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Adsorption of copper (II) onto molecular sieves NaY

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ABSTRACT

The adsorption of Cu^{2+} onto NaY zeolite was investigated. The effects of pH, initial concentration, solid/liquid ratio and temperature were studied in batch experiments. The Freundlich and the Langmuir models were applied and the adsorption equilibrium followed Langmuir adsorption isotherm. The uptake distribution coefficient (K_d) indicated that the Cu^{2+} removal was the highest at maximum concentration. Thermodynamic parameters were calculated. The negative values of standard enthalpy of adsorption revealed the exothermic nature of the adsorption process whereas the negative activation entropies reflected that no significant change occurs in the internal structure of the zeolites solid matrix during the sorption of Cu^{2+}. The negative values of Gibbs free energy were indicative of the spontaneity of the adsorption process. Analysis of the kinetic and rate data revealed that the pseudo second-order sorption mechanism is predominant.

Keywords: Adsorption; Copper (II) ions; NaY zeolite; Kinetic; Thermodynamic; Diffusion

1. Introduction

The general composition of aluminosilicates such as zeolites was represented by $M_{y/z}[(SiO_2)_x(AlO_2)_y]$ nH_2O where M is the exchangeable ion metal with a valency z. Zeolites are a suitable choice as they have a great ion exchange capacity and an affinity for heavy metals [1–6]. They are widely used as adsorbents [7–11] and ion exchangers [12–14]. The NaY zeolite ions are located in the sodalite super cage and double hexagonal rings of the zeolite framework. Super cages are able to accommodate many ions, even those with high hydrated radii, due to their aperture (7.5 Å) and diameter (12.5 Å). Sodalite and double hexagonal rings having an aperture of 2.2 Å, are less favourable to ion exchanging, because of steric factors [15].

Mondale et al. [16] studied the exchange of K^+, Na^+ and Ca^{2+} present in zeolites 3A, 4A and 5A respectively for Cu^{2+} and reported the poor response of these adsorbents for Cu^{2+} removal. Biskup et al. [17] studied the exchange ions processes of Cu^{2+} on zeolite A and showed that the exchange processes are controlled by chemical reaction rather than by diffusion. Other authors [6,11,18,19] carried out detailed kinetics investigations about the ion exchange in zeolites, and developed models to describe the effect of degree of ion exchange on the interdiffusion coefficients.

Taking into consideration these approaches, we focus our attention to the use of NaY zeolite in copper (II) adsorption and to use models based on Fick's law in the analysis of experimentally obtained data, and to determine the step describing the mechanism of the reaction according to Eq. (1).

$$Cu^{2+}_{(solution)} + 2Na_{(zeolite)} \leftrightarrow Cu_{(zeolite)} + 2Na^{+}_{(solution)} \qquad (1)$$

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Values of pseudo first order and pseudo second order rate constants were determined and interpreted. The effects of various parameters such as initial metal concentration, pH, solid-liquid ratio (*R*) and temperature on the exchange percentage were investigated. The equilibrium isotherms of zinc ions sorption are also evaluated using Langmuir and Freundlich models. Thermodynamic parameters, i.e., enthalpy of adsorption ΔH°_{ads}, entropy change ΔS°_{ads} and Gibbs free energy ΔG°_{ads} for the sorption of copper ions onto NaY were examined.

2. Materials and methods

NaY zeolite was prepared from aluminosilicate gel with molar composition of $4.8Na_2O$: $1Al_2O_3$: $3.8SiO_2$: $224H_2O$. A typical preparation for NaY was performed in previous work [3]. NaY zeolite was characterized by X-ray powder diffraction (Philips PW 1800, using CuKα radiation), at a scan range 2θ from 5 to 50°. Thermogravimetry and differential thermal analysis (M2 BDL-Setaram) were carried out with a heating rate of 5°C/min in the range from 25–900°C. Surface area measurements were conducted using Micrometrics ASAP 2010 apparatus.

Solution of copper (II) were prepared by dissolving weighed amounts of $CuSO_4 \cdot 7H_2O$ (Merck) in distilled water at the needed initial concentration.

