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Modelling and adsorption studies of removal uranium (VI) ions on synthesised zeolite NaY

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ABSTRACT

The adsorption of uranium (VI) from aqueous solutions on synthesised zeolite NaY has been studied and the effect of the solution pH, the initial concentration *C*, the solid/liquid ratio *R* and the temperature *T* was investigated. The adsorption process has been modelled using a 2^3 full factorial design in order to study the influence of the main effects and interaction parameters and to optimise the adsorption process. The pH is the most significant parameter affecting uranium (VI) ions' distribution on zeolite NaY. The equilibrium isotherm has been found to follow the Langmuir model. Kinetic studies showed that the pseudo-second-order model correlates our experimental data. Thermodynamic parameters showed the exothermic heat of adsorption and the spontaneity of the adsorption process.

Keywords: Adsorption; Uranium (VI) ions; NaY zeolite; Modelling; Kinetic; Thermodynamic.

1. Introduction

The aluminosilicates with microporous structures are excellent inorganic ion exchangers, having high stability under radioactive irradiation [1–2]. Zeolite exchangers have been widely studied and used in the full-scale separation of ^{137}Cs in waste solutions from nuclear power and fuel reprocessing plants. Harjula et al. [3] studied the effect of Na (I) and K (I) ions on Cs (I) adsorption from nuclear power plant waste solutions on synthetic zeolites. Olmez Aytas et al. [4] have studied the distribution of uranium on zeolite X. Some zeolites, such as mordenite, chabazite and phillipsite, have been used for processing of radioactive liquid wastes, owing to their high ion-exchange capacity and selectivity for Cs [5]. In the literature concerning uranium (VI) adsorption, the synthetic zeolites were limited to a narrow range and relatively few species such as NaY zeolites were investigated [6–8]. Recently, the removal of UO_2^{2+} ions from aqueous solutions on synthetic zeolite NaA was investigated by Nibou et al. [9].

The zeolite Y is of utmost importance in heterogeneous catalysis; for example, it is the active component in catalysts for fluid catalytic cracking [10–11]. Its porous system is relatively complicated and consists of spherical cages, referred to as supercages, with a diameter of 13 Å connected tetrahedrally with four neighbouring cages through windows with a diameter of 8 Å [12]. Supercages are able to accommodate many cations, even those with high hydrated radii, due to

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their aperture and diameter. The exchange of Na^+ with La^{3+} occurs preferably in the supercavities and only a few cations of lanthanum may enter the sodalite cage as reported by Chen et al. [13]. Weckuysen et al. [14] stated that Cr^{3+} cations are preferably available in the supercavities of zeolites NaY as an hexahydrated form $Cr(H_2O)_3{}^{6+}$. Oda et al. [15] reported that the uranium (VI) is present in aqueous solution as an uranyl ion, $UO_2{}^{2+}$, and as in its hydrated state ($UO_2(H_2O)_5{}^{2+}$). The radius of the hydrated uranyl cations was estimated by Krestou et al. [16] at about 6.5 Å. It is less than the mean dimension of NaY zeolite channels (8 Å) indicating that the uranium (VI) bearing species in the solution can have access to the exchangeable sites. To date, the potential application of synthetic NaY in nuclear waste effluents to remove excess uranium (VI) has not yet been fully assessed.

The present investigation deals with the application of NaY zeolite in the removal of uranium (VI) from aqueous solutions. The amount of uranium removed was determined on the basis of the following parameters: solution pH, initial uranium concentration, solid/liquid ratio and temperature. The process has been modelled by means of a 2^3 full factorial design to study the effect of the main and interaction parameters and to optimise the adsorption process. The optimal factors obtained have been applied to nuclear waste effluents. Three most common kinetic models and three adsorption isotherm models were applied to the adsorption of uranium (VI) ions on the synthesised NaY zeolite. They are the pseudo-first-order, the pseudo-second-order and the intraparticle diffusion kinetic models. The thermodynamic parameters were also determined.

2. Materials and methods

2.1. Zeolite synthesis and characterisation

Zeolite NaY is synthesised from aluminosilicate gel with molar composition of $1.1Na_2O$ $1Al_2O_3$ $1.26SiO_2$ $92H_2O$ as previous method [17]. The gel was hydrothermally reacted in Teflon-lined stainless steel autoclaves at 100˚C for 24 h. The product was recovered by filtration, washed with distilled water and dried at 100˚C overnight. The as-synthesised form of zeolite NaY was calcined by heating at 600˚C during 6 h in air.

