

Removal of nickel ions from aqueous solutions using natural zeolite; kinetic, equilibrium and thermodynamic studies

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Abstract

The aim of the present study is to investigate the removal of nickel ions from aqueous solutions using natural zeolite. Batch experimental studies were conducted to evaluate by changing relevant parameters such as initial pH of solution, dosage of adsorbent, contact time, initial nickel ion concentration and temperature. The experimental isotherm data are analyzed using Langmuir and Freundlich equations. The Langmuir model fits the equilibrium data better than the Freundlich model. According to the Langmuir equation, the maximum uptake for nickel ions is 18.09 (mg/g). Pseudo-first-order and pseudo-second-order models are used to represent the kinetics of the process. The results indicate that the pseudo-second-order model is the one that best describes the kinetics of the adsorption of metal ions. The calculated thermodynamic parameters (ΔG° , ΔH° , and ΔS°) show that the adsorption process is feasible, spontaneous and endothermic at 20-50°C. Based on the experimental results, it can be concluded that natural zeolite has the potential of application as an efficient adsorbent for the removal of heavy metals from aqueous solutions.

Keywords: Adsorption; Batch method; Nickel ion; Isotherm; Kinetic; Natural zeolite.

1- Introduction

Nickel ions are among the most harmful pollutants in several industrial wastewaters. Nickel is being discharged into the environment as industrial wastes, causing serious soil and water pollution [1]. Nickel is employed in several industrial activities, including mineral processing, electroplating, production of paints and batteries, and manufacturing of sulphate and

porcelain enameling [2-4]. Human exposure to this heavy metal at significant levels is associated with serious health effects. Nickel is associated with dermatitis, nausea, coughing, chronic bronchitis, gastrointestinal distress, reduced lung function and lung cancer [5-10]. Therefore, removal of nickel from natural and industrial wastewater has been drawing

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more and more attention [11-15]. During the last few years, many techniques have been proposed by which to remove unwanted cations from wastewater, such as ion exchange, precipitation, adsorption, membrane processes, reverse osmosis, sedimentation, and electro-dialysis [16–18]. Among these methods, adsorption is currently considered to be very simple and cost-effective method [19-21]. Various materials are generally used as adsorbents among which zeolites have been widely used to adsorb high amount of heavy metals [22]. Besides that, zeolites have a net negative structural charge, which makes them suitable for ion exchange process and selective for cations. Zeolite is a naturally occurring crystalline aluminosilicate mineral that are aluminosilicates consisting of a framework of tetrahedral molecules, linked with shared oxygen atoms. Natural zeolites are safe, environmentally friendly, low-cost, and has a large surface area and high cation exchange capacities [20] and are considered effective materials for the removal of heavy metal ions such as Cd^{2+} , Pb^{2+} , Mn^{2+} and Zn^{2+} from wastewater [21]. Due to their favorable structural characteristics and valuable properties. In Iran, large piles of zeolite exist with no disposal options. The zeolite samples from different regions show different characteristics in ion exchange and adsorption processes [22- 26].

In this study, the adsorption potential of the natural zeolite to remove nickel ions from aqueous solution has been investigated using batch method. Optimum adsorption conditions are determined as a function of initial pH of solution, dosage of adsorbent, contact time and initial nickel ion concentration. Furthermore, the adsorption is modeled by using the Langmuir, and Freundlich models and also, the adsorption mechanisms of Ni(II) onto natural zeolite are evaluated in terms of thermodynamics and kinetics.

2-Materials and methods

2.1. Characteristic of clinoptilolite

The particular ion exchanger of interest in this study is clinoptilolite. The clinoptilolite used as an adsorbent in this experiment was obtained from Shahin Dejh City in

the south of Western Azarbaijan, Iran. The clinoptilolite sample was characterized using Rigaku D-Max III X-ray diffractometer (XRD) and chemical analysis. The chemical composition was determined by analytical methods usually applied for silicate materials. The chemical composition of the clinoptilolite used in this study is shown in Table 1.

Table 1. Chemical and mineralogical composition of natural Western Azarbaijan zeolite.

