

Equilibrium ion exchange studies of Ni²⁺ on homoionic forms of clinoptilolite

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A natural zeolite (clinoptilolite) that is mined in KwaZulu-Natal, South Africa, was evaluated for the removal of Ni²⁺ from wastewater. In particular, the effect of zeolite modification on Ni²⁺ removal from synthetic wastewater was investigated. The natural clinoptilolite was pretreated with 2 M metal chlorides for 24 h to yield near homoionic Na⁺, K⁺ and Ca²⁺ forms. A comparison of the isotherms for the Na⁺-Ni²⁺, K⁺-Ni²⁺, Ca²⁺-Ni²⁺ and natural-Ni²⁺ systems gave insight into how the displaced ion affects the selectivity of the clinoptilolite for Ni²⁺. The Na⁺, K⁺ and natural forms show highly selective convex isotherms whereas the Ca²⁺ form has a concave graph suggesting that the selectivity series is Ca²⁺ > Ni²⁺ > (Na⁺, K⁺, natural). Thermodynamic properties revealed that the Ni²⁺ sorption capacity increases as the values of the equilibrium constant and Gibbs free energy increase with increasing temperature from 298.15 K to 348.15 K. The enthalpy change was positive for all forms of clinoptilolite; values of 26.00 kJ/mol, 18.72 kJ/mol and 42.05 kJ/mol were obtained for exchange of Ni²⁺ into Na⁺, K⁺ and Ca²⁺ forms, respectively. The positive changes in enthalpy provide an indication that the sorption reaction is endothermic for Ni(II). The Gibbs free energy values were all negative except for Ca²⁺-exchanged clinoptilolite at 298.15 K and 308.15 K, for which the values were positive 3.10 kJ/mol and 0.53 kJ/mol, respectively. The entropy values for Ni²⁺ sorption were also positive; values of 0.12 kJ/mol.K, 0.08 kJ/mol.K and 0.14 kJ/mol.K were obtained for the Na⁺, K⁺ and Ca²⁺ forms, respectively. As expected, the enthalpy obtained from the Van't Hoff plot is dependent not only on the metal ion being adsorbed, but also on the ion being displaced. Pretreatment of the zeolite enhances the removal efficiency provided that monovalent ions are used for the pretreatment. Thus clinoptilolite is an effective low-cost adsorbent for the removal of Ni²⁺ from aqueous solutions.

Introduction

Heavy metal pollution is an environmental problem of concern worldwide. The increasing levels of heavy metals in the environment represent a serious threat to human health and ecological systems. Soluble and mobile heavy metal species are non-biodegradable and tend to bioaccumulate in living organisms causing various diseases and disorders. The Ni²⁺ ion is one such heavy metal which is frequently encountered in raw wastewater streams from industries, such as those for the manufacture of magnetic tape, electroplating, jewellery, welding rods, dental procedures and pigments; Ni²⁺ is also used as a catalyst in oil hydrogenation.¹ Several methods – such as ion exchange, solvent extraction, reverse osmosis, precipitation and adsorption – have been proposed for the treatment of wastewater contaminated with heavy metals.²⁻⁴ Among several chemical and physical methods, the adsorption of heavy metals onto zeolites has been found to be superior to other techniques because of the capability of the zeolite to remove several cations simultaneously from an aqueous solution through ion exchange.³⁻⁷ The history of ion exchange on zeolites has been reported by several authors.^{3,8-10} One of the important properties of zeolites is that they show selectivity in adsorption, i.e. they possess different affinities for different ions.^{11,12}

The effect of converting the zeolite initially to a homoionic form for the removal of heavy metal ions from wastewater has been studied by many authors.¹³⁻¹⁹ These authors pointed out that zeolite in homoionic forms exhibits a significantly increased ability to remove heavy metals from wastewater. NaCl is most often used as the pretreatment agent. Prior to any ion-exchange application, most exchangeable ions from the structure of the material are removed by pretreatment and replaced by more easily removable ones. Pretreatment of natural zeolites with, for example, acids, bases and surfactants, is also used to improve their ion-exchange capacity. Most pretreatment operations increase the content of a single cation, called a homoionic form.