The ion exchange of copper (II) onto NaY zeolite was carried out using the batch method. Batch adsorption experiments were conducted using different amounts of adsorbent with 100 ml of solution containing copper metal ions. The content was agitated with a constant stirring rate at 200 rpm. The concentration of Cu (II) in solutions was measured using a Carl Zeiss model FMD atomic adsorption spectrophotometer. The exchanged sodium Na^+ ions were monitored by ion selective potentiometric method [12] using a sodium and Ag/AgCl reference electrodes and Radiometer potentiometer model.

The adsorption uptake (Eq. (2)) was calculated by using the following equation:

$$\text{Adsorption uptake}(\%) = (C_i - C_{eq})\,100 / C_i \tag{2}$$

where C_i and C_{eq} are the initial and the final concentration of the studied metal ion in its aqueous solution.

The linearized forms of Langmuir and Freundlich models for equilibrium study are given by Eq. (3) and Eq. (4).

$$C_e / q_e = 1 / Q_0 b + C_e / Q_0 \tag{3}$$

$$\text{Log } q_e = \text{Log } K_f + 1 / n \text{ Log } C_e \tag{4}$$

where q_e is the equilibrium uptake (mg/g), C_e is the equilibrium copper ions concentration (mg/l), Q_0 (mg/g) (saturated monolayer sorption capacity), b (l/g) (sorption equilibrium constant) are the Langmuir constants and K_f (l/g) and *n* are Freundlich constants.

In order to study the adsorption dynamics, the pseudo first-order and pseudo second order equations were used (Eq. (5) and Eq. (6)). The integrated forms of these equations are expressed as follows:

$$\text{Log}\,(q_e - q_t) = \text{Log } q_e - K_{1\text{ads}} t / 2.303 \tag{5}$$

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

$$1 / (q_e - q_t) = (1 / q_e) + k_{2\text{ads}} t \tag{6}$$

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

The diffusion coefficients D_i were determined using the Eq. (7):

$$\frac{q_t}{q_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(- \frac{D_i \cdot n^2 \pi^2 \cdot t}{r_0^2} \right) \tag{7}$$

where q_t/q_∞ is the fractional attainment of equilibrium at time *t* of amounts of exchange; r_0 is the radius of crystallite particles assumed to be spherical and *n* is an integer. For short time, Eq. (7) can be rearranged to obtain Eq. (8).

$$\frac{q_t}{q_\infty} = \frac{6}{r_0} \left(\frac{D_i \cdot t}{\pi} \right)^{1/2} \tag{8}$$

3. Results and discussion

3.1. Characterization of elaborated zeolites

Fig. 1 shows XRD patterns of the NaY and copper exchanged NaY samples. The relative intensities and relative broadness in the peaks of the two samples patterns were used to compare their crystallinity. The adsorption of Cu^{2+} on the zeolite NaY sites does not affect its framework. Table 1 shows some characteristics of NaY zeolite. TG characterization in air flow shows total weight losses at 900°C of 27 wt.%. DTA profile shows an endothermic transformation at 50–270°C

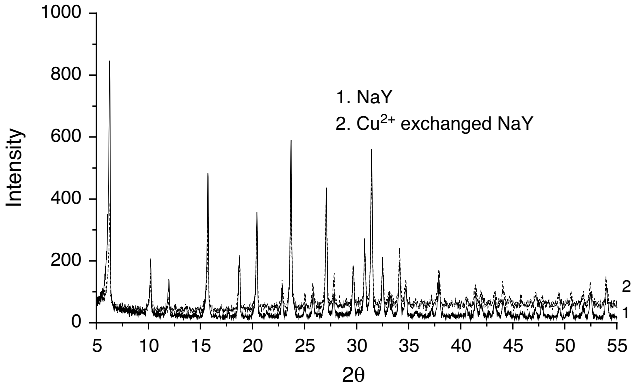

Fig. 1. XRD patterns of (1) NaY and (2) Cu^{2+} exchanged NaY.

which are ascribed to desorption of water and impurities occluded within the NaY zeolite channels. The surface areas of prepared samples were measured by BET method [20]. The results show that high value was obtained for NaY zeolite (453 m^2/g).