Parameter	Value (%)
SiO_2	67.5
Al_2O_3	12.5
Na_2O	3.1
K_2O	4.4
CaO	1.6
Fe_2O_3	0.2-0.9
L.O.I	10-13
XRD analysis	
<i>Major mineral: Clinoptilolite – Quartz - Cristobalite</i>	
<i>Minor mineral: Calcite – Montmorillonite</i>	

The crystalline phase composition of the used natural zeolite was characterized by Scanning Electron Micrograph (VEGA II TSCAN Co. Czech. Republic). The SEM analysis of natural Western Azarbaijan zeolite reveals important information on the surface morphology (Fig. 1). As seen in Fig. 1, the adsorbent has some cavities in its structure capable of up taking nickel ions. After metal ion binding, the surface of natural zeolite flattened in comparison of raw sample. Apart from that, no further significant morphological changes were apparent in the SEM images.

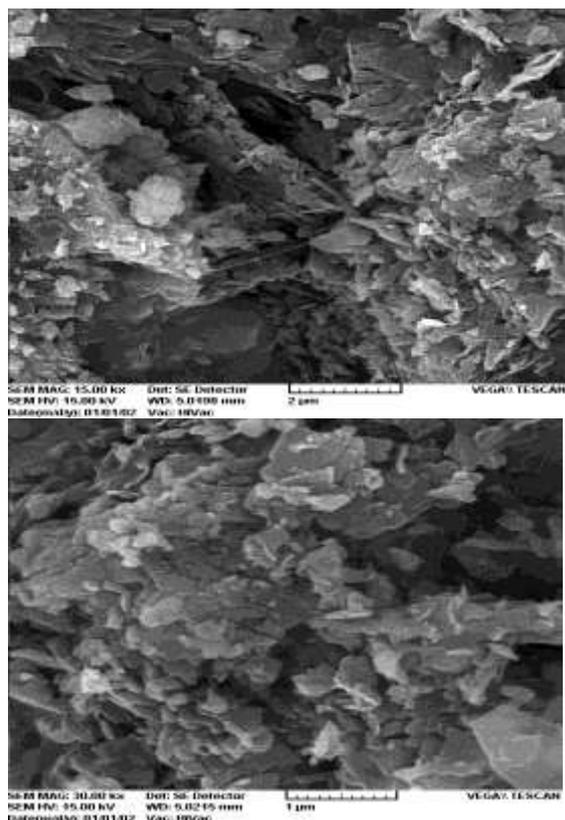


Fig 1. SEM images of natural Western Azarbaijan zeolite

2.2. Reagent

All chemicals used were of analytical grade from Merck (Darmstadt, Germany) and the solutions were prepared with freshly double distilled water. Synthetic wastewaters of nickel ion concentrations (10-200 mg/L) were used in this study. Nickel stock solutions (1000 mg/L) were prepared separately from $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in double distilled water. The working solutions were prepared by diluting the stock solutions to appropriate volumes.

2.3. Batch experiments

The adsorption of nickel ion on natural zeolite was studied using the batch procedure. All experiments were carried out in triplicate and the mean value was used in all cases. In this studies, the experiments were conducted using a shaker apparatus (Model 3017, GFL Co., Germany) to investigate the effects of relevant parameters such as initial nickel ion concentration (10-200 mg/L), contact time (5-120 min), pH (2-8) and dosage of adsorbent (0.1 to 0.7 g/L) on removal efficiency by natural zeolite.

In batch method, the adsorbent is contacted with a synthetic solution of nickel ion in a suitable vessel with stirring. The ion removal reaction proceeds in this closed system and shaken at 200 rpm until the equilibrium between the adsorbent and the nickel ions in solution is established. After equilibrium is obtained, the adsorbent is separated from the solution phase by filtration through centrifuge. A centrifuge (4000rpm, Urom Azma Company, Urmia, Iran) with 15ml calibrated tubes (Superior, Germany) was used to accelerate the phase separation process. At last, the amount of nickel ion was determined by inductivity coupled plasma (ICP) using an ICP-OES Varian Vista-Pro CCD spectrometer. A Metrohm model 713 pH-meter with a combined glass electrode was used for pH measurements. The removal efficiency (%) was calculated using the relation:

$$\text{Removal efficiency (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

Where C_0 and C_e are the initial and final concentrations of nickel ion in solution (mg/L).

Equilibrium studies were conducted at optimum conditions with six different initial concentrations of 10, 30, 50, 75, 100 and 200 mg/L. The adsorption experiments were also carried out at 20, 30, 40 and 50°C to determine the adsorption thermodynamic parameters.