The evaluation of the ion-exchange properties of zeolites is based on equilibrium data for a particular exchange reaction. On the basis of these data, the main thermodynamic properties, such as the equilibrium constant (K_{eq}) and Gibbs free energy ΔG° , can be computed using a suitable model. The use of a reliable model for the exchange process is particularly important when one needs to predict the ion-exchange behaviour of the zeolites for varying compositions of the aqueous phase based on experimental data. Much research has been done with regard to modelling the equilibria of ion exchange in zeolites.²⁰⁻²⁴

Fitting of adsorption isotherm equations to experimental data is often an important aspect of data analysis. In most previous studies, Ni²⁺ adsorption with clinoptilolite was generally examined with the Langmuir, Dubinin–Radushkevitch and Freundlich isotherms.²⁵⁻²⁷

The Langmuir equation assumes that the adsorbed species forms a monolayer. But monolayer formation is possible only for a dilute solution. Under high concentration conditions the assumption is no longer valid as adsorbates accumulate to form multiple layers. The Langmuir equation also assumes that adsorbed molecules do not interact with each other laterally. This is impossible as weak forces of attraction exist even between molecules of the same type. Another assumption is that all the sites on the solid surface are equivalent in size and shape and have equivalent affinity for adsorbate molecules, i.e. the surface of the solid is homogeneous. But real solid surfaces are heterogeneous. Because clinoptilolite minerals have high surface irregularities, the adsorption models (Langmuir and Freundlich) should not be used to explain the adsorption equilibrium phenomenon.²⁸

Zeolites have been found to be highly efficient in removing heavy metals from wastewater and the costs involved are still significantly below competing technologies. Although major breakthroughs have been made towards the use of zeolites in environmental remediation, most researchers have focused on heavy metal ions such as Pb^{2+} , Cu^{2+} and Co^{2+} rather than on Ni^{2+} removal. Two interesting observations with respect to Ni^{2+} adsorption on clinoptilolite have been made by Sprynskyy et al.²⁹ After its initial fast uptake from mixed metal feed concentrations, the second phase of adsorption is characterised by desorption and is referred to as an 'inversion phenomenon'. It is thought that this phenomenon is caused by the counter-diffusion of displaced extra-lattice cations from the deeper layers of the zeolite. As high concentrations of these counter-ions diffuse out of the zeolite pores, the Ni^{2+} is displaced and re-adsorbed. This displacement indicates that Ni^{2+} adsorbs in the mesopores, rather than in the zeolite channels. It was observed by Sprynskyy et al.²⁹ that when metal ions like Pb^{2+} are adsorbed on clinoptilolite, there is usually only a slight difference between the loading capacities of these metal ions when single component feeds are compared to mixed feeds. This finding implies that metal ions are sorbed on specific sites. However, with Ni^{2+} , adsorption significantly decreases in mixed feeds as a consequence of competition with other metals. Sprynskyy et al.²⁹ concluded that the adsorption of Ni^{2+} ions is not site specific. Moreover, the zeolite selectivity for Ni^{2+} is generally low, hence improvements in Ni^{2+} selectivity are important for industrial applications, especially when implementation of more stringent standards for discharge of heavy metals into receiving environments are taken into consideration. It has been proven that converting zeolite to homoionic forms improves selectivity, but we are not aware of any study which compares different homoionic forms for the removal of Ni^{2+} from aqueous solutions. In this study, physical (i.e. pore diameter and volume) and thermodynamic differences between these forms have been found; such data have not been published before.

Theory: Ion-exchange isotherms

Ion-exchange isotherms are plots of the equilibrium fraction of an exchanging ion in solution against the equilibrium fraction of the same ion in the zeolite at the same temperature. The isotherms are plotted in terms of equivalent cation fraction of the ion in the solution (X_{sol}) against that in the solid (X_{zeo}) in accordance with the analysis of Inglezakis et al.²³ The equivalent cation fraction in solution and on the clinoptilolite is calculated by using Equations 3 and 4 given below.

