Equilibrium and Kinetics Study of Nitrate Removal from Water by Purolite A100 Resin

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In this study, removal of nitrate from aqueous solutions was investigated by anion exchange resin Purolite A100, using batch method. The experimental equilibrium data were modelled by Langmuir and Freundlich isotherms. The Langmuir equation describes sorption isotherm of nitrates with high correlation coefficients, and better than Freundlich model. According to the Langmuir model, at room temperature the maximum uptake capacity of resin for nitrates was obtained as 19.38 mg/g at 334 K. The effect of temperature on the nitrates ion exchange process onto resin was also investigated, and various thermodynamic parameters, such as ΔG, ΔH, ΔS and E_a have been calculated. The experimental data were analyzed using two kinetics models: pseudo-first order and pseudo-second order. On the basis of these models the kinetics parameters (rate constants and equilibrium sorption capacities) were calculated.

Keywords: equilibrium study, kinetic, ion exchange, nitrates pollution, Purolite A100

Water pollution by nitrate from routine agricultural practices is a common and growing problem in the major agricultural areas of the world. In regions where pesticide contamination is a problem, nitrate concentrations are often high [1]. Nitrate can bring in severe problems, including eutrophication [2] and infection diseases, such as cyanosis [3]. Among several techniques for nitrate removal, such as biological de-nitrification [4], reverse osmosis [5] electro-dialysis [6] and ion exchange [7, 8]. Compared with these methods, ion exchange seems to be simple, effective, and relatively low cost method [9]. As with other candidate technologies such as reverse osmosis and electro-dialysis highly concentrated brine is produced containing the target pollutant, sulphate, bicarbonate and chloride [10].

Several research projects were developed on the nitrates removal from drinking water by exchanging resins of anions; on macroporous resins, type IMAC HP-555 resins [11] type macro-reticuled Amberlite IRA900 [12], type Purolite A850 [13]. Resins whose selectivity is better for nitrates than for sulphates (Duolite A196, Amberlite IRA996) were developed in 1985 with the specific resin Purolite A520-E [9, 14]. The resins are considered the most promising owing to their chemical stability and ability to control surface chemistry [15]. The characteristics of adsorption behaviour are generally inferred in terms of both sorption kinetics and equilibrium isotherms.

The objective of this study was to investigate equilibrium and kinetic parameters for the removal of nitrates from aqueous solutions by adsorption onto new case of anion exchange resin, namely, Purolite A100 resin. The Langmuir and Freundlich equations were used to fit the equilibrium isotherms. Thermodynamic parameters were also evaluated through sorption experiments.

Experimental part

Materials and methods

Purolite A100 resin is a macroporous polystyrenic weak base anion resin having tertiary amine functional groups. Because of its special porosity characteristics Purolite A100 shows excellent properties for removal of naturally occurring organic species from waters along with superior elution efficiency of the organics during regeneration [16].

Experiments were performed with synthetic solutions of nitrate using batch method. Stock solution of 1254 mg/L of sodium nitrate was prepared by salt dissolving in twice-distilled water. Working solutions were obtained by dilution from the stock solution with twice-distilled water. All other reagents were of analytical reagents degree, and were used without further purifications.

The experiments for ion exchange of nitrates from aqueous solutions by resin Purolite A100 were performed in batch technique at constant resin amount of 6 g/L, and various initial nitrate concentrations between 25 – 250 mg NO_3^-/L (± 0.1 mg/L), in 150 mL conical flasks. The effect of temperature on the nitrate ions retention was studied at three different values of temperatures (276, 298, 315 and 334 K). The ion exchange kinetics of nitrates experiments was performed by changing the mixing contact for probes containing 0.3 g resin in 50 mL of 22 mg/L nitrate solution.