The amount of nickel ion adsorbed by the natural zeolite was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e) \times V}{M} \quad (2)$$

Where q_e is the ion uptake (mg/g), M is the mass of the adsorbent (g), C_0 and C_e are the initial and equilibrium of the nickel ion concentrations in the solution (mg/L), respectively, V is the volume of solution (L).

The average absolute value of relative error, AARE, is used to compare the predicted results with the experimental data. This is defined as follows:

$$\text{AARE} = \frac{1}{\text{NDP}} \sum_{i=1}^{\text{NDP}} \frac{|\text{Predicted value} - \text{Experimental value}|}{\text{Experimental value}}$$

In which NDP is the number of data points.

3. Results and discussion

3.1. Effect of pH

It is well recognized that the pH is an important parameter affecting the adsorption process. In order to determine the effects of pH on the removal of nickel ions from aqueous solutions using clinoptilolite, batch equilibrium experiments were carried out using 50 mg/L initial Ni(II) concentration and 0.1 g/L adsorbent at different pH levels ranging from 2 to 8. The effect of pH on adsorption of nickel ions onto natural zeolite is presented in Fig.2.

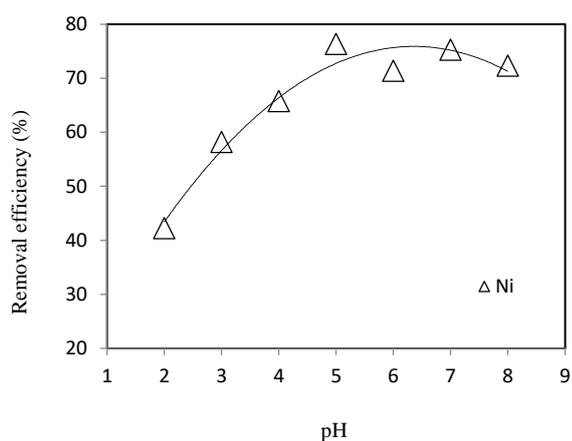


Fig 2. Effect of pH on the adsorption of Ni(II) on natural zeolite (C_0 : 50 mg L⁻¹; Contact time: 90 min; adsorbent dosage: 0.1 g/L) As shown in this figures, nickel ion removal from solution is increased when the pH rises from 4 to about 7 and achieves a maximum in the pH range of 6.50-7.50. After reaching this pH, the removal efficiency reduced slowly.

At low pH values, the low adsorption observation can be explained due to increase in positive charge density on the surface sites, and thus, electrostatic repulsion occurs between the nickel ions and the edge group with positive charge on the surface. Thus resulting, the surface charge developed at low pH is not suitable for adsorption of the nickel ions. When the pH was increased, the competing effect of H⁺ ions decreased and the positively charged Ni²⁺ ions hook up the free binding sites. Hence, the nickel ion uptake was increased on the surface of the adsorbent with the increase in pH [27-31]. In the experiments, the pH of 7 was selected to be the optimum pH for further experimental studies.

3.2. Effect of adsorbent dosage

One of the parameters that strongly affect sorption capacity is the quantity of the contacting sorbent in the liquid phase [20]. The effect of adsorbent dosage on the adsorption of Ni(II) onto natural zeolite is indicated in Fig 3. The results illustrated that the removal efficiency increases with an increase in adsorbent dosage. This is because of the availability of more binding sites and making easier penetration of metal ions to the sorption sites. The maximum adsorption is found to be at 0.7 g/L for nickel ions. Further increment in the adsorbent of dosage does not cause significant improvement in the adsorption capacity. This may be due to the binding of almost all ions to the sorbent and the establishment of equilibrium between the ions bound to the adsorbent and those remaining in the solution. Therefore, the optimum adsorbent dosage is taken as 0.4 g/L and this is used for all further experiments.