NaY was characterised by X-ray powder diffraction (Philips PW 1800, using CuKα radiation), at a scan range 2θ from 5 to 50˚. Surface morphology was observed by using scanning electronic microscopy (Philips XL 30) equipped with energy dispersive spectrometry for chemical analysis. Surface area and micropore volume measurements were conducted using Micrometrics ASAP 2010 apparatus. Before each adsorption experiment, the calcined samples were outgassed at 300˚C overnight. Thermogravimetry and differential thermal analysis (M2 BDL-Setaram) were carried out with a heating rate of 5˚C/min in the range from 25 to 900˚C.

Infrared spectroscopy measurements of framework vibrations were conducted using Philips PU 9800 equipment. The samples were diluted in KBr and compressed to give zeolite self-supported pellets.

2.2. Batch adsorption studies

The adsorption of uranium (VI) on NaY zeolite was carried out using the batch method [18]. The solutions of uranium (VI) were prepared by dissolving $UO_2(NO_3)_2.6H_2O$ salt in distilled water at the desired initial concentration. Adsorption experiments were conducted using different amounts of adsorbent with 100 mL of solution containing uranium ions. The content was agitated with a constant stirring rate at 350 rpm. The final uranium (VI) concentration was measured using UV spectrophotometer in presence of Arsenazo III.

The adsorption uptake was calculated by using the following equation:

$$\text{Adsorption uptake } (\%) = (C_0 - C_e)100/C_0 \tag{1}$$

where C_0 and C_e are the initial and the determined final (equilibrium) concentration of studied metal ion in its aqueous solution.

The uptake distribution coefficient K_D is defined as the concentration of the species adsorbed per gram of the adsorbent divided by its concentration per mL in the liquid phase:

$$K_D(\text{mL/g}) = (C_0 - C_e)\,V/C_e m \tag{2}$$

where, V is the volume of the solution in mL and m is the mass of adsorbent in g.

The instantaneous adsorbed uranium quantity in mg/g is determined by the equation:

$$q_e = (C_0 - C_e)V/m \tag{3}$$

3. Results and discussion

3.1. NaY zeolite characterisation

Fig. 1 shows the XRD pattern of the NaY sample; it is obtained with high purity and a good crystallinity. These characteristics are in good agreement with those reported in the literature [17,19–23].

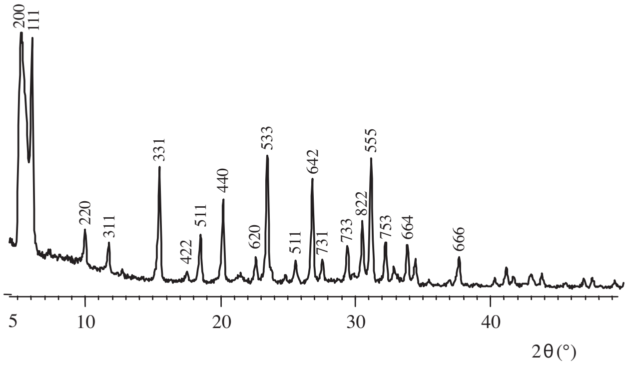

Fig. 1. XRD pattern of pure NaY zeolite.

Scanning electronic micrograph (Fig. 2) shows that NaY zeolite crystallize as rather fine particles with cubic shape with average size of about 1 μm.

TG characterisation of synthesised NaY in air flow shows total weight losses at 900˚C of 29 wt.%. DTA profile shows a large peak at 145˚C which are ascribed to desorption of water located in the zeolite channels. The second peak appears at 265˚C and is due to the decomposition of organic template used as aluminium reagent during the synthesis of NaY zeolite.

Fig. 3 shows FT-IR spectrum of NaY zeolites where the bands at 1,200–450 cm^{-1} are known to assignable to Si–O–Al, Si–O–Si, Si–O, Si–Al and T–O species [12]. In the other hand, the bands at 3,750–3,450 cm^{-1} are attributed to Si–OH, Si–OH–Al and –OH hydroxyl groups. The band at 660 cm^{-1} is known to assignable to Si–O–M where M is the exchangeable Na^+ and UO_2^{2+} ions species [12].

The surface area of the synthesised NaY zeolite was 362 m^2/g and the micropore volume has been found to be 0.118 cm^3/g.

