Adsorption of Ni\(^{2+}\) Ions onto NaX and NaY Zeolites: Equilibrium, Kinetics, Intra Crystalline Diffusion and Thermodynamic Studies

Ferhat, Djawad; Nibou, Djamel*; Elhadj, Mekatel; Amokrane, Samira
Laboratory of Materials Technology, University of Science and Technology Houari Boumediene, B.P. 32, El-Alia, Bab-Ezzouar, Algiers, ALGERIA

ABSTRACT: This paper focus on intra crystalline diffusion of Ni\(^{2+}\) ions onto NaX and NaY zeolites. The zeolites are obtained by hydrothermal synthesis method. The samples were characterized by several techniques: X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) coupled with Energy Dispersive Spectroscopy (EDS) and Infrared Spectroscopy (FT-IR). Physical parameters such as pH solution (2 - 7), adsorbent dose (0.25 - 2 g/L), initial concentration of Ni (II) ions (50 - 200 mg/L) and temperature (298 - 323 K) are optimized. The maximum uptake is 99% and 97% for NaX and NaY zeolite respectively under the optimum conditions: pH ~ 7 and adsorbent dose of 1 g/L for initial concentration of 50 mg/L at 298 K. The best interpretation of the experimental data is obtained by the Langmuir isotherm with a maximum adsorption capacity of 111.85 and 77.57 mg/g for NaX and NaY respectively. The results show that the kinetic data for both zeolites follow the pseudo second order model, indicating the presence of physical adsorption. The free energy (\(\Delta G^\circ\)), enthalpy (\(\Delta H^\circ\)) and entropy (\(\Delta S^\circ\)) are evaluated. The process has proved its spontaneous and endothermic. Diffusion mechanisms of Ni (II) ions adsorption onto NaX and NaY has shown that intra particle diffusion is the limiting step of the process. The NaX and NaY have been applied to wastewater from the Algerian industrial zone in order to eliminate the Ni\(^{2+}\) effluents using the optimal parameters. It has been found that the Ni\(^{2+}\) ions removal yield was 77.81% for NaX and 83.86% for NaY.

KEYWORDS: Adsorption; Nickel ions; Zeolite; kinetic; diffusion; thermodynamic.

INTRODUCTION

Nowadays, the problem of heavy metals is becoming more worrying, because they are difficult to eliminate such as the industrial wastewater, contained different types of heavy metal ions and organic pollutants, which may cause a serious environmental problems that can affect the public health. Many methods such as ion exchange, precipitation, membrane processes, ultra-filtration, electro dialysis and reverse osmosis have been performed for toxic metal ions and organic pollutants removal [1-5]. Among these processes, adsorption is one of the most efficient techniques owing to its various advantages such as high relatively easy regeneration,
adsorption capacity, fast kinetics and the use of a large variety of adsorbent materials (zeolites, clays and biomasses) [6,7]. Zeolites are microporous materials, which have been extensively used in various applications, e.g. as catalysts, for separating and sorting various molecules, for water and air purification, including removal of radioactive contaminants, for harvesting waste heat and solar heat energy, for adsorption refrigeration, as detergents, etc. The growth of zeolites for environmental applications depends primarily on their physical properties and especially on the specific surface area [8-10].

The properties of extremely wide zeolites such as their hydrophilic and hydrophobic properties, high surface area, tunable chemical properties, high thermal stability and eco-friendly nature. Zeolites are microporous microcrystalline inorganic materials capable of adsorbing organic molecules [11]. The NaX and NaY Zeolites are suitable for adsorptions due to the high cation exchange capacity and the affinity for heavy metals as Ce$^{3+}$, La$^{3+}$, UO$_2^{2+}$, Co$^{2+}$, Sr$^{2+}$, Pb$^{2+}$, Ti$^+$ [2], Zn$^{2+}$ [6] and Cu$^{2+}$ [12].

Moreover, the main contents of zeolites are aluminum and silicon oxides. They are an open structure with compensation charge cations as Na$^+$ and K$^+$. Theses cations are readily exchangeable with other present in the solution [13]. Zeolite are classified into two major groups of natural and synthetic, X and Y are two most famous synthetic zeolites [14-18]. The Si/Al of NaX: 1<Si/Al<1.5 and NaY : Si/Al > 1.5 ratio directly influences the position and the number of the compensating cations on the type of crystal [19].

The kinetics of adsorption has also an important impact on the performance of the zeolites. The adsorption contains three phases of transfer of the zeolite and a reaction phase. The first represents the migration of the solute from the aqueous phase to the surface of the zeolite (external diffusion). The second related to intra-particle diffusion, and finally the surface chemical reaction between these functions of the zeolite and the metal ions [20-21]. Therefore, chemical exchange is slow comparing to other diffusion processes, which involve the determination step of the mechanism [6,22]. Several mathematical models describing a system of a particle at constant pressure and volume have been used by some authors in the literature [23-25]. They have assumed that the kinetic order of the chemical exchange is two and reported that the exchange process is characterized by a linear relationship between $1/(q_t - q_\infty)$ and $t$ where $q_\infty$ and $q_t$ are the adsorption capacity at $\infty$ and at time $t$ respectively. Contrary, other authors [26-28] have achieved the result that the variation of $\ln(1/q_t - q_\infty)$ in function time $t$ should be linear if the chemical reaction is crucial, taking in consideration its approaches.