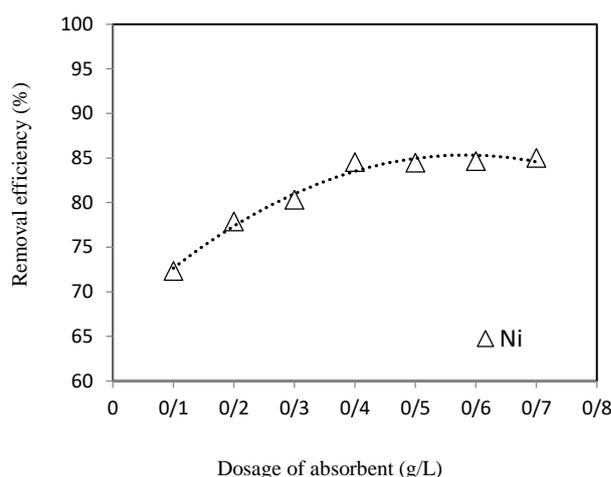


Fig 3. Effect of adsorbent dosage on the adsorption of Ni(II) on natural zeolite (C_0 : 50mg/L; Contact time: 90 min)

3.3. Effect of contact time

Due to equilibrium nature of the removal process of nickel ion by the natural zeolite, it seems that contact time affects the removal efficiency of the used sorbent. Hence, the effect of contact time on the removal extent of nickel ions by natural zeolite was studied in batch experiment. The corresponding results are given in Fig 4. As seen in this figure, the uptake of nickel ions increases with increase in contact time and reached to nearly constant amount at equilibrium conditions after 60 min. Hence, this obtained equilibrium time was selected for the next adsorption experiments.

Experimental kinetic data coincides with this aspect because more than 75% of total removal occurs within the first 45 min. This initial quick phase is followed by the slow attainment of equilibrium. These two different phases are common in the most sorption systems because the sorbent contains a high concentration of exchangeable binding sites for the metal binding in the beginning. As time increases, these binding sites get saturated and subsequently uptake decreases [32-34].

3.4. Effect of initial ion concentration

The corresponding results for the study of the effect of the initial nickel concentration on the removal efficiency using natural zeolite are shown in Fig 5. As shown, nickel ion removal from solution gets increased when the initial concentration rises from 5 to about 15 and achieves to a maximum amount of 10. Then, the removal efficiency reduced slowly.

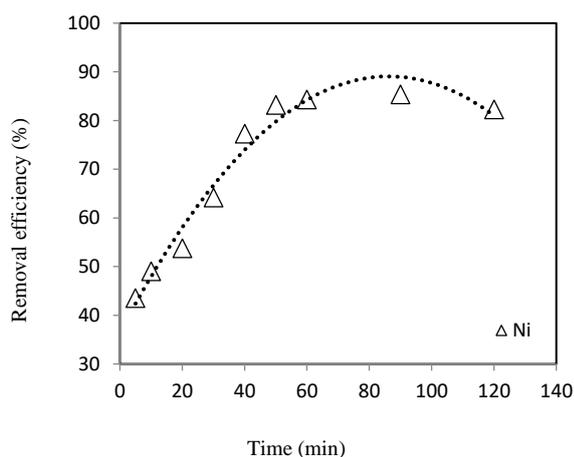


Fig4. Effect of contact time on adsorption of Ni(II) ions on natural zeolite (C_0 : 50mg/L)

The initial concentration of metal ion provides an important driving force to overcome all mass transfer resistances of metal ions between the aqueous and solid phases [15]. Fig. 5 clearly shows that by increasing the concentration gradually there is a decrease in the removal efficiency. As the ratio of sportive surface to ion concentration decreased with increasing metal ion concentration and so metal ion removal was reduced. At low initial concentration of metal ions, more binding sites are available. But as the concentration increases, the number of ions competing for available binding

sites in the adsorbent increased [16]. A further increase in metal concentration results in saturation of adsorption sites and surface precipitation is the main uptake mechanism.

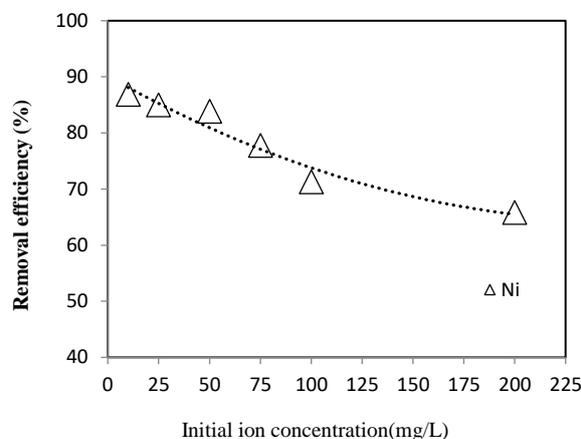


Fig 5. Effect of initial ion concentration on adsorption of Ni(II) ions on natural zeolite

3.5. Adsorption isotherm models

Adsorption isotherms are important for the description of how molecules or ions of adsorbate interact with adsorbent surface sites, and also, are critical in optimizing the use of adsorbent. The isotherm equations are tested in the present study, namely, Langmuir, and Freundlich isotherm models.