Construction of ion-exchange isotherms

In general, the ion-exchange reaction between a solution containing the cation A^{z_A+} (where A is a cation of valence z_A) and the B form of clinoptilolite (B being a cation of valence z_B) may be written as³⁰:



in which L is a portion of the clinoptilolite framework holding a unit negative charge and the subscript *aq* denotes the solution phase. The equivalent fraction of the exchanging cation in the solution (X_{sol}) is therefore given by:

$$X_{sol} = \frac{z_A m_s^A}{z_A m_s^A + z_B m_s^B} \quad \text{Equation 2}$$

where m_s^A and m_s^B are the molarities of the ions A and B in solution, respectively. The equivalent cation fraction in the clinoptilolite is given by:

$$X_{zeo} = \frac{z_A (M_{A,i} - M_{A,f})V}{W.CEC} \quad \text{Equation 3}$$

where W is the zeolite mass in grams, V is the solution volume used in litres, $M_{A,i}$ and $M_{A,f}$ are the initial and final concentrations of the exchanging

ion (in moles per litre) and CEC is the cation-exchange capacity of the zeolite (in eq/g).²³

Experimental methods

The raw zeolite sample used in this study was obtained from Pratley (Pty) Limited (Kenmare, South Africa) which mines the zeolite in KwaZulu-Natal (South Africa). All chemicals and reagents used for experiments and analysis were analytical grade supplied by Merck Ltd. (Johannesburg, South Africa).

Zeolite preparation

Small grains of zeolite were obtained by first using a hammer to break the as-received samples into small pieces. These small pieces were then ground using a pestle and mortar and sieved to yield fractions differing in diameter from 0.60 mm to 0.85 mm. Sieving was repeated several times to minimise the retention of smaller grains in a sample with a larger size range. Prior to the batch adsorption experiments, the crushed zeolite was washed with distilled water three times to remove the surface dust, and then dried in an oven at 343.15 K for 24 h until a constant weight was attained.

Preparation of homoionic forms

Near homoionic forms of Na^+ , K^+ and Ca^{2+} clinoptilolite were generated by treating 30-g batches of the purified clinoptilolite with 300 mL of 2 M chloride salts ($NaCl$, KCl and $CaCl_2$ for Na^+ , K^+ and Ca^{2+} , respectively). The mixtures were then placed in a Labex shaking incubator (Edenvale, South Africa) at 298.15 K for 24 h at a speed of 200 rpm. The solutions of the Cl^- salts were replaced with fresh ones for a further 24 h. The treated clinoptilolite grains were washed several times with distilled water to eliminate excess metal chlorides, and dried in an oven at 343.15 K for 24 h. Treated zeolite fractions were used as adsorbents for Ni^{2+} removal. Metal chloride treatment was conducted based on the findings of previous studies that alkali and alkaline earth metals are cheap, commonly available and are the most effective exchangeable ions for heavy metal removal.²

Equilibrium studies

Equilibrium studies were done as follows. A stock solution (1000 mg/L) of Ni^{2+} was prepared by dissolving 2.04 g of $NiCl_2 \cdot 6H_2O$ in 1 L of distilled water. The composition of the synthetic aqueous solution used in this study was based on those used previously and the concentrations were within the range of typical industrial wastewaters, that is, 0.1 mg/L to 100 mg/L.²⁸

Synthetic samples were prepared to give Ni^{2+} concentrations of 20 mg/L, 40 mg/L, 60 mg/L, 80 mg/L and 100 mg/L by adding an appropriate amount of $NiCl_2 \cdot 6H_2O$ stock solution to deionised water. The masses of clinoptilolite used in the experiments ranged from 0.2 g to 1.5 g and the solution volume ranged from 10 mL to 100 mL. Before adding the adsorbents, the pH of the solution was adjusted to 7, i.e. the pH at which H^+ and Ni^{2+} competition is minimal, using either 0.1 M $NaOH$ or 0.1 M HNO_3 solution, following the method of Gaus and Lutze²⁶. The zeolite mass to solution volume ratios and the aqueous mixture compositions used in the experiments were designed to yield a relatively evenly spaced distribution of points along the ion-exchange isotherm as well as significant differences in the initial and final concentrations of the cation in solution. No background electrolyte was added during the ion-exchange experiments.