In the present work some characteristics of NaX and NaY zeolites are investigated by XRD, SEM, EDS and FT-IR techniques. Optimized parameters influencing the adsorption phenomenon as pH solution, zeolite dose, initial concentration of Ni$^{2+}$ ions and the temperature are performed. In order to identify the adsorption mechanism, Langmuir, Freundlich and Temkin isotherms models are used. Kinetic studies using pseudo first-order, pseudo second-order and diffusion models are performed. We have focused on the use of models based on Fick laws during the analysis of the data obtained experimentally and for determining the step which describes the mechanism of the reaction. Thermodynamic parameters i.e. enthalpy of adsorption $\Delta H^o$ entropy change $\Delta S^o$ and Gibbs free energy $\Delta G^o$ for the adsorption of Ni$^{2+}$ ions onto NaX and NaY zeolites were examined. The obtained optimal parameters have been applied to wastewater from the industrial zone (West Algiers, Algeria).

**EXPERIMENTAL SECTION**

The NaX and NaY were obtained by hydrothermal method as illustrated in the previous paper [6, 13]. All reagents used in the present study were analytical grade, Ni(NO$_3$)$_2$·6H$_2$O (98%) from Biochem chemopharma. The NaOH was from Fluka chimika. Both of HCl and KCl were from Sigma-Aldrich. In all experiments, we used distilled water, which is obtained by GFL 2008. The unit cells composition in dry basis of NaX and NaY were Na$_8$(AlO$_2$)$_6$(SiO$_2$)$_{111}$ and Na$_{31}$(AlO$_2$)$_{25}$(SiO$_2$)$_{141}$ corresponding to a CEC of 5.96 and 3.90 meq/g respectively. The surface areas of prepared NaX and NaY were 375 and 304 m$^2$/g.

**Characterization**

The morphological and physico-chemical properties of the samples were characterized by XRD (Panalytical XPert PRO, Germany, using CuK$\alpha$ radiation) at a scanning range 20 from 5 to 50°. The surface morphology was observed by SEM (JEOL 6360, Japan) equipped with EDS. We use carbon to coat our samples with a thin film.
The FT-IR analysis was carried out using Perkin Elmer Spectrum equipment (Version 10.03.06, Germany). Surface area measurements were conducted using Micrometrics ASAP 2010 apparatus.

**Batch adsorption**

Batch adsorption experiments of Ni$^{2+}$ ions were carried out in a double-walled Pyrex reactor of capacity 200 cm$^3$ whose temperature was regulated by a thermostat bath. Preparation of the Ni$^{2+}$ solutions between (50–200 mg/L) were started by dilution of stock solution of (1000 mg/L). The effect of pH was studied in the range of 2 to 7 with optimized condition such as 0.2 g of adsorbent dropped in 200 mL of Ni$^{2+}$ ions with (C$_i$=100 mg/L) in room temperature solution. We use NaOH (0.1 M) or HCl (0.1 M) to adjust our pH. The adsorption kinetics and isotherms of the solutions between (50–200 mg/L) have been performed at different temperatures (25, 30, 40, and 50 °C). The final Ni$^{2+}$ concentration is determined using UV–Vis spectrophotometer (Optizen 2120 UV–Visible, Korea, maximum of wavelength is 465 nm) [1,29]. Using the following relationship, we calculated the removal percentage of Ni$^{2+}$ ions.

\[
\text{Removal of Ni}^{2+} (\%) = \frac{(C_i - C_e)}{C_i} \times 100
\]  

(1)

Where $C_i$ and $C_e$ are the initial and equilibrium Ni$^{2+}$ concentrations (mg/L) respectively. The adsorption capacity of the samples, $q_i$ (mg/g), were determined using the relationship:

\[
q_i = \frac{(C_i - C_e)V}{C_i m}
\]  

(2)

Where $V$ is the volume of the Ni$^{2+}$ solution and $m$ is the weight of our adsorbent. The equilibrium constant $K_e$ is given by [30].

\[
K_e = \frac{(C_i - C_e)}{C_e}
\]  

(3)

**RESULTS AND DISCUSSION**

**Zeolite Characterization**

**X-ray diffraction studies**

Fig. 1 (a, b) shows the XRD patterns of the NaX and NaY zeolites. The identification of the phases was done according to a standard file (JCPDS 00-012-0228) and reveal a cubic structure for both zeolites which promote better ions exchange [31]. The spectra show the presence of all the crystallization planes (hkl) of the NaX and NaY structures. On the other hand, the NaX sample exhibits a strong peak compared to those of NaY showing a good crystallinity.

The crystallite size was determined by the Scherrer Equation (4) [32-33]:

\[
D = \frac{K \lambda}{\beta \cos \theta}
\]  

(4)

Where $K$ is usually 0.89 is the Scherrer constant, $\lambda$ (1.54056 Å) is the wavelength of X-ray radiation, $\beta$ is the peak full width at half maximum in radians and $\theta$ is the Bragg diffraction angle. The estimated values of grain size are 0.20-1.4 nm range for NaX and NaY zeolites.