3.2. Effect of parameters

The adsorption of Cu^{2+} ions onto NaY zeolite as versus the contact time was studied at 25°C by varying the metal concentration from 100 to 500 mg/l while other parameters were kept constant (Fig. 2). The results show that the uptake adsorption of copper (II) decreases with an increase in the solution concentration indicating that sorbents active sites are saturated and further increase of the concentration will have not effect on the uptake. The maximal level of uptake adsorption reached for NaY zeolite was 51% with copper initial concentration of 100 mg/l. In these conditions, the efficiency increases rapidly and over than 40% of the adsorbed copper (II) occurred within 10 min using NaY zeolite. It seems that 60 min are needed to reach the equilibrium. We noticed in the present study that 60 min were taken as adequate time for equilibrium.

In order to study the dependence of the removal efficiency on pH, experiments were conducted in the pH range 2 to 9 and the results are illustrated in Fig. 3.

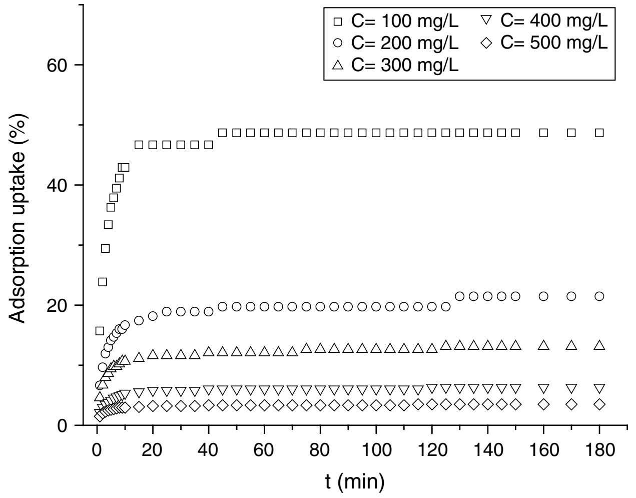

Fig. 2. Adsorption uptake of Cu^{2+} ions onto NaY zeolite as versus the contact time by varying the metal concentration from 100 to 500 mg/l. T = 298 K, pH = 5 and S/L = 2.5.

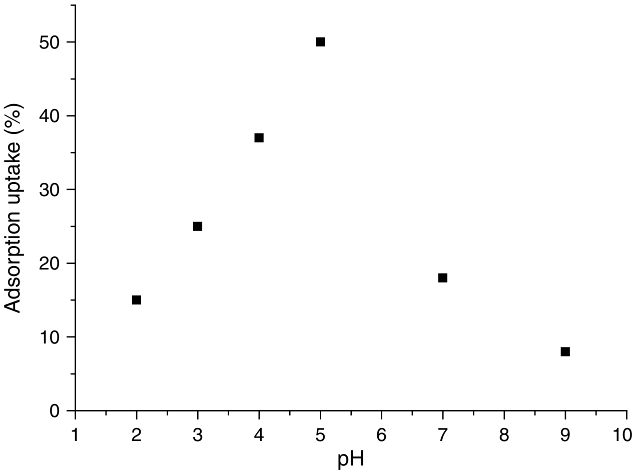

Fig. 3. Effect of pH on the adsorption uptake of copper (II) from aqueous solution onto NaY zeolite. T = 298 K, $[Cu^{2+}]$ = 100 mg/l and S/L= 2.5.

Table 1
Anhydrous chemical composition and characteristics of NaY zeolite

Chemical composition			Surface area (m^2/g)	Microporous volume (cm^3/g)	wt. % loss at 900°C	Dimension of particles (μm)
Na	Si	Al				
4.17	30.50	8.76	453	0.1184	27	3

The maximal level of copper (II) uptake adsorption reached at pH equal 5. In the subsequent investigations, experiments were performed at this solution pH value to avoid any possible hydroxide precipitation [4].

The uptake adsorption of copper (II) ions onto NaY at different temperatures (25 to 50°C) is presented in Fig. 4. The results showed that the uptake adsorption decrease with the increase in temperature.

3.3. Equilibrium isotherms

The Langmuir and Freundlich adsorption isotherms of copper (II) on zeolites NaY are shown in Fig. 5. The model parameters and the statistical fits of the sorption data to these equations are given in Table 2. The results show that Langmuir model describes better the sorption data with a correlation factor R^2 values > 0.99. It can be concluded that the Langmuir isotherm was more suitable than the Freundlich. Thus, indicating the homogeneity of the active sites.