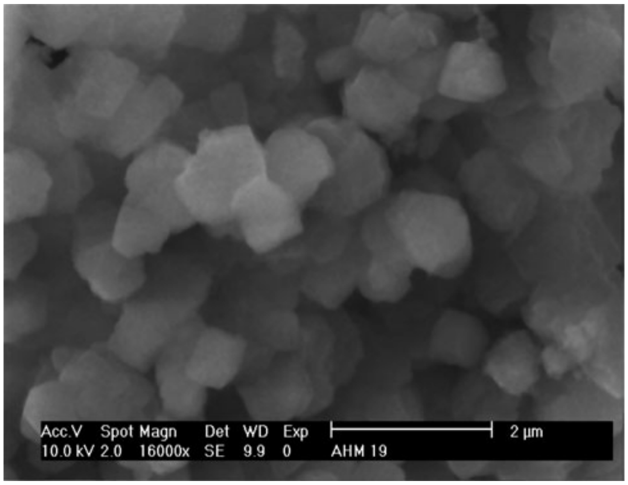

Fig. 2. Scanning electronic micrograph of NaY zeolite.

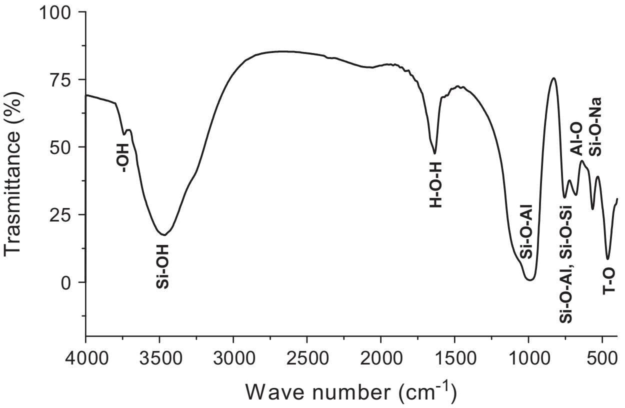

Fig. 3. FT-IR spectrum of NaY zeolite.

3.2. Modelling results

In order to obtain the optimum condition for the adsorption process [24,25], a full factor design of the type 2^3 has been used, where 2 is the number of levels and 3 is the number of factors. Thus, the total number of trial experiments needed for an investigation is 8. If Y_{mod} is the response variable, then the regression equation with 3 parameters and their interaction is given by Akhnazarova and Katarov [26]:

$$\begin{aligned} Y_{\mathrm{mod}} &= a_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_{12}X_1X_2 \\ &\quad + a_{13}X_1X_3 + a_{23}X_2X_3 + a_{123}X_1X_2X_3 \end{aligned} \tag{4}$$

where a_0, a_1, a_2 and a_3 are the linear coefficients, a_{12}, a_{13} and a_{23} are the second-order interaction terms and a_{123} is the third-order interaction term. X_1, X_2 and X_3 are the dimensionless coded factors for the contributions of pH, uranium (VI) concentration and temperature, respectively.

The relations between the coded and actual values are given as:

$$X_1 = (\mathrm{pH} - \mathrm{pH_m})/\Delta\mathrm{pH} \tag{5}$$

$$X_2 = (C - C_{\mathrm{m}})/\Delta C \tag{6}$$

$$X_3 = (T - T_{\mathrm{m}})/\Delta T \tag{7}$$

where $\mathrm{pH_m} = (\mathrm{pH_{sup}} + \mathrm{pH_{inf}})/2$, $\Delta\mathrm{pH} = (\mathrm{pH_{sup}} - \mathrm{pH_{inf}})/2$, $C_{\mathrm{m}} = (C_{\mathrm{sup}} + C_{\mathrm{inf}})/2$, $\Delta C = (C_{\mathrm{sup}} - C_{\mathrm{inf}})/2$, $T_{\mathrm{m}} = (T_{\mathrm{sup}} + T_{\mathrm{inf}})/2$ and $\Delta T = (T_{\mathrm{sup}} - T_{\mathrm{inf}})/2$ and $\mathrm{pH_{sup}}$, $\mathrm{pH_{inf}}$, C_{sup}, C_{inf}, T_{sup} and T_{inf} are the maximum and minimum values of the three variables in the range studied, given in Table 1.

The adsorption percentage (Y_{exp}) was calculated by using the following equation:

Table 1
The 2^3 factorial design for uranium (VI) adsorption onto NaY zeolite

Reduced variables	Factors	Level	
		−1	+1
X_1	pH	2.5	11
X_2	Concentration (ppm)	10	100
X_3	Temperature (℃)	20	60

$$Y_{\exp} = (C_{\mathrm{i}} - C_{\mathrm{f}})100/C_{\mathrm{i}} \tag{8}$$

where C_{i} and C_{eq} are the initial and the determined final (equilibrium) concentration of studied metal ion in its aqueous solution at the beginning and at the end of adsorption experiments, respectively.

The matrix 2^3 using reduced variables and corresponding uranium (VI) adsorption percentage is shown in Table 2.