**SEM micrographs analysis**

Fig. 2 shows the SEM micrographs of NaX (a) and NaY (b) with respective EDS analysis. The form of obtained particles seems to be cubic with clearly visible facets and with a homogeneous size distribution of about 10 and 5 μm respectively.

The EDS analysis shows the presence of the main essential elements of the NaX and NaY framework Si and Al and the compensation cations Na. From the results, the values of Si/Al atomic ratio of NaX and NaY samples are 1.28 and 2.63 respectively. It can be observed that the value of NaY ratio is superior to that NaX. These results are in good agreement with those cited in the bibliography [13,14]. The NaY ratio directly influences
the atomic percentage of the cations compensating (10.53) compared to the NaX sample (20.44) as shown in Fig 2.

**FT-IR spectral analysis**

The NaX and NaY samples were characterized by FT-IR to observe the absorption bands grouped in Table 1 and illustrated in Fig 3. In general, the vibration spectrum of the NaX and NaY zeolites consists of two types of bands. First bands due to the internal vibrations of the TO$_4$ (T = Si, Al) tetrahedra which constitute the primary unit of the structure [6,14]. They are not very sensitive to structural vibrations. Second bands corresponding to the vibrations of the TO$_4$ tetrahedra with respect to one another. They are obviously sensitive to the way in which the tetrahedra are both attached. The samples analyzed show bands at 1200 to 450 cm$^{-1}$ which correspond to the vibrations of Si-O-Al, Si-O-Si, Si-O, and Al-O. Other absorption bands between 3800 to 3450 and 1600 cm$^{-1}$ are also present and are attributed to the vibrations of the hydroxyl groups Si-OH and H$_2$O respectively [20,33,34,35].

**Determination of zero point charge pHpzc of NaX and NaY zeolite**

The pH at which the charge of the adsorbent surface is zero is referred to as the zero point of charge (pHpzc). The pH$_{pzc}$ is one of the important parameters for discussion of pH effect. The pH$_{pzc}$ of NaX and NaY zeolite samples was determined by the method cited in [36-38]. KCl solution (0.001 M) was transferred to a series of Erlenmeyer flasks who are made up to exactly 50 mL. The initial pH of each flasks was adjusted by adding either HCl (0.1 M) or NaOH (0.1 M) to decrease
Adsorption of Ni$^{2+}$ Ions onto NaX and NaY Zeolites: Equilibrium, Kinetic, ...  

Table 1: Infrared absorption bands characteristic of NaX and NaY.

<table>
<thead>
<tr>
<th>Type of bond</th>
<th>Frequencies (cm$^{-1}$) from Breck [14]</th>
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</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>NaX NaY</td>
</tr>
<tr>
<td>Asymmetric elongation Si-O-Al, Si-O-Si</td>
<td>1250-950</td>
<td>989 989</td>
</tr>
<tr>
<td>Symmetrical elongation Al-O</td>
<td>720-650</td>
<td>679 717</td>
</tr>
<tr>
<td>Vibration of tetrahedral vertices Si, Al-O</td>
<td>650-500</td>
<td>565 659</td>
</tr>
<tr>
<td>Symmetrical elongation Si-O-Al, Si-O-Si</td>
<td>820-750</td>
<td>755 788</td>
</tr>
<tr>
<td>Asymmetric elongation Si-O-Al</td>
<td>1150-1050</td>
<td>- -</td>
</tr>
</tbody>
</table>

Fig. 3: FT-IR spectra of NaX (a) and NaY (b) zeolites.

Table 1: Infrared absorption bands characteristic of NaX and NaY.

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<td>1150-1050</td>
<td>- -</td>
</tr>
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</table>

Fig. 3: FT-IR spectra of NaX (a) and NaY (b) zeolites.

Adsorption study

The pH of solution as parameter of control is used which powerfully affects the adsorption of Ni$^{2+}$ ions on the adsorbent surface. The influence of pH has been studied between 2 until 8. Fig. 5 (a) shows a maximum removal of Ni$^{2+}$ ions (91% NaX and 63% NaY) at pH ~ 7. At lower pH values the adsorbents have a net positive charge but a minimum elimination of Ni$^{2+}$ ions is obtained at lower pH. Probably, it may be due to the electrostatic attractions between the positively charged adsorbent surface and the negatively functional groups charge located on Ni$^{2+}$ [39-40].

The uptake of Ni$^{2+}$ ions by NaX and NaY samples was fast at the beginning due to a larger surface area of adsorbent and gradually decreases with time until it reaches saturation. As we can see in Fig. 5 (b), the first stage is the faster until reaching 15 min. The second (15-120 min) is slower because of the saturation of active zeolite sites. The equilibrium which is the last step is due to the occupation of all active sites.

