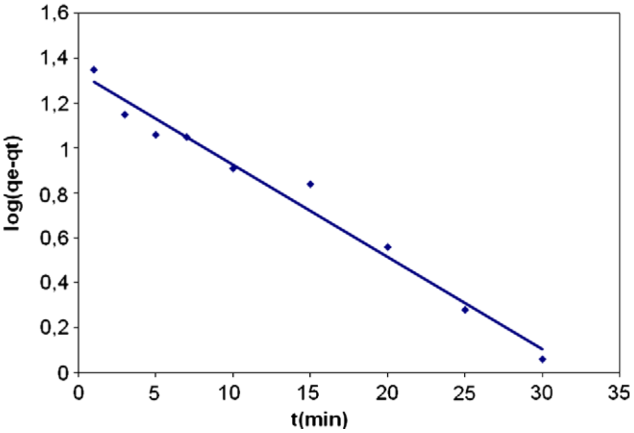

Fig. 4. Linear kinetic plots for nitrate adsorption pseudo-first-order model.

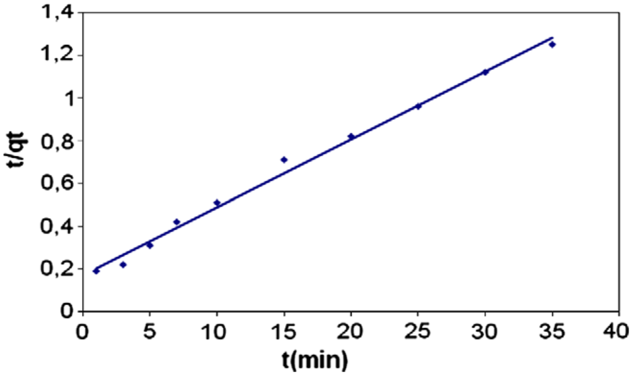

Fig. 5. Linear kinetic plots for nitrate adsorption pseudo-second-order model.

Similar results were also reported by other workers [22,2]. According to the intra-particle diffusion model, a plot of q_t vs. $t^{1/2}$ should be linear if intra-particle diffusion is involved in the adsorption process, and if this line passes through the origin then intra-particle diffusion is the rate controlling step. When the plot does not pass through the origin, this is indicative of some degree of boundary layer control and this further shows that the intra-particle diffusion is not the only rate-limiting step, but other kinetic models may also control the rate of adsorption, all of which may be operating simultaneously [23]. As can be seen from Fig. 6, the linear plot did not pass through the origin. The plot has an initial curved portion, followed by an intermediate linear portion. The first sharper portion is the external surface adsorption or instantaneous adsorption stage. The second portion is the gradual adsorption stage, where the intra-particle diffusion is rate controlled. It was demonstrated by Boyd et al. [24] who proposed a model for the study of sorption behavior, which is in accordance with the observations of Reichenberg [25]. The linearity test of B_t [26] vs. time plots (Fig. 7) is employed to find out the particle diffusion control mechanism. At the lower concentration, the B_t vs. t plots pass through the origin indicating the sorption to be a particle diffusion in nature, but at higher concentrations the line does not pass through the origin signifying the adsorption to be film diffusion.

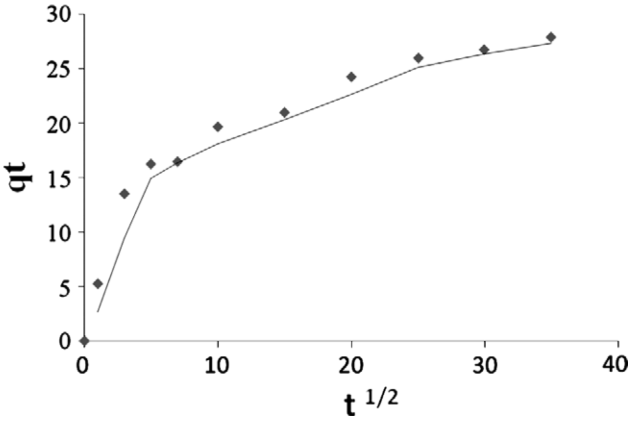

Fig. 6. Linear kinetic plots for nitrate adsorption intra-particle diffusion model.