The clinoptilolite-zeolite samples were put in 250-mL Erlenmeyer flasks and agitated in a Labex shaking incubator at 298.15 K, 308.15 K, 323.15 K, 333.15 K or 348.15 K for 24 h.² After equilibrium was established, the clinoptilolite was separated from the solution by centrifugation and the pH of the supernatant was adjusted to 7. The equilibrium concentration of the exchangeable ions (Na^+ , K^+ , Ca^{2+}) and Ni^{2+} in the samples was determined by atomic absorption spectrometry (AAS, Varian 55B). In order to calculate the experimental error, all adsorption experiments were performed in triplicate, which enabled us

to account for the errors caused by instability of the isothermal bath temperature and the calibration of the AAS.

The metal concentration in the liquid phase was determined at the beginning (C_o) and at the end (C_f) of the adsorption. The following equation was used to compute the percentage uptake of the metal by the clinoptilolite:

$$\text{Sorption \%} = \frac{(C_o - C_f)100}{C_o} \quad \text{Equation 4}$$

Results

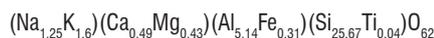
The chemical analysis of the natural and homoionic clinoptilolite samples is given in Table 1.

Table 1: Chemical composition (wt %) of treated clinoptilolite samples determined by X-ray fluorescence

Component	Weight (%)			
	Natural	Na form	K form	Ca form
SiO ₂	77.24	77.37	76.13	76.50
Al ₂ O ₃	13.30	13.18	13.09	12.93
Fe ₂ O ₃	0.14	0.13	0.14	0.12
FeO	1.09	1.01	1.14	0.12
MnO	0.04	0.01	0.02	0.02
MgO	0.86	0.71	0.67	0.80
CaO	1.40	0.77	0.87	3.35
Na ₂ O	1.94	3.84	0.23	1.43
K ₂ O	3.78	2.94	7.78	3.77
TiO ₂	0.14	0.14	0.14	0.14
Total	100.44	100.01	100.00	99.97

The elemental analysis of the natural and pretreated clinoptilolite revealed that it is mainly composed of SiO₂, Al₂O₃ and Fe₂O₃ with very low amounts of MnO and TiO₂ in the framework. The extra-framework ions Na⁺, K⁺, Mg²⁺ and Ca²⁺ showed considerable variation depending on the pretreatment agent used and this change was mainly at the expense of Na⁺ and Ca²⁺ content. SiO₂ ranged from 76.13% to 77.37% and Al₂O₃ ranged from 12.93% to 13.30%.

In the natural sample about 50% of the exchangeable ions were K⁺. Complete exchange of cations was impossible to achieve, especially for the Na⁺- and Ca²⁺-treated clinoptilolite as it is assumed that K⁺ present in the clinoptilolite did not exchange significantly with other cations. This behaviour is attributed to the location of K⁺. Based on the chemical composition of the natural clinoptilolite used in this study, the molecular formula for the natural zeolite was:



The pretreatment process led to the production of different forms of zeolite depending on the treatment agent used. The molecular formulae of the pretreated samples were as follows:

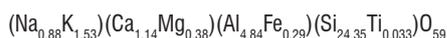
Na⁺-clinoptilolite:



K⁺-clinoptilolite:



Ca²⁺-clinoptilolite:



The cation-exchange capacity (CEC, milliequivalents (meq) per gram) of the zeolite samples was derived from the analysis given in Table 1. The calculation of CEC was based on the assumptions that (1) Al³⁺ and Fe³⁺ substitute for Si⁴⁺ in the tetrahedral sites and result in a negatively charged structure, (2) this negative charge is balanced by the alkali and alkaline earth ions in the intracrystalline cation-exchange sites and (3) any other exchangeable ions present in a homoionic form of clinoptilolite are assumed to occupy inaccessible sites; for instance, the K⁺, Ca²⁺ and Mg²⁺ present in the Na⁺-clinoptilolite are in inaccessible exchange sites and do not participate in the ion-exchange process. An additional assumption is that negligible mineral impurities are present in the sample.²²

Experimental CECs of clinoptilolite were determined and were found to range from 1.38 meq/g to 2.29 meq/g for all forms of clinoptilolite (for natural and pretreated clinoptilolite).