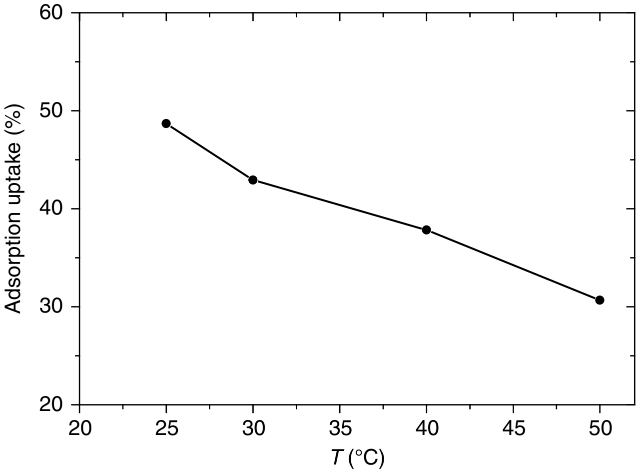

Fig. 4. Effect of temperature on the adsorption uptake of copper (II) from aqueous solution onto zeolite NaY. $[Cu^{2+}]$ = 100 mg/l, pH (Cu^{2+}) = 5 and S/L = 2.5.

3.4. Adsorption dynamics

The values of log ($q_e - q_t$) (Eq. (5)) were linearly correlated with t. The plot of log ($q_e - q_t$) versus t should give a linear relationship from which k_{1ads} and q_e can be determined from the slope and intercept of the plot, respectively (Fig. 6 (a)).

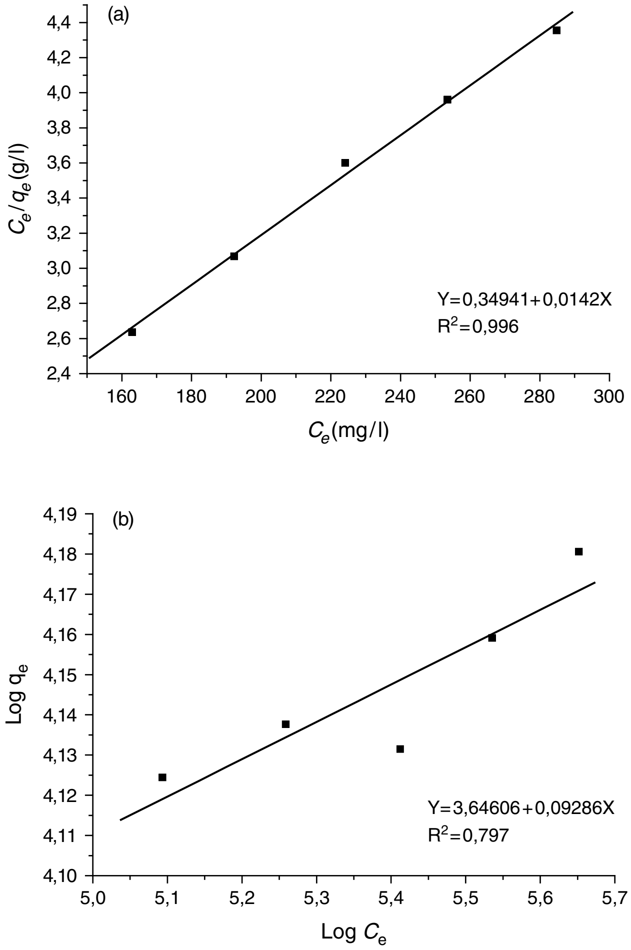

Fig. 5. Langmuir (a) and Freundlich (b) isotherms for adsorption of copper (II) on zeolite NaY. T = 298 K, $[Cu^{2+}]$ = 100 mg/l, S/L = 2.5 and pH = 5.