3.2.1. Effect of initial concentration

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 [27]. Preliminary experiments showed high initial rates of adsorption of nitrates followed by lower rates near equilibrium. Kinetics of nitrates removal at 300 K showed high rates during the initial 15 min and decreased thereafter until nearly constant values after 40 min of adsorption (Fig. 8).

3.2.2. Effect of agitation rate

As can be seen from Fig. 9, there is a small effect of shaking rate on uptake capacity but a great effect on the adsorption rate. At a strong agitation rate, the resistance of the boundary layer surrounding the adsorbent weakens. The rate constants of pseudo-second-order and pore diffusion are calculated in Table 4. As can be shown by the k_2 constant, nitrates are adsorbed faster at higher shaking rate, and kp increases with agitation rate. The highest sorption was at 500 rpm.

Table 3
Kinetic parameters for adsorption rate expressions

q_e(exp) mg/g	First-order kinetic model			Second-order kinetic model			Intra-particle diffusion model	
	k_1 (1/min)	q_e(cal) (mg/g)	R_2	k_2 (g/mg min)	q_e(cal) (mg/g)	R_2	k_p (mg/g min$^{1/2}$)	R^2
25.17	.0944	21.65	0.9782	0.0058	31.54	0.9936	5.3196	0.9117

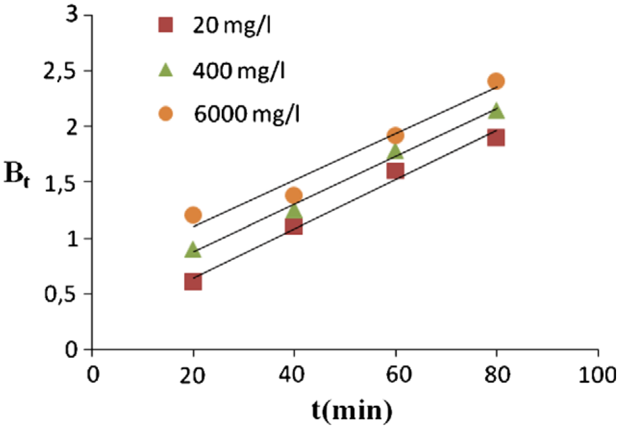

Fig. 7. B_t vs. t plots for nitrate solution of: 20 mg/L; 400 mg/L; and 6,000 mg/L concentrations.

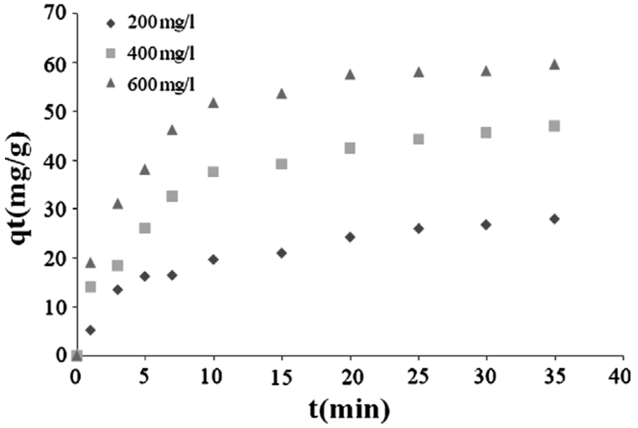

Fig. 9. Time courses of nitrates adsorption for different initial concentrations of nitric nitrogen.

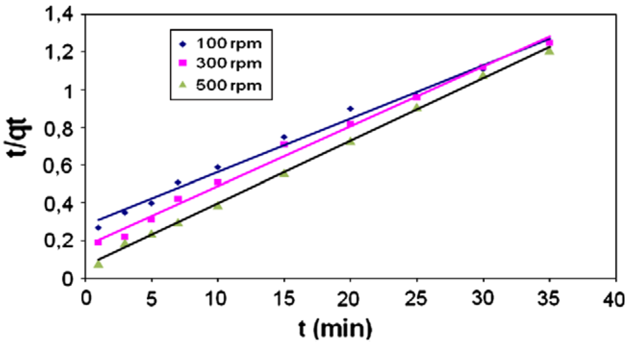

Fig. 8. Effect of agitation rate on adsorption on PUROLITE A 520E.