Previous studies showed that the South African zeolite comprises mainly clinoptilolite (80–85%) and coexists with impurities of opaline, cristobalite, K-feldspar and traces of sanidine.² From the X-ray fluorescence results, the Si:Al ratio was calculated to be 5.14. The chemical composition, the theoretical exchange capacity and the Si:Al ratio (generally ranging from 4 to 5.5) are typical for clinoptilolite.³¹ Low SiO₂ members are enriched with Ca²⁺, whereas high SiO₂ clinoptilolite is enriched with K⁺, Na⁺ and Mg²⁺. It was found that the natural zeolite was predominantly clinoptilolite.

Effects of ion exchange

The surface area and pore volume data for Na⁺, K⁺ and Ca²⁺ form clinoptilolite are presented in Table 2. The ionic radii taken from Cotton and Wilkinson³² have also been included in Table 2. The data for the Na⁺ and Ca²⁺ forms are within experimental error, while the K⁺ form has a higher surface area and pore volume.

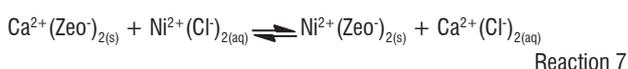
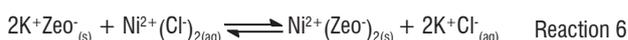
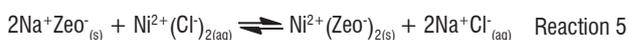


Table 2: Structural characteristics of different homoionic forms of the zeolite

Adsorbent	Surface area	Pore volume	Ionic radii (Å)
	S _{BET} (m ² /g)	V ₁ (cm ³ /g)	
Na form	13.54	3.11	Na ⁺ (1.16) ³²
K form	16.49	3.79	K ⁺ (1.52) ³²
Ca form	14.31	3.28	Ca ²⁺ (1.14) ³²

Note: The surface area and pore volume data were obtained from Brunauer Emmett Teller (BET) analysis. The ionic radii are values from Cotton and Wilkinson³².

Figures 1 to 4 present the experimental ion-exchange results. The initial and final concentration of Ni²⁺ was measured as well as the concentration of the displaced ions, Na⁺ for the Na⁺ form, K⁺ for the K⁺ form and Ca²⁺ for the Ca²⁺ form. These measured concentrations, zeolite masses and the volumes of solutions were used in the construction of ion-exchange isotherms.

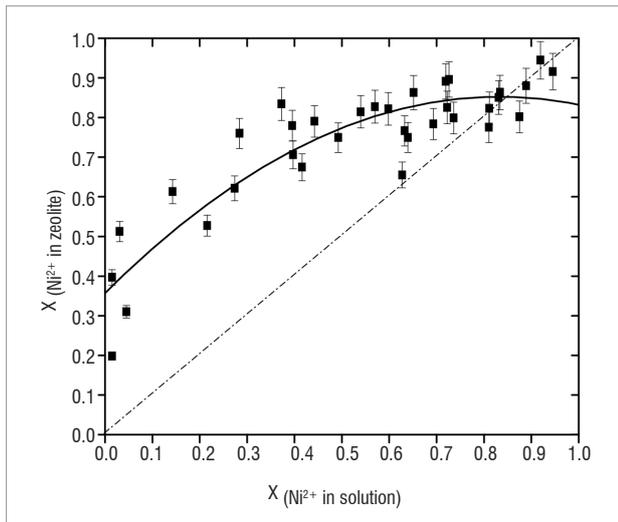


Figure 1: The Na⁺-Ni²⁺ isotherm at 298.15 K. $X_{(Ni^{2+} \text{ in soln})}$: equivalent fraction of ingoing nickel in the liquid phase. $X_{(Ni^{2+} \text{ in Zeo})}$: equivalent fraction of ingoing cation in the solid phase. Percentage error bars for all points are indicated. The solid curve is a polynomial fit of order 2.