After shaking the flasks for 4 h, the phases were separated by filtration, and the nitrate concentration in filtrate was analyzed spectrophotometrically (Digital Spectrophotometer S104D/WPA, chromotropic acid, 1x1 cm glass cell, λ = 412 nm, against a blank solution) [17] using a prepared calibration graph. The IR spectra have been recorded with a Bio-Rad IR Spectrometer, in 400 – 4000 cm^{-1} spectral domain (4 cm^{-1} resolution, KBr pellet technique), before and after the retention of nitrate. The analysis of FT-IR was carried out by examining the spectral bands that are modified, after ion exchange process.

The amount of nitrate retained by the Purolite A100 resin at each temperature was calculated using equation 1:

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad (1)$$

where:

q_e is the the amount of nitrates retained per unit mass of resin (mg/g), at equilibrium;

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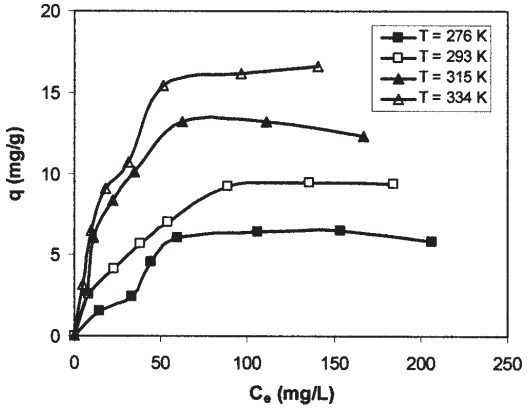


Fig. 1. Effect of temperature on NO_3^- equilibrium sorption to Purolite A100 resin

C_0 and C are the initial and equilibrium concentration of nitrate ions in solution, respectively, (mg/L),

V – volume of initial nitrates solution used (L) and m is the mass of dry resin used (g) [18].

The analysis of equilibrium data was carried out by fitting them to different isotherm models. This is important for an estimation of the practical ion exchange capacity and optimization of the design of retention process. Two models were used to describe the experimental ion exchange isotherms: Langmuir and Freundlich models.

Results and discussions

In a previous study [24] it has been shown that the ion exchange process of NO_3^- on Purolite A100 resin depends on several experimental parameters (initial solution *p*H, resin dose, initial nitrate concentration, and temperature). On the basis of experimental conditions which establish the NO_3 water content at 25 – 200 mg/L, we have considered that a good experiment operation for the retention of NO_3^- on this resin are neutral *p*H and a resin dose of 6 g /L.

Effect of temperature – Ion exchange isotherm

The ion exchange isotherms of NO_3^- on Purolite A100 are show in figure 1. It can be seen that the retention of nitrates on Purolite A100 increases with the increase of temperature. This is because with the increasing of temperature, the attractive forces between positive charged functional groups of resin and nitrate ions become stronger, and the ion exchange process is improved.

The retention equilibrium occurs rapidly at lower nitrates concentration, for all studied temperatures and becomes relatively constant at higher concentrations. We show that for a liquid NO_3^- concentration of 150 mg/L the resin concentration of fixed NO_3^- is 6.49 mg/g for T = 276 K, 9.41 mg/g for T = 298 K, 13.18 mg/g for T = 315 K and respectively 16.59 mg/g for T = 334 K. This fact shows that the increase of temperature improves significantly the efficiency of nitrate removal process. If we consider the temperature effect on resin degradation, the utilization of high operating temperature is not recommended.

The experimental equilibrium data were processed with two isotherm models (Langmuir and Freundlich models) with the aim to establish the best-fit equilibrium.

The Langmuir isotherm model is based on the monolayer adsorption onto homogeneous surface. This model assumed that adsorption forces are similar to the forces in chemical interactions, and can be used to estimate the maximum retention capacity (q_{max}, mg/g), corresponding to ion exchange resin surface saturation. The linear forms of Langmuir equation are:

$$q_e = q_{\max} \frac{K_L C_e}{1 + K_L C_e} \quad (2)$$

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}} \quad (3)$$

where:

K_L is a constant related to the sorption/desorption energy (L/mg);

q_{max} - the maximum retention upon complete saturation of the resin surface (mg/g).