The regression coefficients were estimated by using the following equations:

$$a_0 = \left[\sum_{1}^{8} Y_i/_8\right] \tag{9}$$

$$a_j = \left[\sum_{1}^{8} X_i Y_i/_8\right] \tag{10}$$

$$a_{ij} = \left[\sum_{1}^{8} X_{ni} X_{ji} Y_i/_8\right] \tag{11}$$

$$a_{ijk} = \left[\sum_{1}^{8} X_{ni} X_{ij} X_{ki} Y_i/_8\right] \tag{12}$$

Table 2
Experimental matrix 2^3 for uranium (VI) adsorption onto NaY zeolite

Experiences	pH	C (ppm)	T (℃)	X_1	X_2	X_3	$Y_{\exp}$
1	2.5	10	20	−1	−1	−1	98.84
2	11	10	20	+1	−1	−1	16.47
3	2.5	100	20	−1	+1	−1	96.52
4	11	100	20	+1	+1	−1	1.91
5	2.5	10	60	−1	−1	+1	99
6	11	10	60	+1	−1	+1	20.23
7	2.5	100	60	−1	+1	+1	98.42
8	11	100	60	+1	+1	+1	3.86

The values of calculated coefficients (Table 3), when incorporated in Eq. (4), take the form of Eq. (13):

$$\begin{aligned} Y_{\mathrm{mod}} = {} & 54.44 - 43.83X_1 - 4.19X_2 + 1.01X_3 \\ & - 3.54X_1X_2 + 0.42X_1X_3 - 0.03X_2X_3 \\ & - 0.48X_1X_2X_3 \end{aligned} \tag{13}$$

Fig. 4 shows the scatter diagram of the investigated adsorption model of uranium (VI) with the model residual variance S^2_{res} value. The residual values do not exceed 10^{-2}%. The significance of each coefficient was assessed using the Fisher's test and Student's t-test methods [26–27]. The regression equation was tested to see how it fitted with the observations, using Fisher's adequacy test at 95% confidence level ($\alpha = 0.05$) and Student's t-test (Fig. 4). Table 4 shows the calculated values F_0 and t^* of different coefficients.

Using tabulated data, values of $F(0.95, 1, 8) = 5.32$ and $t(0.975, 8) = 2.306$ were deduced from respective tables. The coefficients whose F_0 and t are greater than 5.32 and 2.306 only have significant effects. From Table 4 and Fisher's test, it seems that only pH is a significant parameter for uranium (IV) adsorption and Student's t-test confirms it (Fig. 5).

The insignificant terms were neglected from Eq. (13) and our regression equation will have the following form:

$$Y_{\mathrm{mod}} = 54.44 - 43.83X_1 \tag{14}$$

where the pH value of about 2.5 is the optimum.

3.3. Parametric study on uranium (VI) uptake from aqueous solution

3.3.1. Determination of equilibrium time

The kinetic studies were carried out in order to determine the equilibrium time as shown in Fig. 6. The adsorption equilibrium was reached within 120 min under the conditions in Fig. 6.

3.3.2. Effect of pH

The pH values were varied between 2 and 11 using operating conditions: $T = 298$ K, $S/L = 2$ and $[\mathrm{UO_2}^{2+}] = 10$ mg/L. The Fig. 7 shows two maximum pH values at 2.5 and 7, then the uranium (VI) percentage adsorption declines rather rapidly with further increase in pH. The higher adsorption of uranium (VI) on NaY zeolite at pH value 2.5 may be due to the

Table 3
Values of calculated regression coefficients

Exp.	Average	Factors			Interaction factors				Y_{exp}
		1 (pH)	2 (C)	3 (T)	12	13	23	123	
1	+1	−1	−1	−1	+1	+1	+1	−1	98.84
2	+1	+1	−1	−1	−1	−1	+1	+1	16.47
3	+1	−1	+1	−1	−1	+1	−1	+1	96.52
4	+1	+1	+1	−1	+1	−1	−1	−1	1.91
5	+1	−1	−1	+1	+1	+1	−1	+1	99
6	+1	+1	−1	+1	−1	+1	−1	−1	20.23
7	+1	−1	+1	+1	−1	−1	+1	−1	98.42
8	+1	+1	+1	+1	+1	+1	+1	+1	3.86
	(a_0) 54.44	(a_1) −43.83	(a_2) −4.19	(a_3) 1.01	(a_{12}) −3.54	(a_{13}) 0.42	(a_{23}) −0.03	(a_{123}) −0.48	

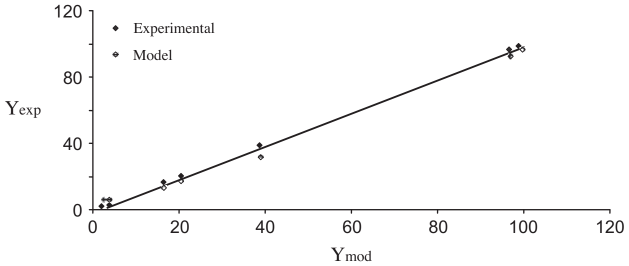

Fig. 4. Scatter diagram of the investigated adsorption model of uranium (VI) on NaY zeolite.