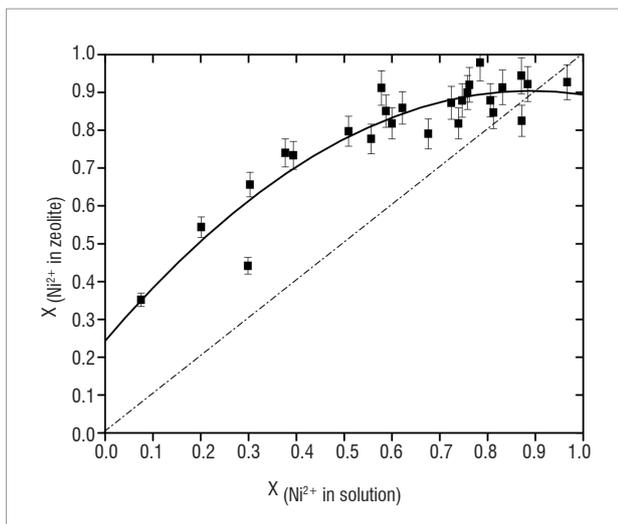


Figure 2: The K⁺-Ni²⁺ isotherm at 298.15 K. $X_{(Ni^{2+} \text{ in soln})}$: equivalent fraction of ingoing nickel in the liquid phase. $X_{(Ni^{2+} \text{ in Zeo})}$: equivalent fraction of ingoing cation in the solid phase. Percentage error bars for all points are indicated. The curve was fitted to the isotherm data using a polynomial of order 2.

A comparison of the isotherms (Na⁺-Ni²⁺, K⁺-Ni²⁺, natural-Ni²⁺ and Ca²⁺-Ni²⁺) gives insight into how the displaced ion affects the selectivity of the clinoptilolite for Ni²⁺. The Na⁺-Ni²⁺ isotherm indicates a strong selectivity for Ni²⁺ through the entire range of zeolite composition. It is observed that the isotherms shown in Figures 1 to 3 do not proceed to completion (that is, do not attain $X_{\text{solution}} = 1$ for $X_{\text{zeolite}} = 1$). This result is attributed to the fact that in these systems only a fraction of the total CEC is available to the incoming cations as a result of crystallite occlusion; nonetheless the CEC is close to 1 (0.9 ± 0.1). The same observation was reported by Breck³³. When the isotherm exhibits a convex profile, e.g. for Na⁺-Ni²⁺, K⁺-Ni²⁺ and natural-Ni²⁺ systems, the uptake of Ni²⁺ from the solution is known to follow a Langmuir-type isotherm.³⁴ The Na⁺, K⁺ and natural forms show highly selective convex graphs, whereas the Ca²⁺ form has a concave graph, suggesting the selectivity series to be Ca²⁺ > Ni²⁺ > (Na⁺, K⁺, natural). This selectivity series is in agreement with the investigation done by Colella³⁴ on Italian clinoptilolite. Figure 4 demonstrates that the clinoptilolite has a greater affinity for Ca²⁺ than for

Ni²⁺. This observation is consistent with the expectation that the Ca²⁺ ion has a relatively lower desorption ratio than Na⁺ and K⁺ because of the strong interaction (ionic in nature) between clinoptilolite and Ca²⁺ (it is difficult to destroy the Ca²⁺-O-Al bonds). A similar observation was made by Ćurković et al.³⁵ for Serbian clinoptilolite. A remarkably high selectivity of natural-, K⁺- and Na⁺-exchanged clinoptilolite for Ni²⁺ is observed.