These constants were determined by plotting C_e/q_e against C_e.

The Freundlich model was chosen to estimate the adsorption intensity of the nitrates towards resin, and it is defined by equation (4) and (5), respectively.

$$q_e = K_f \cdot C_e^{(1/n)} \quad (4)$$

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_f \quad (5)$$

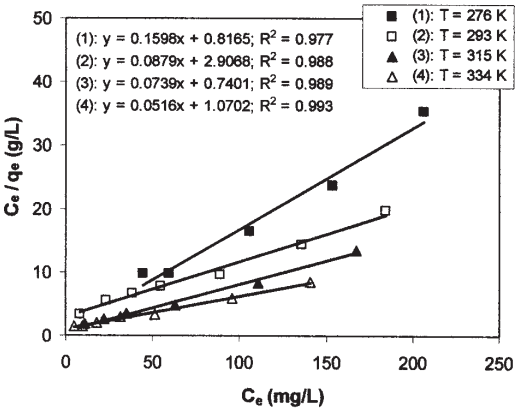
where:

K_f – Freundlich constant, is an indicator of the sorption capacity;

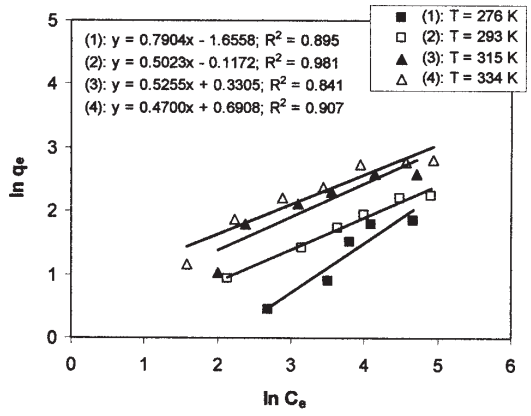
n – constant that characterizes the affinity of the nitrates towards the resin.

A plot of $\ln q_e$ in function of $\ln C_e$, yielding a straight line, indicated the confirmation of the Freundlich sorption isotherm. The Freundlich constants, K_f and n, can be determined from the intercept and slope, respectively [19, 20, 21].

The linear representation of Langmuir and Freundlich isotherms models for nitrates retention on Purolite A100, obtained at studied temperature values 276, 298, 315 and 334 K, are presented in figures 2 (a) and (b).



(a)



(b)

Fig. 2. Experimental data in linearized forms of Langmuir (a) and Freundlich (b) isotherms

Table 1
CONSTANTS OF LANGMUIR AND FREUNDLICH ISOTHERMS AND CORRELATION COEFFICIENTS FOR NITRATES SORPTION BY PUROLITE A100

T (K)	Langmuir constants			Freundlich constants		
	q_{max} (mg/g)	K_L (L/mg)	R^2	n	K_f [(mg/g)/(mg/L)]$^{1/n}$	R^2
276	6.2578	0.0195	0.9772	1.265	0.1909	0.8948
297	11.3765	0.0302	0.9878	1.991	0.8894	0.9813
315	13.5318	0.0425	0.9895	1.903	1.3916	0.8409
334	19.3798	0.0482	0.9930	2.128	1.9953	0.9071

The isotherm models parameters (K_L, q_{max}, K_f and n), computed from the intercept and slope of these linear observed dependencies, and the correlation coefficients (R^2), are summarized in table 1 having temperature as parameter. The values of correlation coefficients (R^2) indicate that the nitrates retention is very well represented by the Langmuir isotherm model ($R^2 > 0.97$) in case of Freundlich model, these have lower values. This means that the resin surface is made up of homogeneous retention patches. The values of maximum adsorption capacity (q_{max}, mg/g) of Purolite A100 resin (table 1) calculated from Langmuir isotherm equation increase with the increasing of temperature, the highest value of 19.38 mg/g being obtained at 334 K.