Table 2
Langmuir and Freundlich constant values for the adsoption of Cu^{2+} species onto NaY zeolite. T = 298 K, pH = 5 and S/L = 2.5

	Q_0 (mg/g)	b (l/g)	Langmuir		Freundlich	
			R^2	n	K_f (l/g)	R^2
Cu^{2+}	70.423	7.21 10^{-2}	0.996	9.30	37.99	0.797

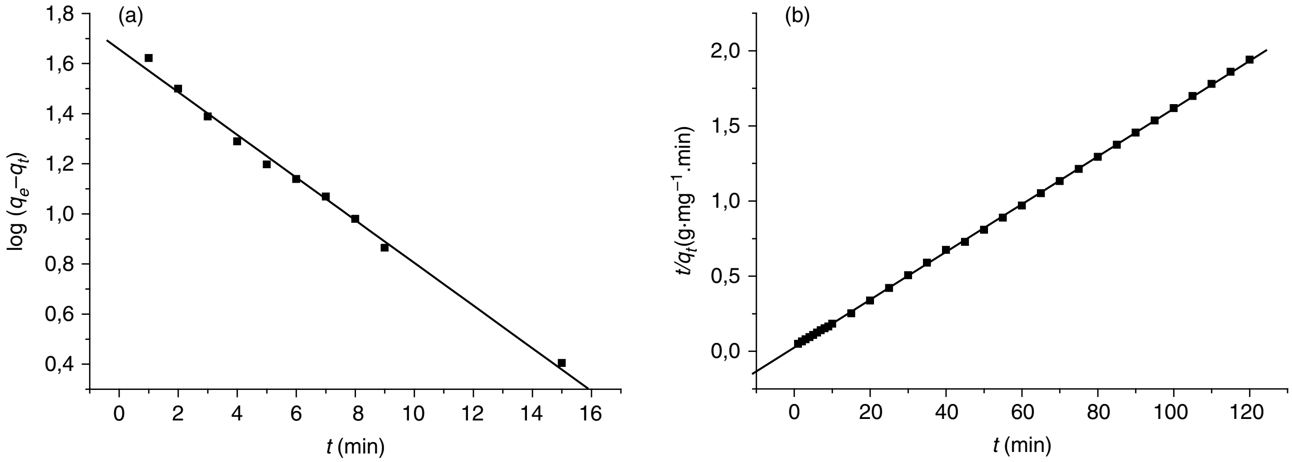

Fig. 6. Pseudo-first order (a) and Pseudo-second order (b) kinetic plots for the sorption of copper (II) ions from aqueous solutions on zeolite NaY. T = 298 K, [Cu^{2+}] = 100 mg/l, pH = 5 and S/L = 2.5.

The plot of (t/q_t) and t of Eq. (6) should give a linear relationship from which q_e and k_{2ads} can be determined from the slope and intercept of the plot, respectively (Fig. 6(b)). The results of fitting experimental data with the pseudo first-order and pseudo second-order models for adsorption of copper (II) onto NaY are presented in Table 3. As can be seen, the correlation coefficients (R^2) are 0.999 for the pseudo second-order model and 0.994 for the pseudo first-order model, indicating a better fit with the pseudo second-order model. The better fit of this model to the experimental data is also seen in the much closer agreement between the experimental values for $q_{e(exp)}$ and those from the second-order model ($q_{e(cal)}$), when compared to the $q_{e(cal)}$ values generated from the first-order model. These results explain that the pseudo second-order sorption model is predominant and that the rate constant of the ion exchange process appears to be controlled by the chemical sorption process.

3.5. Rate limiting

In this study, a quantitative data and models based on the Fick's law were applied. The initial diffusion coefficients D_i, which assume a particle diffusion mechanism to be rate-limiting, were calculated from Eq. (8). The D_i values obtained at different temperatures and concentrations for copper (II) ions are presented in Table 4. It can be shown that D_i decreases with increasing of temperature and concentration of Cu^{2+} ions indicating that the sorption process is governed by particle diffusion. Coker et al. [4] investigated the kinetics of ion exchange in zeolites and described the variation of diffusion coefficients for ion exchange reactions. Nibou et al. [21] conducted studies into the inter diffusion for the adsorption of zinc (II) ions onto zeolites. They have found that the diffusion of metal (II) ions is governed by two distinct diffusion coefficients, relatively fast and slower kinetics. They attributed this phenomenon

Table 3
Kinetic parameters for the adsorption Cu^{2+} species onto NaY zeolite. T = 298 K, [Cu^{2+}] = 100 mg/l, S/L = 2.5 and pH = 5