Table 4
Values F_0 and t^* of different coefficients of the Fisher's and student's t-tests

Coefficient	Effect	F_0	t^*
a_1	−43.83	15.742	3.967
a_2	−4.19	0.1438	0.379
a_3	1.01	0.0083	0.91
a_{12}	−3.54	0.1027	0.320
a_{13}	0.412	0.0014	0.037
a_{23}	0.03	7.375E-06	0.003
a_{123}	−0.48	0.0019	0.043

neutralisation of surface charge by an excess of hydrogen ions, thereby, facilitating the diffusion of uranium ions and their adsorption [28]. However, the increase of adsorption uptake at the narrow range of pH ($5 \leq \mathrm{pH} \leq 7$) is mainly due to the precipitation of uranium (VI) species [9,29,30].

3.3.3. Effect of initial uranium (VI) concentration

The uranium concentration was varied between 10 and 100 mg/L using operating conditions: $T = 298\,\mathrm{K}$, $S/L = 2$ and $\mathrm{pH} = 2$. From the results shown in Fig. 8, it appears that the concentration has a little effect on the uranium adsorption uptake in this interval. The adsorption percentage values varied only from 95 to 67.7 in studied range 10–100 mg/L. The uptake adsorption of uranium ions decreases with an increase in the solution concentration indicating that fewer favourable sites become involved when the solution concentration rises. This result is similar to that reported by Nibou et al. [9]. The uranium (VI) ions move towards sodium (I) cations located in the microporous of zeolite and displaces it through the two well-known processes, the ion exchange and the adsorption [9]. However, the adsorption capacity increases with increasing initial uranium concentration. On the other hand, the modelling results showed that the concentration was not a significant parameter for uranium (IV) adsorption.

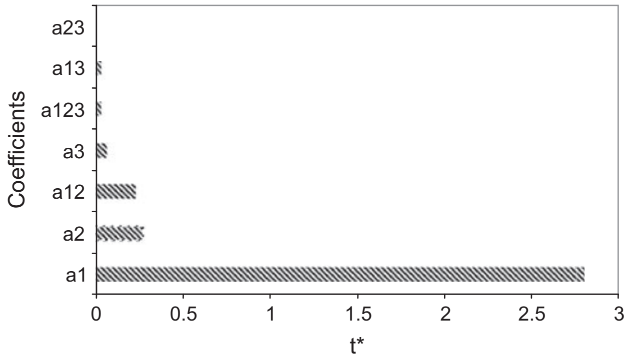

Fig. 5. Significant main and interaction empirical coefficients for uranium (VI) adsorption yields.

3.3.4. Effect of temperature

The effect of temperature on the adsorption of uranium (VI) by NaY zeolite was studied within the

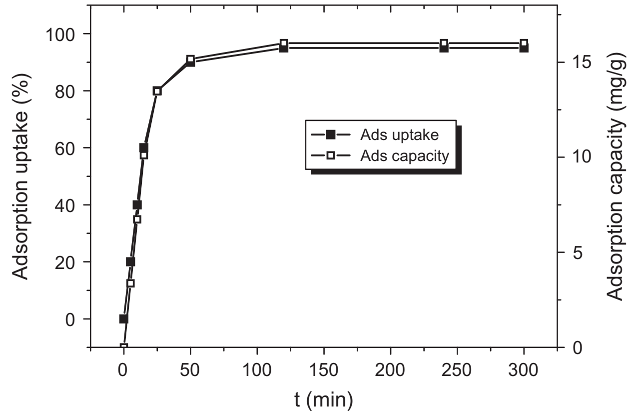

Fig. 6. Effect of contact time on the adsorption uptake and capacity of uranium (VI) from aqueous solution onto zeolite NaY. $[UO_2^{2+}] = 10\,mg/L$, $pH = 2.5$, $S/L = 2$ and $T = 298\,K$.