On the other hand, the Freundlich constants (n) which estimate the retention intensity of nitrate ions on resin surface, is higher than 1 (table 1), at all studied temperatures, indicating favourable ion exchange process, even at higher nitrates concentration. The values of K_f (table 1), which is a measure of the retention degree, suggest that between nitrates ions from aqueous solution and functional groups of resin, electrostatic interactions occur.

Thermodynamic parameters of retention process

In these systems, the free Gibbs energy change (ΔG) is the driving force and the fundamental criteria of spontaneity. As is known, the processes occur spontaneously, at a given temperature if ΔG is a negative quantity. The free energy of the sorption process was calculated from the Langmuir constant using equation (6):

$$\Delta G = -RT \ln K_L \quad (6)$$

where:

R is the universal gas constant, (8.314 J/mol K);

T is absolute temperature, (K).

The other thermodynamic parameters, such as enthalpy change (ΔH) and entropy change (ΔS) may be determined [18, 19], from the slope of linear dependence $\ln K_L$ against T^{-1}, and using equation (7) and equation (8) respectively:

$$T \cdot \Delta S = \Delta H - \Delta G \quad (7)$$

$$\ln K_L = -\left(\frac{\Delta H}{R}\right)\frac{1}{T} + \left(\frac{\Delta S}{R}\right) \quad (8)$$

The activation energy (E_a) was obtained from the slope of $\ln(1 - \theta)$ against 1/T, dependence where the surface coverage (θ) was computed [22] from relation:

$$\theta = (1 - C_e/C_0) \quad (9)$$

where:

C_e C_0, are the initial and residual concentration of nitrates in solution, respectively.

The thermodynamic treatment of the equilibrium experimental results shows that ΔG values were negative at all temperatures investigated. The negative values of ΔG (table 2) indicate the spontaneous nature of nitrates retention on resin.

The values of ΔH and ΔS were obtained from the slope of plots $\ln K_L$ vs 1/T (fig. 3) and from equation (6), and are presented in table 2. The positive values of ΔH for nitrates onto resin confirm the endothermic nature of the sorption process. The positive values of ΔS (table 2) show that the freedom of nitrate ions is not too restricted at the resin surface.

In order to further support the assertion that ion-exchange is the predominant mechanism, the values of activation energy (E_a, kJ/mol) were estimated from experimental data. According with the modified Arrhenius equation, the plot of $\ln(1 - \theta)$ against 1/T gave a linear plot with slope of Ea / R, as it is shown in figure 4.

Table 2
THERMODYNAMIC PARAMETERS OF THE STUDIED NITRATES SORPTION ONTO PUROLITE A100 RESIN

T (K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol K)	E_a (kJ/mol)
276	- 16.286	12.026	102.579	12.183
293	- 18.355		103.689	
315	- 20.628		103.663	
334	- 22.220		102.533	

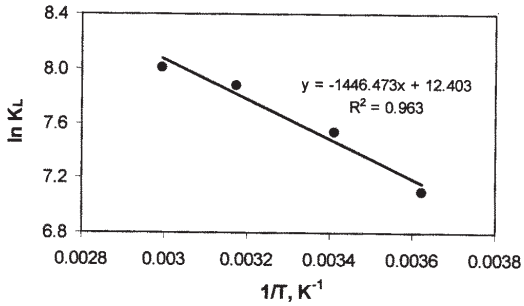


Fig. 3. Plot ln K_L against 1/T for nitrates sorption on resin Purolite A100

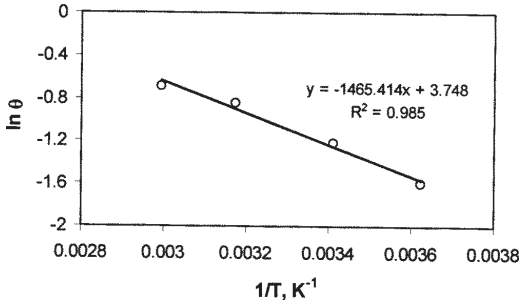


Fig. 4. The dependence ln(1 – θ) against 1/T nitrates sorption on resin Purolite A100

The positive values of E_a indicate that the higher temperature favours the nitrates removal by sorption onto resin. On the other hand, the high values of these thermodynamic parameters suggest that the nitrate retention is chemically controlled process (see also the observation concerning the re-organization of water molecules around resin active sites).