	Pseudo first-order			Pseudo second-order			
	$q_{e(cal)}$ (mg/g)	k_{1ads} (min^{-1})	R^2	$q_{e(cal)}$ (mg/g)	k_{2ads} (g/mg · mn)	R^2	$q_{e(exp)}$ (mg/g)
Cu^{2+}	45.357	19.60 10^{-2}	0.994	62.932	9.71 10^{-3}	0.999	68.32

Table 4
Coefficient diffusion D_i values of exchanged NaY zeolite at different temperatures and concentrations of copper (II)

	Temperature (°C)				Initial concentration (mg/l)				
Coefficient diffusion,	25	30	40	50	100	200	300	400	500
Di × 10^{17} (m²/s)	10.874	9.683	6.078	4.829	9.686	6.508	5.954	4.723	4.424

to entering metal (II) ions occupying 8-ring (NaA) and 12-ring (NaX) oxygen sites which partially obstruct the pore mouths and thus increasing energy for further exchange. They calculated the initial and final diffusion coefficients of zinc (II) adsorbed onto these zeolites. The initial diffusion coefficients D_i values presented in Table 4 are in agreement and comparable to those reported elsewhere [4,22].

Using the Arrhenius equation ($D_i = D_0\, exp^{(-Edif/RT)}$), the diffusion energy E_{dif} and D_0 (pre-exponential constant) for the adsorption of copper (II) onto NaY were determined. The activation entropy ΔS^* for the adsorption of copper (II) was also calculated using the equation: $D_0 = (2.72\ d^2\ kT/h)exp(\Delta S^*/R)$ where k is the Boltzmann constant, h is the Planks constant, d is the average distance between two successive positions, R is the gas constant and T is the absolute temperature. The energy E_{dif} and D_0 values are estimated to be 13.62 Kj/mol and 1.7110^{-14} m^2/s respectively, indicating that a chemical sorption process consisting of strong interaction between NaY zeolite and Cu^{2+} and illustrate that each sorption process has a low potential energy. The activation entropy ΔS^* value of −168,47 J/mol K reflects that no significant change occurs in the internal structure of the NaY during the adsorption of Cu^{2+}.

3.6. Thermodynamic parameters

Thermodynamic parameters as enthalpy of adsorption ΔH°_{ads}, entropy change ΔS°_{ads} and free energy ΔG°_{ads} for the adsorption of copper ions onto NaY zeolite were calculated (Table 5). The results show that ΔG°_{ads} values are negative indicating that the system reached a more stable energy level after ion exchange. The negative value of ΔH°_{ads} at 298 K indicates that the copper (II) ions can maintain their hydration and mobility in the supercages of NaY zeolite. At 303, 313 and 323 K, the ion exchange is endothermic because some energy must be supplied to the ion as it undergoes dehydration to occupy the less accessible sites located in the small cages [22,23].

Table 5
Thermodynamic parameters for adsorption of copper (II) ions onto NaY zeolite. S/l = 2.5, $[Cu^{2+}]$ = 100 mg/l and pH = 5

Temperature (K)	ΔH° (kJ /mol)	ΔS° (J /mol K)	ΔG° (kJ /mol)
298	–23.225	–28.789	–14.641
303	8.697	0.125	–12.564
313	76.980	0.309	–28.321
323	602.562	1.879	–46.567

4. Conclusion

In the present work, we reported the adsorption of copper (II) ions onto NaY zeolite from aqueous solution. The X ray diffraction analysis shows that the adsorption of Cu^{2+} on the exchangeable sites does not affect the structure of NaY. The optimized parameters for adsorption copper (II) onto NaY have been found: T = 25°C, pH = 5, $[Cu^{2+}]$ = 100 mg/l and t_{equi} = 60 min. The equilibrium studies show that the adsorption process followed Langmuir adsorption model.

The analysis of the kinetic and rate data revealed that that the pseudo second-order sorption is predominant for adsorption of copper (II). The rate limiting investigations using the Fick's law show that the intraparticle diffusion of copper (II) ions through the NaY particles was the determining step.

The negative values of the adsorption Gibbs free energy ΔG°_{ads} within the range of temperature investigated, indicating that the adsorption process are spontaneous while, the negative values of ΔS^* indicate that the copper (II) ions are more stable within the framework NaY. The NaY zeolite was found to be very effective in removing copper (II) from aqueous solutions.

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