The effect of NaX and NaY dosage of removal of Ni$^{2+}$ ions at $C_i = 100$ mg/L was studied and filled in Fig. 5 (c). The adsorbent dose was varied from 0.25 to 2 g/L for each zeolite, keeping the concentration of metal ion fixed. Theoretically, increasing the adsorbent dose increases the adsorption and improve more metal ion elimination. The main reason that governs this supposition is the availability of more adsorption sites due to large surface area available for adsorption initially [41]. Fig. 5 c shows that high doses positively influence the adsorption removal of Ni$^{2+}$ ions; this is attributed to the increased available sites with increasing the amount of the zeolite where the adsorption increases progressively to peak at 99.86% for NaX and 95.15% for NaY. From these results, it can be concluded that the best Ni$^{2+}$ ions adsorption by NaX occurs for an optimal dose of 2 g/L.

Adsorption of Ni$^{2+}$ ions on NaX and NaY is affected by the initial concentration at 25°C between 50 and 200 mg/L. Results mentioned in Fig. 5 (d) illustrated that the adsorption of Ni$^{2+}$ decreased when the concentration of the solution increased. This indicates that less favorable sites occur when the concentration of solution achieving a maximum removal of 99.67% and 97.40% at 50 mg/L.
Fig. 4: Point of zero charge of NaX (a) and NaY (b) zeolites.

Fig. 5: Factors affecting Ni$^{2+}$ ions adsorption onto NaX and NaY: (a) pH effect, (b) contact time, (c) adsorbent dose and (d) initial concentration effect.
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Table 2: Results of the equilibrium isotherm models of NaX and NaY (pH \(\sim 7\), \(C_i = [50 – 200 \text{mg/L}]\), adsorbent dose = 1 g/L and \(T = 298 \text{K}\)).

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameters</th>
<th>Value</th>
<th>NaX</th>
<th>NaY</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>(q_m) (mg/g)</td>
<td>111.85</td>
<td>77.57</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(b) (L/mg)</td>
<td>0.482</td>
<td>0.186</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(R^2)</td>
<td>0.9970</td>
<td>0.9864</td>
<td></td>
</tr>
<tr>
<td>Freundlich</td>
<td>(K_f) (L/g)</td>
<td>62.61</td>
<td>46.32</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(1/n)</td>
<td>0.128</td>
<td>0.093</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(R^2)</td>
<td>0.9490</td>
<td>0.9320</td>
<td></td>
</tr>
<tr>
<td>Temkin</td>
<td>(k_f) (L/mg)</td>
<td>783.38</td>
<td>3032.18</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(b_f) (J/mol)</td>
<td>254.53</td>
<td>440.19</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(R^2)</td>
<td>0.9103</td>
<td>0.8501</td>
<td></td>
</tr>
</tbody>
</table>

for NaX and NaY samples respectively. A minimum of removal of 60 and 40% at 200 mg/L was also obtained from the respective samples. This retention for low initial Ni$^{2+}$ ions concentrations might be explained by the active sites available on the adsorbent. The increase of the Ni$^{2+}$ ions concentration leads to a rapid saturation of active sites, resulting in a decreased removal efficiency [42-44].

**Equilibrium isotherms**

Three well-known models Langmuir [45], Freundlich [46] and Temkin [47-49] have been tested in this work. The Equations (5), (6) and (7) have been used for each model respectively.

\[
\frac{C_e}{q_e} = \frac{1}{q_m} + \frac{C_e}{q_m b} \quad (5)
\]

Where \(C_e\) is the equilibrium concentration of Ni$^{2+}$ (mg/L) and \(q_e\) is the amount of adsorbed Ni$^{2+}$ (mg/g). The monolayer adsorption capacity \(q_m\) (mg/g) and the Langmuir constant related to the free adsorption energy \(b\) (L/mg) (Table 2) were evaluated from the slope and intercept of the linear plots of \(C_e/q_e\) versus \(C_e\) respectively (Fig. 6 (a)).

\[
\ln q_e = \ln K_F = \frac{1}{n} \ln C_e \quad (6)
\]

Where \(K_F\) (mg/g) and \(n\) are the Freundlich constants related to adsorption capacity and adsorption intensity respectively. The values of \(K_F\) and \(n\) (Table 2) were determined from the intercept and slope of the linear plot of \(\ln q_e\) versus \(\ln C_e\) (Fig. 6 (b)).

\[
q_e = \frac{R T}{b_T} \ln K_F + \frac{R T}{b_T} \ln C_e \quad (7)
\]

Where \(k_f\) (L/mg), \(R\) (8.314 J/mol k), \(T\) (K) and \(b_f\) (J/mol) are the Temkin constants related to the binding equilibrium isotherm, universal gas constant, the temperature and the variation of adsorption energy respectively. The constants were determined from the slope and the intercept (Fig. 6 (c)).

The adsorption isotherms of Ni$^{2+}$ ions onto NaX and NaY are tested. As illustrated in Table 2, Langmuir isotherm was more suitable than the Freundlich and Temkin isotherms. In the most cases, the correlation coefficients were higher, indicating the applicability of monolayer coverage of the Ni$^{2+}$ on the surface of adsorbents. The Langmuir model describes the sorption data with a correlation factor \(R^2\) values greater than 0.997. According to the saturated monolayer sorption capacity \(q_m\) and \(b\), the NaX adsorbs better compared to NaY. On the other hand, the equilibrium data were analyzed using Freundlich and Temkin isotherm models and \(R^2\) values were estimated as shown in Table 2. The values of \(1/n\) for NaX and NaY were inferior to 1, indicating that adsorption capacity is only slightly suppressed.