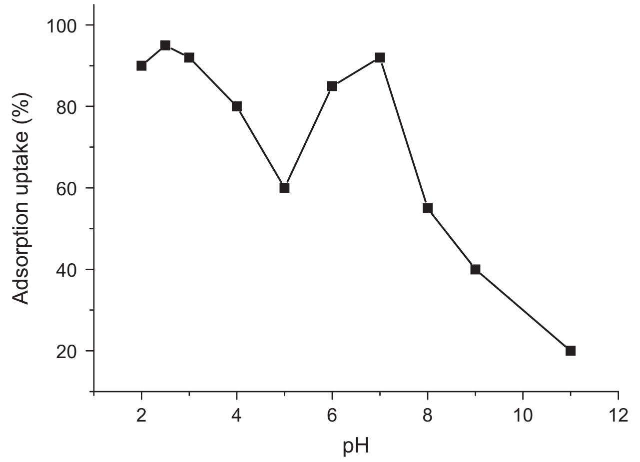

Fig. 7. Effect of pH on the adsorption uptake of uranium (VI) from aqueous solution onto zeolite NaY. $T = 298\,K$, $[UO_2^{2+}] = 10\,mg/L$ and $S/L = 2$.

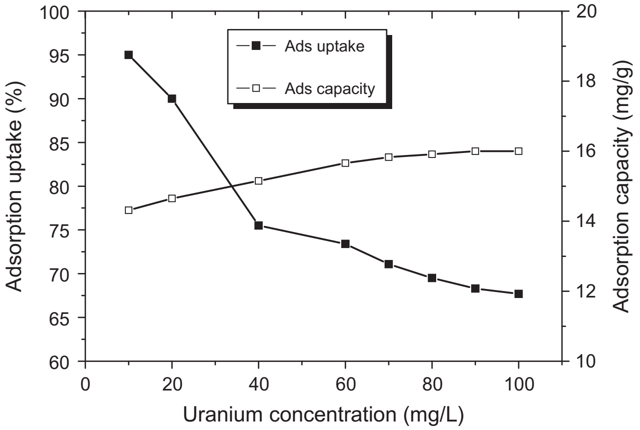

Fig. 8. Influence of initial concentration on the adsorption of uranium (VI) ions on NaY zeolite. $T = 298\,K$, $pH = 2.5$, $t = 2\,h$ and $S/L = 2$.

range from 298 to 343 K while the other parameters were kept constant. Fig. 9 shows that the adsorption uptake decreased with increasing temperature indicating that the process is exothermic.

3.4. Adsorption isotherms

The most common equilibrium isotherms, namely, Dubinin–Radshkevich (D–R), Freundlich or Langmuir models, were used and their linearised forms may be expressed, respectively, by Eq. (15), Eq. (17) and Eq.(18) [31].

$$\mathrm{Log}\, q_e = \mathrm{Log}\, Q_{max} - K_{ads}\, \varepsilon^2 \tag{15}$$

where q_e is the equilibrium uptake (mg/g), Q_{max} is the capacity of saturation theory (mg/g), K_{ads} is the constant of adsorption energy ($J^2/mole^2$) and ε is the potential Polaniyi defined by:

$$\varepsilon = RT \log(1 + 1/C_e) \tag{16}$$

where R is the gas constant (8.314 J/mole K), C_e is the equilibrium metal ions concentration (mg/L) and T is the absolute temperature.

$$\mathrm{Log}\, q_e = \mathrm{Log}\, K_f + 1/n\, \mathrm{Log}\, C_e \tag{17}$$

where K_f (L/g) and n are Freundlich constants

$$C_e/q_e = 1/Q_0 b + C_e/Q_0 \tag{18}$$

where Q_0 (mg/g) (saturated monolayer sorption capacity) and b (L/g) (sorption equilibrium constant) are the Langmuir constants.

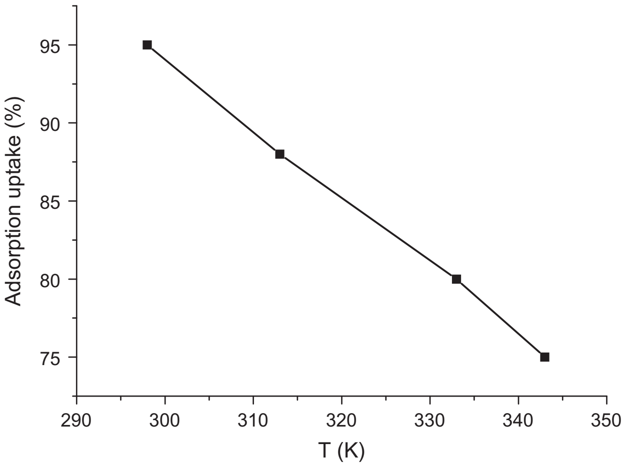

Fig. 9. Effect of temperature on the adsorption uptake of uranium (VI) from aqueous solution onto zeolite NaY. $[UO_2^{2+}] = 10\,mg/L$, $pH = 2.5$ and $S/L = 2$.