Effect of contact time

Other parameters displaying the efficiency of an exchange process of nitrate ions by anionic resins is the contact time. The influence of contact time between Purolite A100 resin and a nitrates aqueous solution, with an initial concentration of 50.16 mg NO_3^-/L and *p*H = 6.5, at 298 K, on nitrates retention efficiency, is show in figure 5.

As it can be seen from figure 5 the capacity of retention evolves with the contact time in three stages. The removal of nitrates process is very fast during the first stage (I), when for 30 min the values of retention capacity is 4.063 mg/g. In stage two (II), the ion exchange process become slower, the values of retention capacity increasing from 4.063 to 6.93 mg/g, to reach a equilibrium steady state value in about 120 min. After this value the capacity of

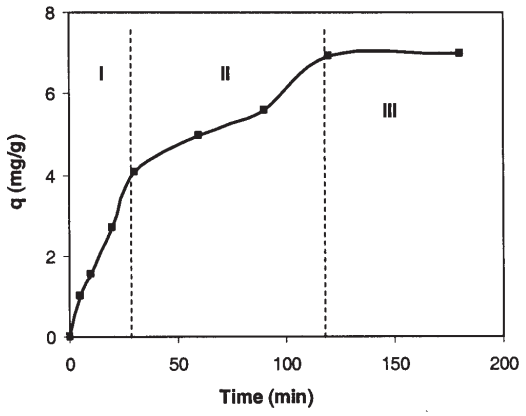


Fig. 5. Effect of contact time for removal of nitrate ion from aqueous solution (resin concentration: 6 g/L)

retention remains approximately constant, (stage III) indicating to reach the equilibrium state. Thus it can be said that the time to removal of nitrates, under the specified conditions is minimum 120 min. The relative low values of contact time required to reach equilibrium state sustain the hypothesis that the retention process of nitrate ions on Purolite A100 resin is controlled by the electrostatic (ion exchange) interactions.

The importance of electrostatic interactions in the retention mechanism of nitrate ions onto Purolite A100 resin is shown by IR spectra recorded before and after nitrate retention (fig. 6). It can be observed that after retention of nitrate ions, do not appear supplementary adsorption bands, so the nitrate retention is not a results of some complexation processes. The comparison of obtained spectra indicates that after nitrate retention, the band at 3439 cm^{-1} corresponding to O–H bond from water molecules hydrogen bonded on resin, is shifted to 3423 cm^{-1}. This modification suggests that after nitrate retention only the re-organization of water molecules around resin surface occurs.

6 g/L)