The Langmuir adsorption isotherm suggests monolayer sorption on a homogeneous surface without interaction between adsorbed molecules. This model can be written as follows [35]:

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

Where, q_e (mg/g) is the equilibrium metal ion concentration on the sorbent, C_e (mg/L) is the equilibrium metal ion concentration in the solution, q_m (mg/g) is the monolayer sorption capacity of the sorbent (mg/g), and K_L is the Langmuir sorption constant (L/mg) relating the free energy of sorption.

The shape of the isotherm can be considered when predicting whether an adsorption system is favorable or unfavorable. The essential characteristic of a Langmuir isotherm can be expressed in terms of dimensionless

separation factor or equilibrium parameter R_L , which is defined as:

$$R_L = \frac{1}{1 + K_L C_0} \quad (4)$$

There are four probabilities for R_L value: for favorable adsorption, $0 < R_L < 1$, (2) for unfavorable adsorption, $R_L > 1$, (3) for linear adsorption, $R_L = 1$, and (4) for irreversible adsorption, $R_L = 0$.

The Freundlich isotherm model proposes a monolayer sorption with a heterogeneous energetic distribution of active sites, accompanied by interactions between adsorbed molecules. The Freundlich model can be expressed as [36]:

$$q_e = K_F C_e^{1/n} \quad (5)$$

Where, K_F (mg/g)(L/mg) $^{1/n}$ is a constant relating the sorption capacity and $1/n$ is an empirical parameter relating the sorption intensity, which varies with the heterogeneity of the material.

The Langmuir and Freundlich model constants, along with the correlation coefficient (R^2) are presented in Table 2.

Table 2. Langmuir and Freundlich constants for the adsorption of Ni(II) ions on natural zeolite

Langmuir model			Freundlich models		
q_m (mg/g)	K_L (L/mg)	R^2	$1/n$	K_F	R^2
18.09	0.0613	0.982	0.854	2.650	0.940

A comparison of the Langmuir and Freundlich isotherm models (Figures 6 and 7) shows that the sorption characteristics of Ni(II) onto natural zeolite follow more closely the Langmuir isotherm equation. The maximum uptake capacity (q_m) of natural zeolite for nickel ions are found to be 18.09 (mg/g). Therefore, it can be noteworthy that natural zeolite has remarkable potential for the removal of Ni(II) from aqueous solution. The adsorption capacities of different adsorbents for adsorption of nickel ions are given in Table 3. This table shows that natural zeolite has remarkable potential for the removal of nickel ions

from aqueous solution compared to some previously developed adsorbents.

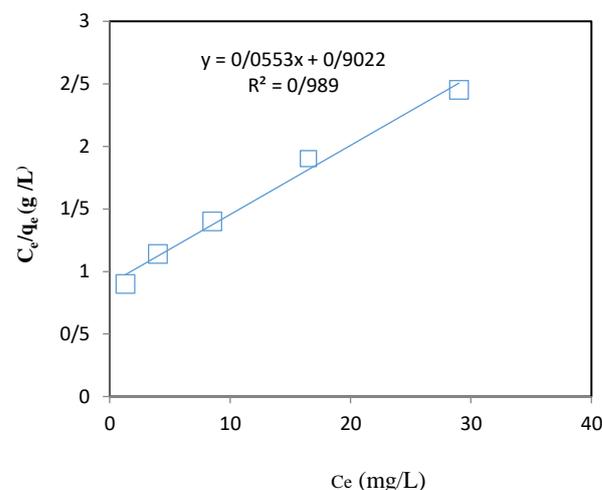


Fig 6. Langmuir isotherm plot for the adsorption of Ni(II) ions on natural zeolite