3.2.3. Effect of pH

pH is an important controlling parameter in all the adsorption processes. A typical experiment with 8.4 mg/l of nitric nitrogen solution, 2 g of adsorbent, and at a temperature of 300 K shows interesting adsorption capacities for a pH range from 2 to 12. PUROLITE A 520E shows therefore a good stability at acidic and alkaline pH. Aqueous phase pH governs the dissociation of active functional sites on the sorbent. Hence, nitrates sorption is critically linked with pH. The highest sorption capacity was at pH 11 and the decrease in sorption capacity for decreasing pH may be attributed to the dissociation of functional groups on the sorbent. The decrease in sorption capacity at alkaline pH values may be due to the competitiveness of NO_3^- and OH^- ions in the bulk. At acidic pH, some functional groups are positively charged when protonated and may electrostatically bind with negatively charged nitrates. The increase in the adsorption for increasing pH may be due to the increase in electrostatic force of attraction between the sorbent and sorbate ions. As can be seen in Table 5 from k_2 and k_p constants, the higher rates of adsorption were obtained at pH 11 in the range of alkaline pHvalues and at pH 4.5 in the range of acidic pH values tested.

3.3. Thermodynamic parameters

The thermodynamic constants free energy change (ΔG^0), enthalpy change (ΔH^0), and entropy change (ΔS^0) were calculated to confirm the nature of the adsorption process. The equilibrium constants (b) obtained from Langmuir model were used to determine the Gibbs free energy changes by the following equation [28–30].

Table 4
Kinetic model parameters for the adsorption of nitrates at different agitation rates on PUROLITE A 520E

Kinetic model parameters		Speed agitation (rpm)		
		100	300	500
Pseudo-first-order	k_1	9.99	9.44	9.16
	R^2	0.9652	0.9782	0.9041
Pseudo-second-order	k_2	4.539	7.44	17.57
	R^2	0.9904	0.993	0.9986
Intraparticular diffusion	k_p	4.9946	5.3196	6.0351
	R^2	0.9898	0.9117	0.6348

Table 5
Kinetic model parameters for the adsorption of nitrates at different pH values on PUROLITE A 520E

Kinetic model parameters		pH		
		3	6.7	8
Pseudo-first-order	k_1	10.01	9.44	10.8
	R^2	0.9177	0.9782	0.9894
Pseudo-second-order	k_2	6.63	7.44	4.66
	R^2	0.9936	0.993	0.9928
Intraparticular diffusion	k_p	5.1767	5.3196	4.8527
	R^2	0.922	0.9117	0.9718

$$Lnb = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} = -Lnk_d \tag{11}$$

The values of enthalpy ΔH^0 and entropy ΔS^0 were obtained from the slope and intercept of $\ln(k_d)$ vs. $1/T$ plot. The enthalpy ΔH^0 and entropy ΔS^0 changes can also be estimated by the last equation. The negative values of ΔG^0 (−7.81, −8.40 and −8.93 kJ/mol) indicate the spontaneous nature of the adsorption for nitrate in the range 27–70°C. The negative value of ΔH^0 (−14.88 kJ/mol) suggests that the adsorption is exothermic. The positive value of ΔS^0 (1.08 kJ/mol K^{-1}) indicates that there is an increase in the randomness in the solid/solution interface during the adsorption process. The resultant effect of complex bonding and steric hindrance of the sorbed species probably increased the entropy of the system.

4. Conclusion

In this study, removal of nitrate from aqueous solutions was investigated by using nitrate selective anion-exchange resin, PUROLITE A 520E. The obtained results show that the last resin is an effective adsorbent for the removal of nitrates from aqueous solution. The equilibrium between nitrates and resin was achieved in approximately 25 min, leading to 97% removal of nitrates. The correlation coefficient showed that Langmuir model gave a better fit of experimental data than Freundlich and Dubinin–Radushkevich models. Adsorption kinetics was found to follow second-order reversible model expression. The film diffusion was the main rate-limiting step. Temperature variations were used to evaluate enthalpy ΔH^0, entropy ΔS^0, and Gibbs free energy ΔG^0 values. The negative value of ΔG^0 showed the spontaneous nature of adsorption. In the temperature range 300–343 K, ΔH^0 were negative and ΔS^0 were positive, and the reaction was exothermic and irreversible.

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