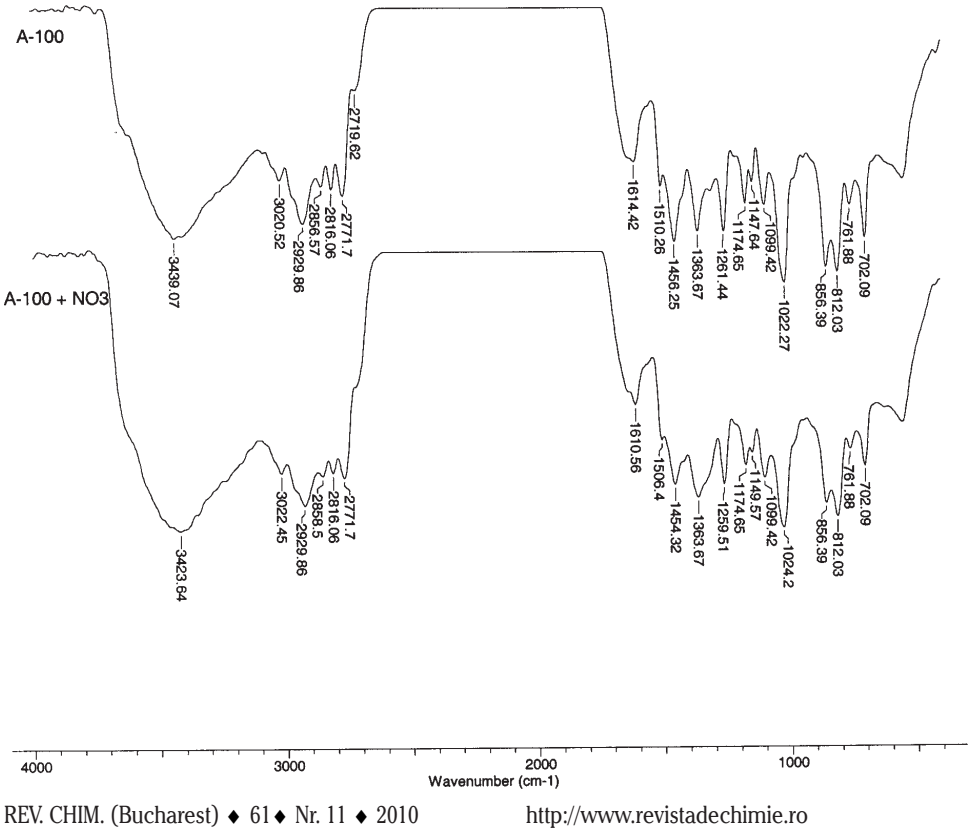


Fig. 6. IR spectra of Purolite A100 resin before and after NO_3^- sorption

Kinetics of the retention process

In agreement with the studies regarding the kinetic modelling of the ion exchange processes occurring on the porous grains of organic ion exchangers [19,23], in the case of removal of NO_3^- ions three rate limiting stages may exist: (i) external diffusion of NO_3^- ions in solution to the grain surface; (ii) internal diffusion of NO_3^- ions in solution from the grain pores; (iii) chemical reactions of ion exchange at the level of functional groups of the ion exchangers , written in the form:

$$R\text{–}N(CH_3)_2]^+OH^- + NO_3^- \rightarrow R\text{–}N(CH_3)_2]^+NO_3^- + OH^- \quad (9)$$

In these conditions, for kinetic modelling of the process, two methods may be used: (a) accomplishment of research for determining the rate controlling (limiting) stage and mathematical description using the corresponding kinetic model; (b) extension of application of the equations of the chemical reactions of ion exchange for the whole process through inserting the effective constant rate that will contain the influences of the external and internal diffusion on the process rate. Since the experimental requirements carried-out in static conditions do not allow the establishment of the rate controlling stage within the study, the second way for kinetic modelling of the ion exchange process was used.

Pseudo-first order model and pseudo-second order model were used to fit the batch contacting ion exchange kinetic data.

The pseudo-first order kinetic equation is expressed by equation (10) and it integral form (11):

$$\frac{dq_t}{dt} = k_1 \cdot (q_e - q_t) \quad (10)$$

$$\lg(q_e - q_t) = \lg q_e - \frac{k_1}{2.303} \cdot t \quad (11)$$

Here k_1 is the effective rate constant for the pseudo-first order kinetic equation; q_e and q_t are the amounts of nitrates retained on weight unit of resin at equilibrium and at time t, respectively.

The rate equation for the pseudo-second order kinetic model may be formulated as differential equation (12) and it integral form (13):

$$\frac{dq_t}{dt} = k_2 \cdot (q_e - q_t)^2 \quad (12)$$

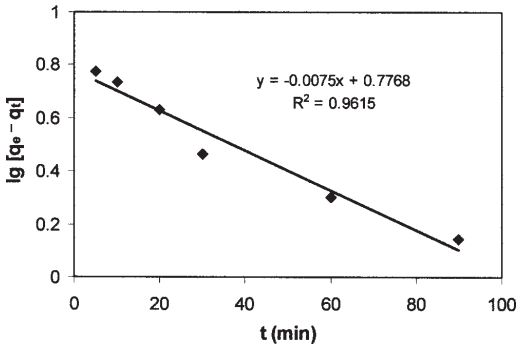
$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e} \quad (13)$$

In the above relations k_2 is the effective rate constant of pseudo-second order kinetic equation, q_e and q_t are the amounts of nitrates retained on weight unit of resin at equilibrium and at time t, respectively [21, 24].