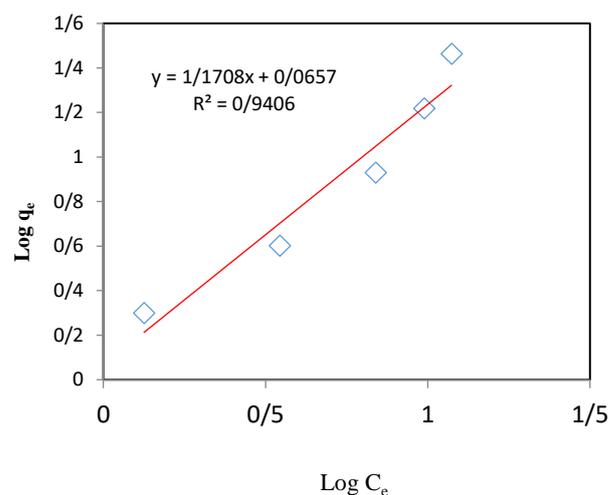


Fig 7. Freundlich isotherm plots for the adsorption of Ni(II) ions on natural zeolite

Table 3. Comparison of maximum adsorption capacity of various adsorbents for nickel removal from aqueous solution

Nickel		
Adsorbent	q_m (mg/g)	Reference
Clinoptilolite	0.48	[37]
Chabazite	4.5	[38]
Natural clinoptilolite	2.04	[39]
Turkish clinoptilolite	5.2	[40]
Ukraine clinoptilolite	6.6	[41]
Synthetic zeolite	20.1	[42]

Expanded perlite	2.24	[43]
Na-montmorillonite	۳,۶۴	[44]
NaOH pretreated	۰,۹۶	[45]
Dolomite	۱,۷۰	[46]
Clinoptilolite	۱۳,۰۰	[47]
Iranian clinoptilolite	18.09	This study

3.6. Adsorption kinetics

In order to examine the controlling mechanism of the adsorption process, kinetic models are used to test the experimental data. Three different kinetic models namely pseudo-first-order and pseudo-second-order models are applied for the experimental data to predict the adsorption kinetics.

The pseudo-first-order equation is one the most widely used rate equations to describe the adsorption of an adsorbate from the liquid phase. The non-linear pseudo-first-order equation is given as follows [48]:

$$q_t = q_e \left(1 - e^{-k_1 t}\right)$$

(6)

Where, q_e and q_t (mg/g) are the amount of metal ions adsorbed at equilibrium and at time t (min), respectively and k_1 is the pseudo-first-order rate constant (min^{-1}).

The pseudo-second-order model is more suitable for the description of the kinetic behavior of adsorption in which chemical sorption is the rate-controlling step.

The pseudo-second-order equation is given by [48]:

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

(7)

Where, k_2 ($\text{g}/(\text{mg}\cdot\text{min})$) is the rate constant of the pseudo-second-order equation.

The pseudo-first-order and pseudo-second-order models rate constants along with correlation coefficients and AARE values presented in Table 4. Fig.8 shows the agreement between experimental data with calculated values using Eq (7) for Ni(II) ions. As can be seen, the AARE values are 11.27% for the pseudo-first-order model and 7.246% for pseudo-second-order model, indicating a better fit with the pseudo-second-order model.

The better fit of this model to the experimental data is also observed in the much closer agreement between the experimental values of q_t and those obtained from the pseudo-second-order model, when compared to q_t values calculated from the pseudo-first-order model. This suggests that the pseudo-second-order kinetic model based on the assumption that the rate-limiting step may be chemical sorption involving valence forces through sharing or exchange of electrons between sorbent and sorbate.

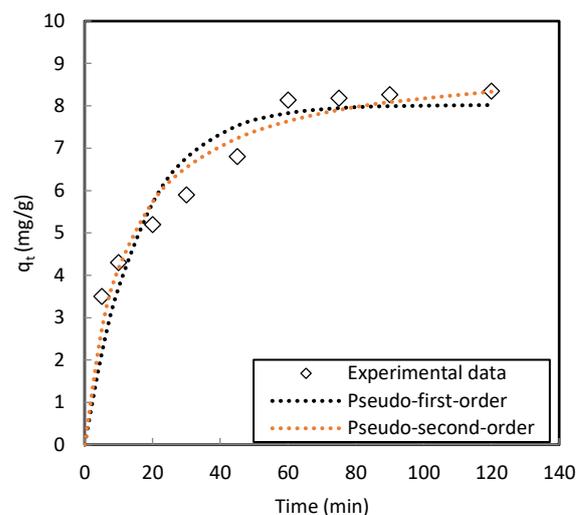


Fig 8. Plot of pseudo-first order and pseudo-second order kinetic models for adsorption of Ni(II) onto natural zeolite