To confirm the performance of the Ni$^{2+}$ ions adsorption onto NaX and NaY, the separation factor \(R_L\) was calculated using the following Eq. (8).

\[
R_L = \frac{1}{1 + b C_i} \quad (8)
\]

Where \(b\) (L/mg) constant Langmuir. The \(R_L\) value indicates the nature of adsorption process. In fact,
Adsorption kinetics

In this part of the study, the mechanism of Ni$^{2+}$ ions adsorption onto NaX and NaY was defined by a pseudo-first-order, pseudo-second-order and intra-particle diffusion models.

A pseudo-first-order Lagergren model is based on the hypothesis that the rate of adsorbate seizing the adsorption sites is proportional to the amount of intake adsorption sites. It can be expressed by Eq. (9).

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1t$$  \hspace{1cm} (9)

Where $q_e$ is the adsorption capacity at equilibrium (mg/g); $q_t$ is the adsorption capacity (mg/g) at the time $t$ and $k_1$ is the first order rate constant (1/min). The values of kinetic constants $q_e$ and $k_1$ are defined experimentally from the slope and the intercept of the linear plot of $\ln (q_e - q_t)$ versus $t$, respectively (Fig.7 and Fig.8).

The pseudo-second-order model was deduced, based on the hypothesis that the sorbent absorbed the adsorbate chemically [50]. It can be expressed by Eq (10).

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}$$  \hspace{1cm} (10)

Where $k_2$ is the second order rate constant (g/mg min). The values of kinetic constants $q_e$ and $k_2$ are defined experimentally from the slope and intercept of the linear plot of $t/q_t$ versus $t$, respectively (Fig.9 and Fig.10).

In order to confirm if Ni$^{2+}$ ions adsorption into the pores of NaX and NaY is dominated by particle diffusion, the empirical data were analyzed using the intra-particle diffusion model [51]. The results showed in Table 4 suggest that pseudo-second order model is the most reliable to determine the order of the adsorption kinetics of Ni$^{2+}$ ions onto NaX and NaY which represents a good correlation coefficient ($R^2 > 0.999$). Similarly, we note that the values of $q_e$ calculated by the pseudo-second order model is very close to those determined experimentally which further justifies that the kinetics of

Fig. 6: Langmuir (a) Freundlich (b) and Temkin (c) isotherms for adsorption of Ni$^{2+}$ ions onto NaX and NaY (pH ~7, $C_i = [50-200$ mg/L], adsorbent dose = 1 g/L and $T = 298$ K).
Table 3: Dimensionless factor $R_L$ of the adsorption of the $\text{Ni}^{2+}$ ions onto NaX and NaY.

<table>
<thead>
<tr>
<th>$C_i$ (mg/L)</th>
<th>NaX</th>
<th>NaY</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.0398</td>
<td>0.0970</td>
</tr>
<tr>
<td>75</td>
<td>0.0269</td>
<td>0.0668</td>
</tr>
<tr>
<td>100</td>
<td>0.0203</td>
<td>0.0510</td>
</tr>
<tr>
<td>150</td>
<td>0.0136</td>
<td>0.0346</td>
</tr>
<tr>
<td>200</td>
<td>0.0103</td>
<td>0.0261</td>
</tr>
</tbody>
</table>

Fig. 7: Application of the Pseudo-First Order kinetic model for the adsorption of $\text{Ni}^{2+}$ ions onto the (a) NaX and (b) NaY zeolites at different concentrations ($\text{pH} \approx 7$, adsorbent dose = 1 g/L and $T = 298$ K).

Fig. 8: Application of the Pseudo-First order kinetic model for the adsorption of $\text{Ni}^{2+}$ ions onto the (a) NaX and (b) NaY zeolites at different Temperatures ($\text{pH} \approx 7$, $C_i = 50$ mg/L, adsorbent dose = 1 g/L).
these ions are pseudo second order. We also notice a decrease in the rate constant \( k_2 \) with the increase of the initial concentration of \( \text{Ni}^{2+} \) ions which can be explained by the solute-solute interactions. We also observe an increase in the constant of velocity \( k_2 \) as a function of the temperature which would indicate an increase of the interactions between the \( \text{Ni}^{2+} \) ions \([52-54]\).

The good adaptation of the experimental results to the pseudo second order model suggest that the fixation of the \( \text{Ni}^{2+} \) ions on the two zeolites studied is mainly due to chemical adsorption. Indeed, Ho and McKay indicate that the adsorption kinetics of most metal ions on adsorbents are consistent with the hypothesis of the pseudo-second order model according to the metal ions interact with the different functional groups on the surface of the materials. Therefore we can conclude that the pseudo-second order model represents the experimental results, this model was often adopted to model the adsorption kinetics of heavy metals on both NaX and NaY zeolites \([20, 22, 55]\).