The model's parameters and the statistical fits of the sorption data to these equations are given in Table 5. By comparing the correlation coefficients, we can conclude that the Langmuir isotherm was more suitable than the D–R and Freundlich isotherms; as in most cases, the correlation coefficient was higher than 0.99. By using the Langmuir model, the uranium (VI) equilibrium uptake, q_e, for each experiment was calculated and there was a good agreement between Q_0 (15.87 mg/g) and $q_{e(\mathrm{exp})}$ (14 mg/g).

According to Langmuir model, the essential characteristics of the isotherm can be quantified by means of a dimensionless constant separation factor, R_L, represented by:

$$R_L = 1/(1 + bC_0) \tag{19}$$

The value of R_L describing the type of Langmuir isotherm as irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavourable ($R_L > 1$) has been determined and shown in Table 5. It indicated that the adsorption of uranium (VI) onto NaY zeolite was more favourable.

From D–R model results, the value of adsorption energy E_a (10.54 kJ/mol) indicates that the adsorption process is chemical sorption reaction.

3.5. Adsorption dynamics

The pseudo-first-order, pseudo-second-order and intraparticle diffusion models were used to test the experimental data. The linear pseudo-first-order kinetic equation is given as:

$$\ln(q_e - q_t) = \ln q_e - k_{1\mathrm{ads}} t \tag{20}$$

where q_e and q_t are the adsorption capacity at equilibrium and at time t, respectively (mg/g), and $k_{1\mathrm{ads}}$ is the rate constant of pseudo-first-order adsorption (min^{-1}).

The values of $\ln(q_e - q_t)$ were linearly correlated with t. The plot of $\ln(q_e - q_t)$ vs. t should give a linear relationship from which $k_{1\mathrm{ads}}$ and q_e can be determined from the slope and intercept of the plot, respectively. The calculated value of the adsorption capacity, $q_{e,\mathrm{cal}}$ (1.08 mg/g), was lower than the value of experimental adsorption capacity, $q_{e,\mathrm{exp}}$ (14.05 mg/g) (Table 6).

The linear pseudo-second-order kinetic equation is expressed as:

$$t/q_t = (1/k_{2\mathrm{ads}} q_e^2) + (t/q_e) \tag{21}$$

where $k_{2\mathrm{ads}}$ is the rate constant of pseudo-second-order adsorption (g/mg min).

The plot of (t/q_t) and t has been linearly regressed with a correlation coefficient of 0.995 (Table 6); however, the calculated value of the adsorption capacity, $q_{e,\mathrm{cal}}$ (15.13 mg/g), was close to the value of experimental adsorption capacity, $q_{e,\mathrm{exp}}$ (14.05 mg/g).

The intraparticle diffusion model is given as:

$$\ln Y_{\mathrm{id}} = \ln k_{\mathrm{id}} + a \ln t \tag{22}$$

where k_{id} is the rate constant of intraparticle diffusion (min^{-1}) and a is the gradient of linear plots. The plot of intraparticle diffusion obtained by linear regression showed a correlation coefficient of 0.569 suggesting the non-applicability of this model to fit the experimental data (Table 6). Therefore, the adsorption of uranium (VI) on NaY zeolite best followed the pseudo-second-order model and assumes that the rate-limiting step may be chemical adsorption.

3.6. Thermodynamics studies

The thermodynamic parameters obtained for the sorption process were determined by using the following equations:

$$\ln K_D = \Delta S^\circ_{\mathrm{ads}}/R - \Delta H^\circ_{\mathrm{ads}}/RT \tag{23}$$

where K_D is the distribution coefficient (mL/g), $\Delta S^\circ_{\mathrm{ads}}$ is the standard entropy of adsorption (J/mol K), $\Delta H^\circ_{\mathrm{ads}}$ is the standard enthalpy of adsorption (kJ/mol), T is the absolute temperature (K) and R is the gas constant (8.314 J/mol K). The experiments were carried out at

Table 5
Langmuir, Freundlich and Dubinin–Radshkevich (D–R) constant values for the adsoption of UO_2^{2+} species onto NaY zeolite

Langmuir					Freundlich			Dubinin–Radshkevich (D–R)			
Q_0 (mg/g)	$q_{e\ (\mathrm{exp})}$ (mg/g)	b (L/g)	R_L	R^2	n	k_f mg/g	R^2	$Q_{\max}$ mg/g	k_{ads} J^2/mole^2	R^2	E_a kJ/mol
15.87	14.05	0.391	0.113	0.998	0.7	4.04	0.957	279.6	4.9×10^{-9}	0.856	10.54

$S/L = 2$, $[UO_2^{2+}] = 10$ mg/L, pH = 2.5 and $T = 298$ K.