Table 4. Kinetic parameters of pseudo-first order and pseudo-second order models for adsorption of Ni(II) onto natural zeolite

pseudo-first-order kinetic model			
k_1 (min^{-1})	q_e (mg/g)	R^2	AARE%
0.618	8.02	0.854	11.27
pseudo-second-order kinetic model			
k_2 ($\text{g}/\text{mg}\cdot\text{min}$)	q_e (mg/g)	R^2	AARE%
9.04×10^{-3}	9.167	0.931	7.246

3.7. Adsorption thermodynamics

Thermodynamic behavior of the adsorption of nickel ions onto natural zeolite is investigated using the thermodynamic parameters that include the change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°). These parameters are calculated from the following equations:

$$\ln K_D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (8)$$

Where K_D is the distribution coefficient (mL/g), ΔH° is the enthalpy change, ΔS° is the entropy change, T is the temperature (K), and R is the universal gas constant (8.314 J/mol.K). The free energy change (ΔG°) is determined using the following equation:

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (9)$$

Based on Eq. (8), the ΔH° and ΔS° parameters can be calculated from the slope and intercept of the plot of $\ln K_D$ vs. $1/T$, respectively (Fig. 9).

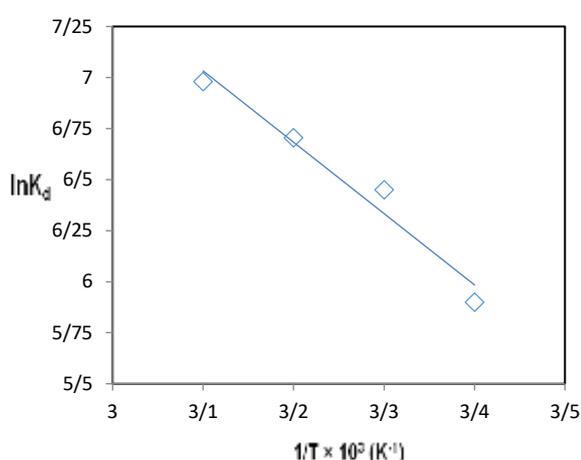


Fig 9. Plots of $\ln K_D$ vs. $1/T$ for the nickel ion adsorption on natural zeolite

The values of ΔG° , ΔH° , and ΔS° are given in Table 5 for Ni(II) adsorption on natural zeolite. The negative values of ΔG° indicate thermodynamically feasible and spontaneous nature of the adsorption. The positive values of ΔH° confirm the endothermic nature of the adsorption of nickel ions onto natural zeolite in the temperature range of 20-50°C. The positive ΔS° values indicate the affinity of the adsorbent for nickel ions.

Table 5. Thermodynamic parameters for the adsorption of nickel ion onto natural zeolite

ΔG° (kJ/mol)				ΔH° (kJ/mol)	ΔS° (J/mol.K)
20°C	30°C	40°C	50°C		
-	-	-	-	29.09	148.52

4. Conclusions

The aim of this study was to investigate the effectiveness of the natural zeolite to remove nickel

ions from aqueous solutions. Batch adsorption studies show that removal is dependent upon process parameters such as pH, dosage of adsorbent, contact time, initial nickel ion concentration and temperature. The maximum Ni(II) loading capacities of natural zeolite is 18.09 (mg/g). It had been found that the adsorption of natural zeolite is strongly affected by the initial pH of the solution. Moreover, the rate of uptake of nickel ions by the zeolite indicated that the process was quite rapid and maximum adsorption occurred within the first one hour of contact. The experimental data were well fitted to the Langmuir equation, with good correlation coefficients. The negative values of Gibbs free energy indicate the feasibility spontaneous nature of the adsorption process. The positive values of ΔH° indicate that the adsorption process is endothermic. Based on the results of the present work, the natural zeolite can be used effectively as an adsorbent/ion exchange material for the removal nickel ions from aqueous solutions and wastewater.

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