**Diffusion kinetics**

**External diffusion**

The external diffusion is modeled starting from the Eq. (11) \([55, 56]\). The variation of the concentration in aqueous solution in the liquid phase can be presented as follows:
Table 4: Pseudo (First, Second) Order adsorption rate constants and the correlation coefficient ($R^2$) values of Ni$^{2+}$ ions onto NaX and NaY.

<table>
<thead>
<tr>
<th>$C_s$(mg/L)</th>
<th></th>
<th>Pseudo first order</th>
<th></th>
<th>Pseudo second order</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$q_{e,exp}$ (mg/g)</td>
<td>$q_{e,cal}$ (mg/g)</td>
<td>$k_1 \times 10^2$ (min$^{-1}$)</td>
<td>$R^2$</td>
<td>$q_{e,cal}$ (mg/g)</td>
<td>$k_2 \times 10^3$ (g/mg min)</td>
</tr>
<tr>
<td>NaX</td>
<td>50</td>
<td>49.48</td>
<td>6.740</td>
<td>5.368</td>
<td>0.6970</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>69.94</td>
<td>11.18</td>
<td>2.201</td>
<td>0.8964</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>91.71</td>
<td>21.81</td>
<td>3.181</td>
<td>0.9767</td>
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<td>7.672</td>
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<td>1.858</td>
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<td>1.004</td>
<td>4.907</td>
<td>0.9471</td>
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\[
\frac{\mathrm{d}C}{\mathrm{d}t} = -k_t S (C_t - C_s)
\]

(11)

Where $C_s$(mg/L): concentration of the Ni$^{2+}$ ions at the surface of the adsorbent; $C_t$(mg/L): Ni$^{2+}$ concentration in the liquid phase at the time $t$; $S$ (cm$^2$): exchange surface concerned with external diffusion; $K_f$(cm/s): external diffusion coefficient and $V$(L): volume of the solution. After integration of the equation (11) for the boundary conditions: $C_s=0$ and $C_s=C_i$ at $t=0$ and $C_s=C_i$ at $t=t$, we obtain the Equation (12):

\[
\ln\left(\frac{C_t}{C_i}\right) = -k_t S V t
\]

(12)

In the case of spherical particles, the report $\left(\frac{S}{V}\right)$ takes the following form (13):

\[
\left(\frac{S}{V}\right) = \frac{3F}{\rho d_p}
\]

(13)

Where $\rho$ is the density of the adsorbent (g/cm$^3$); $F$ is adsorbent dose (g/L) and $d_p$(cm): average particle diameter. The external diffusion coefficient ($k_t$) is obtained from the slope of the linear curve $\ln (C_t/C_i)$ as a function of time. Fig.11 shows the linearization of the curve $\ln (C_t/C_i)$ as a function of time, which makes
Adsorption is a complex phenomenon, which generally follows a path involving the combination of surface adsorption and diffusion in the pores. The extension of a particulate diffusion to the total process can be evaluated by the Weber and Morris model Equation (14). This model was chosen, assuming that the rate of adsorption in the porous adsorbents is often controlled by transport in the pores. The Weber and Morris model shows that surface adsorption is predominant whereas that in the pores is secondary.

$$q_t = k_{in} t^{1/2} + C$$  \hspace{1cm} (14)

Where $k_{in}$ (mg/g min$^{1/2}$); intraparticle diffusion rate constant; C (parameter of Weber and Morris);

The constant $k_{in}$ is deduced from the slope of the linear part of the curve $(q_t)$ as a function of $t^{1/2}$.

The Weber and Morris scattering model were applied for the determination of intra particle diffusion rate constants, the description of the experimental results of the adsorption kinetics by this model is presented in the Fig.12.

According to the results, the modeling of intra-particle diffusion characterized by the Weber-Morris relation between the adsorbed quantity $q_t$ and time $t$ present a multi-linearity, showing an evolution in the adsorption process. Indeed, the first step is very short, corresponds to a limitation of the adsorption by external diffusion. While the second step corresponds to the progressive adsorption of the solute, the phenomenon being then limited by the intraparticle diffusion. The third stage characterized by a plateau corresponds of a state of equilibrium [57]. The values of the intra particle diffusion rate constants for the adsorption of the Ni$^{2+}$ ions onto NaX and NaY are grouped in the Table 5. It is important to note that the intra-particle diffusion constant rate of the NaX is greater than that of the NaY.

### Intraparticle diffusion

In this study Fick’s law model for intra-particular diffusion were applied the initial diffusion coefficients $D_i$ were calculated from the following equations (15):

$$\frac{q_t}{q_e} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left( - \frac{D n^2 \pi^2 t}{r_0^2} \right)$$ \hspace{1cm} (15)

where $q_t/q_e$, $t$, $r_0$ and $n$ are the fractional attainment of equilibrium at time of amounts of adsorption, time, radius of crystalline particles assumed to be spherical, and an integer respectively. In short time, Equation (15) can be rearranged to obtain Eq. (16) [6, 25, 58]. Similar model is developed for the determination of the intra-particle diffusion coefficient ( Eq (17)).