Table 6
Kinetic parameters for the adsorption of UO_2^{2+} species onto NaY zeolite

Pseudo first-order			Pseudo second-order					Intraparticle diffusion	
$q_{e,cal}$ (mg/g)	k_{1ads} (min^{-1})	R^2	q_e(cal) (mg/g)	k_{2ads} (g/mg min)	h (mg/g min)	R^2	$q_{e,exp}$ (mg/g)	K_{id} (min^{-1})	R^2
1.08	0.077	0.845	15.13	5.78×10^{-2}	5.765	0.995	14.05	8.765×10^{-2}	0.569

$S/L = 2$, $[UO_2^{2+}] = 10$ mg/L, pH = 2.5 and $T = 298$ K.

Table 7
Thermodynamic parameters for adsorption of UO_2^{2+} ions on NaY zeolite as function temperature

			ΔG°_{ads} (kJ/mol)			
	ΔH°_{ads} (kJ/mol)	ΔS°_{ads} (J/mol K)	298[a]	313[a]	333[a]	343[a]
UO_2^{2+}	−26.86	−25.00	−19.41	−19.05	−18.54	−18.29

[a] $T(K)$. $T = 298$ K, $S/L = 2$, $[UO_2^{2+}] = 10$ mg/L and pH = 2.5.

293, 313, 333 and 343 K for uranium (VI) concentration 100 mg/L, and the values of $\Delta H^\circ_{ads}$and ΔS°_{ads} were obtained from the slopes and intercepts of linear regression of $\ln K_D$ versus $1/T$.

The standard Gibbs free energy ΔG°_{ads} values (kJ/mol) were determined through the equation:

$$\Delta G^\circ_{ads} = \Delta H^\circ_{ads} - T\Delta S^\circ_{ads} \tag{24}$$

The values of ΔH°_{ads}, ΔS°_{ads} and ΔG°_{ads} are reported in Table 7. One can observe that all ΔG°_{ads} values are negative, indicating that the system reached a more stable energy state after UO_2^{2+} ion exchange. Such results agree with those previously reported for other cations [32]. The observed negative ΔH°_{ads} value confirms the exothermic nature of the process. The chemical adsorption in NaY zeolite is exothermic because UO_2^{2+} ions can maintain their hydration and mobility in the supercages [14].

The entropy ΔS°_{ads} reflects the changes to ion hydration, which occur during the chemical adsorption. Therefore, negative entropy change of such process is possible as reported in the literature [33]. From Table 7, one can observe that ΔS°_{ads} value is negative, which suggests that release of water from the firmly bound hydration of Na^+ contributes to the exchange process as it moves from solid to solution phase [34–36].

3.7. *Treatment of effluent uranium (VI)*

Effluent uranium (VI) samples have been taken from Draria Nuclear Research Centre (Algeria). Then, adsorption uranium (VI) tests have been carried out onto synthesised NaY zeolite using optimal conditions previously determined. Three nuclear waste effluents containing uranium at 100, 85 and 80 mg/L were used. It has been found that the uranium (VI) removal yield was 60.8, 63.5 and 67.2%, respectively, for the three effluents using NaY as adsorbent.

4. Conclusion

The following major conclusions can be drawn based on the above study:

- The synthesised NaY was obtained with high purity and a good crystallinity. After UO_2^{2+} ion exchange, no significant change has been observed neither in the position of the most intense peaks of the NaY nor in its crystallinity.
- The synthesised NaY exhibited a high selectivity towards uranium (VI) removal from aqueous solution.
- The chemical adsorption correlated well with the Langmuir model indicating the applicability of monolayer coverage of the uranium (VI) on the surface of adsorbent.
- The adsorption data were modelled using the pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic equations. It was shown that the pseudo-second-order kinetic model described best the sorption kinetic, indicating that the chemical adsorption reaction was the rate-limiting step.
- Statistical design of experiments for the adsorption of uranium (VI) was an efficient technique to

quantify the effect of variable parameters. The pH is the most significant parameter affecting uranium (VI) adsorption, followed by initial uranium (VI) concentration and temperature. However, the interaction pH - concentration—temperature has a positive effect.

- The thermodynamic parameters showed that the adsorption reaction was a spontaneous process. The negative value of standard enthalpy of adsorption revealed the exothermic nature of the adsorption process. The negative value of entropy reflected that release of water from the tightly bound hydration of sodium Na^+ contributes to the exchange process. The negative values of the Gibbs free energy indicate the feasibility of the process.
- The optimised parameters were applied to three uranium effluents from Draria Nuclear Research Centre (Algeria) and it has been found that synthesised NaY zeolite is an effective adsorbent for UO_2^{2+} ions removal.

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