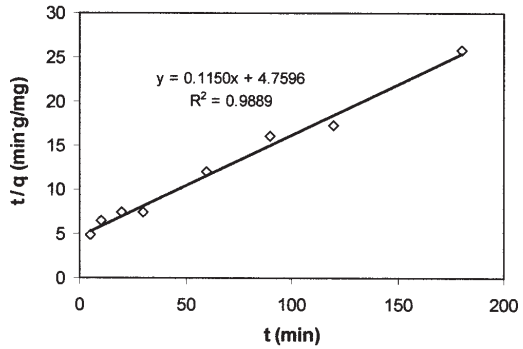
The graphical representation of linear forms for the pseudo-first order and pseudo-second order kinetic models are presented in figures 7 (a) and (b), and the values of kinetic parameters calculated from the slope and intercept of these dependences, together with correlation coefficients (R^2), are summarized in table 3.

It can be seen from table 3 that the equilibrium retention capacity (q_e, mg/g) calculated from the pseudo-first order equation is not far from experimental data (q_e^{exp} = 6.9851 mg/g). But for the pseudo-first order model the correlation coefficient is low; so this model is not suitable to describe the nitrate retention from aqueous solutions on Purolite A100 resin.

The kinetics adsorption data were further fitted by pseudo-second order model and a better fitting was obtained, with high correlation coefficient. In addition, the calculated equilibrium adsorption capacities (q_e, mg/g) are similar with the experimental values suggesting that nitrate retention on Purolite A100 resin are in accordance with the pseudo-second order model. As has been shown it is based on the assumption that the rate-controlling step is the chemical interactions. The good fitting of this model suggests that the rates of ion exchange process is limited only by the availability of nitrate ions and functional groups from resin surface to interact.



a)



(b)

Fig. 7. Pseudo-first order (a) and pseudo-second order (b) models representation for nitrates sorption on Purolite A100 resin (resin concentration: 6 g/L, T = 293 K)

Table 3

THE VALUES OF CORRELATION COEFFICIENTS AND KINETIC PARAMETERS OBTAINED FROM PSEUDO-FIRST ORDER AND PSEUDO-SECOND ORDER KINETIC MODELS FOR NITRATES SORPTION ON PUROLITE A100

q_e^{exp}	Pseudo-first order model			Pseudo-second order model		
(mg/g)	q_e (mg/g)	k_1 (min^{-1})	R^2	q_e (mg/g)	k_2 (g/mg.min)	R^2
6.9851	5.9827	$3.2566 \cdot 10^{-3}$	0.9615	8.6956	$2.7785 \cdot 10^{-3}$	0.9889

Conclusions

The ion-exchange equilibrium and kinetic tests were performed for the case of water NO_3^- removal by Purolite A100 resin. The experimental data were processed by widely used approaches (Langmuir and Freundlich isotherms for equilibrium, pseudo first and second-order models for kinetics). According to the results, the following conclusions can be made: (a) the Langmuir equation describes retention isotherm of nitrates with high correlation coefficients, and better than Freundlich model. According to the Langmuir model, the maximum uptake capacity of resin for nitrates was obtained as 19.38 mg/g, at temperature of 334 K; (b) the values of thermodynamic parameters (ΔG, ΔH and ΔS) indicate that the ion exchange process is spontaneous for all studied temperatures and endothermic; (c) the activation energy (12.183 kJ/mol) further support higher solution temperatures and the obtained value indicates that the nitrate retention is chemically controlled process; (d) the kinetic adsorption data was better fitted by the pseudo-second order kinetic model.

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