$$\frac{q_t}{q_e} = 6 \left( \frac{D t}{r_0^2} \right)^{1/2}$$ \hspace{1cm} (16)
Application of the intraparticle diffusion kinetic model for the adsorption of Ni\textsuperscript{2+} ions onto NaX and NaY (C\textsubscript{i} = 50 mg/L, pH \sim 7, adsorbent dose = 1 g/L and T = 298 K).

\[
-\ln \left(1 - \left(\frac{q_t}{q_e}\right)^2\right) = \left(\frac{4\pi^2D_i}{d_p^2}\right)t
\]  

(17)

Where \(D_i\) and \(d_p\) denote the intraparticle diffusion coefficient (cm\textsuperscript{2}/s) and the average particle diameter (cm) respectively. The initial diffusion coefficients \(D_i\) are obtained from plots of \(-\ln \left(1 - \left(\frac{q_t}{q_e}\right)^2\right)\) vs \(t\) (Fig. 13).

In this study, \(q_e\) value is represented by \(q_\infty\) for our adsorption experiment of Ni\textsuperscript{2+} ions by both NaX and NaY samples.

From the results obtained in Table 5, we note that the intra-particle diffusion coefficients are lower than those of the external diffusion coefficients. Therefore, it can be concluded that adsorption kinetics are controlled by intra-particle diffusion model.

The diffusion coefficient value of Ni\textsuperscript{2+} ions onto our adsorbent show that the diffusion of NaX sample was better than NaY due to the diameter pore. Based on previous work, the calculation of the Biot number made it possible to determine the limiting diffusion mechanism. If this number is greater than 100, the resistance due to the transfer of external matter is negligible in front of that due to the internal transfer. We note that the transfer of matter is controlled by the latter. On the other hand, if this number is less than 100, The resistance due to the transfer of external material becomes the limiting step [56].

The number of Biot (Bi) dimensionless is given by the following formula Eq (18):

\[
\text{Bi} = \frac{k_i \times \frac{d_p}{D_i}}
\]  

(18)

Where \(k_i\), \(D_i\) and \(d_p\) denote respectively the external diffusion coefficient, the intra particle diffusion coefficient and the particle diameter.

The intra-particle diffusion coefficients, the external diffusion coefficients and the Biot numbers for the adsorption of the Ni\textsuperscript{2+} ions on the NaX and NaY are grouped in the Table 5. From the results, we observe that the number of Biot (Bi) is much greater than the value 100, which confirms that the limiting step is the intra particle diffusion.

**Activation Energy**

The activation energy is a criterion of distinction between chemical adsorption and physical adsorption, which is calculated from the Arrhenius law:

\[
K_2 = A_o \exp \left(\frac{-E_a}{RT}\right)
\]  

(19)

Where \(K_2\) (g/mg.min): pseudo second order adsorption rate constant, \(A_o\) (g/mg.min): temperature independent factor, \(E_a\) (kJ/mol): activation energy of adsorption, \(R\) (8.314 J/mol.K): molar gas constant and \(T\) (K): absolute temperature. After linearization of Eq. (19), we obtain Eq. (20) [59].

\[
\ln k_2 = \ln A_o - \frac{E_a}{RT}
\]  

(20)
Table 6: Thermodynamic Parameters of Ni$^{2+}$ ions adsorption onto NaX and NaY.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta H^\circ$ (kJ/mol)</th>
<th>$\Delta S^\circ$ (J/mol K)</th>
<th>$\Delta G^\circ$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>298 K</td>
<td>303 K</td>
<td>313 K</td>
</tr>
<tr>
<td>NaY</td>
<td>8.055</td>
<td>31.584</td>
<td>-1.360</td>
</tr>
</tbody>
</table>

Fig. 14: Characteristic Curves of Arrhenius for the adsorption of Ni$^{2+}$ ions onto the NaX and NaY zeolites Temperatures (pH ~7, Co = 50 mg/L, adsorbent dose = 1 g/L).

By plotting (ln $k_2$) as a function of (1/T). Determining the activation energy ($E_a$). Activation energies of the adsorption of Ni$^{2+}$ ions onto NaX and NaY are summarized in Table 5. From these results, we note that the activation energy values obtained during this study for the adsorption of ions Ni$^{2+}$ onto NaX and NaY are less than 40 kJ/mol. The results show that the adsorption process follows a chemical nature (Fig. 14).

**Thermodynamic Parameters**

The thermodynamic parameters of the adsorption process, free energy ($\Delta G^\circ$), enthalpy ($\Delta H^\circ$) and the entropy ($\Delta S^\circ$) explain the mechanism of the Ni (II) ions adsorption onto NaX and NaY. The variation of the enthalpy ($\Delta H^\circ$) and the entropy ($\Delta S^\circ$) can be obtained from the slope and the interception of the ln $K_c$ plot as a function of (1/T) (Fig. 15).

The values of thermodynamic parameters are listed in Table 6. The free Gibbs enthalpy of adsorption is calculated by the following equation (22):

$$\ln K_c = \left(\frac{\Delta S^\circ}{R}\right) - \left(\frac{\Delta H^\circ}{RT}\right)$$  \hspace{1cm} (21)

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$ \hspace{1cm} (22)

The analysis of these thermodynamic parameters reveals that the adsorption of Ni$^{2+}$ ions is a spontaneous reaction ($\Delta G^\circ < 0$). The decrease of $\Delta G^\circ$ with the increase of the temperature shows that the adsorption is more suitable to high temperature. The values of the entropy variables of the adsorption of Ni$^{2+}$ ions are positive which means that the molecules in the liquid phase and reflect the great affinity of the adsorbent materials NaX and NaY toward Ni(II) ions [20]. The adsorption of Ni(II) ions and water molecules in the zeolite framework to replace Na$^+$ ions contributed to the increasing of the entropy [60]. The $\Delta H^\circ$ values show that adsorption process is endothermic.

**Comparative adsorption capacities onto other material adsorbents**

The maximum Nickel (II) adsorption capacity, according to the Langmuir model shows that the both zeolites NaX and NaY have high potentials compared to others adsorbents tested in several Langmuir Ni$^{2+}$ adsorption research. Table 7 shows the maximum ions capacity comparison of several adsorbents. It is clear
that both zeolites NaX and NaY show significantly better performance than the others adsorbents.

**Treatment of nickel (II) wastewater**

Nickel (II) wastewater samples have been taken from effluent issued from the industrial zone in West Algiers, some physico-chemical properties were obtained and illustrated in Table 8. Then, adsorption Ni^{2+} tests have been carried out onto NaX and NaY zeolites using optimal conditions previously determined.

It has been found that the Ni^{2+} removal yield was 83.86% and 77.81% for NaX and NaY respectively. Comparing the removal efficiencies (percentage) for zeolites, Table 8 shows that the NaX performs considerably better than the NaY. Moreover, NaX have small particles with an average size of 4 and 3 μm. These characteristics allow the Ni^{2+} ions to access and diffuse in the framework structures [61] (Fig. 16).

**CONCLUSIONS**

In this work we successfully prepared two adsorbents NaX and NaY zeolites by hydrothermal method. The characterization results indicate that the zeolites

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>q_m (mg/g)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural zeolite</td>
<td>8.69</td>
<td>[62]</td>
</tr>
<tr>
<td>Na-zeolite</td>
<td>1.30</td>
<td>[63]</td>
</tr>
<tr>
<td>Escherichia coli biofilm supported on zeolite NaY</td>
<td>13</td>
<td>[64]</td>
</tr>
<tr>
<td>kinetic and thermodynamics of nickel removal</td>
<td>10.1</td>
<td>[65]</td>
</tr>
<tr>
<td>citrus limettioides peel and seed carbon (CLSC)</td>
<td>35.54</td>
<td>[66]</td>
</tr>
<tr>
<td>NaX</td>
<td>111.85</td>
<td>This work</td>
</tr>
<tr>
<td>NaY</td>
<td>77.57</td>
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</tbody>
</table>

Table 7: Comparison of maximum adsorption capacities of Ni^{2+} ions by various adsorbents.

<table>
<thead>
<tr>
<th>Physicochemical parameters</th>
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<tbody>
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<td></td>
<td>NaX</td>
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<tr>
<td>Initial pH</td>
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</tr>
<tr>
<td>Final pH</td>
<td>7.5</td>
</tr>
<tr>
<td>Initial Conductivity (mS/cm)</td>
<td>2.5</td>
</tr>
<tr>
<td>Final Conductivity (mS/cm)</td>
<td>0.82</td>
</tr>
<tr>
<td>Ni^{2+} Removal (%)</td>
<td>77.81</td>
</tr>
</tbody>
</table>

Table 8: Some physico-chemical properties of the wastewater from effluent issued from the industrial zone (West Algiers, Algeria).

![Fig. 16: Treatment of Ni^{2+} wastewater with NaX and NaY zeolites (pH ~7, C_i = 50 mg/L, adsorbent dose = 1 g/L and T = 298K).](image)
explained by competition of Ni$^{2+}$ and H$^+$ at the adsorbent sites. The optimum pH to eliminate Ni$^{2+}$ ions using our adsorbents are in the range of 6 - 7. The diffusion coefficient decreases both for NaX and NaY with increasing the concentration of Ni$^{2+}$ ions point out that less favorable media take part when effluent concentration increases. The adsorption isotherm study is represented very correctly by the Langmuir model with maximum adsorption capacity varying from 77 to 120 mg/g for Ni$^{2+}$ ions. Analysis of experimental kinetic data has shown that the pseudo second order model well describes the adsorption. The study of the diffusion mechanisms of Ni$^{2+}$ ions adsorption indicate that intra particle diffusion is the limiting step of the process. The positive value of $\Delta H^\circ$ and $\Delta S^\circ$ related to the adsorption process of Ni$^{2+}$ ions onto the NaX and NaY zeolites showed that the process is endothermic and spontaneous. All optimized parameters have been applied on Algerian industrial wastewater solution and the Ni$^{2+}$ removal yield was 83.86 and 77.81 % for NaX and NaY zeolites respectively. These encouraging results lead us to future large-scale application.

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REFERENCES


Please write complete bibliographic information for Ref. [21] & [46].