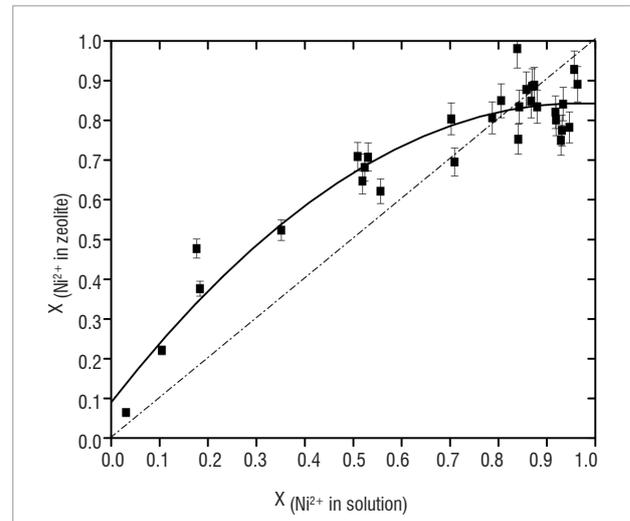


Figure 3: The natural-Ni²⁺ isotherm at 298.15 K. $X_{(Ni^{2+} \text{ in soln})}$: equivalent fraction of ingoing nickel in the liquid phase. $X_{(Ni^{2+} \text{ in Zeo})}$: equivalent fraction of ingoing cation in the solid phase. Percentage error bars for all points are indicated. The curve was fitted to the isotherm data using a polynomial of order 2.

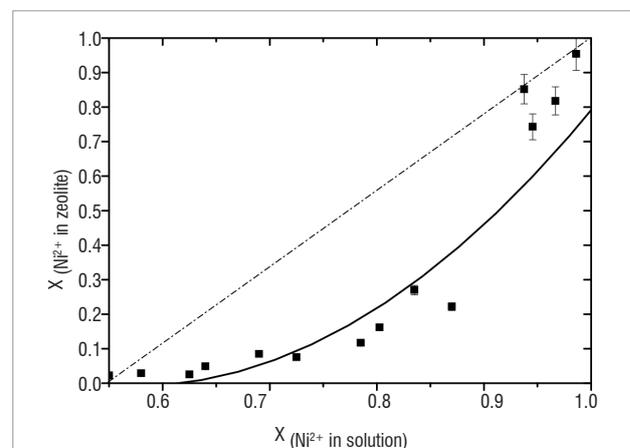


Figure 4: The Ca²⁺-Ni²⁺ isotherm at 298.15 K. $X_{(Ni^{2+} \text{ in soln})}$: equivalent fraction of ingoing nickel in the liquid phase. $X_{(Ni^{2+} \text{ in Zeo})}$: equivalent fraction of ingoing cation in the solid phase. Percentage error bars for some points are indicated. The curve was fitted to the isotherm data using a polynomial of order 2.

In order to obtain the parameter capable of describing the selectivity/non-selectivity of a given form of zeolite, the thermodynamic equilibrium constant (K_{eq}) was evaluated using the following procedure outlined by Khan and Singh³⁶:

$$K_{eq} = a_z/a_s = f_z C_z / f_s C_s \quad \text{Equation 8}$$

where a_z denotes the activity of adsorbed Ni²⁺, a_s is the activity of Ni²⁺ in solution at equilibrium, C_z is the milligrams of Ni²⁺ adsorbed per litre of solution in contact with the clinoptilolite surface, C_s denotes the milligrams per litre of Ni²⁺ in solution at equilibrium, f_z is the activity coefficient of the adsorbed Ni²⁺ and f_s is the activity coefficient of the

Ni²⁺ in solution. The method used to calculate ion activities is the one proposed by Debye and Huckel³⁷ in 1923 in which the ionic strength of the solution is calculated first and then the activity coefficient. Because the activity coefficient approaches unity at very low concentrations, Equation 8 can be re-written as

$$\lim_{C_z \rightarrow 0} \frac{C_z}{C_s} = \frac{a_z}{a_s} = K_{eq} \quad \text{which reduces to} \quad \text{Equation 9}$$

$$K_{eq} = \frac{C_z}{C_s} \quad \text{Equation 10}$$

The values of K_{eq} were calculated as the ratio of the equilibrium concentration of Ni²⁺ on the zeolite and in solution attained after 24 h of adsorption. The standard free energy change on adsorption (ΔG°) was calculated using the following equations:

$$\Delta G^\circ = -RT \ln K_{eq} \quad \text{Equation 11}$$

Several researchers have reported ΔG° values for adsorption in zeolites.^{23,25} In their calculations they only reported ΔG°_{ads} , and did not mention the ΔG°_{des} of the ion being displaced. By considering these two parameters, a true Gibbs free energy of exchange (ΔG°_{exc}) can be computed which is representative of the whole system. Therefore Equation 12 is used to calculate the standard free energy of reaction:

$$\Delta G^\circ_{exc} = \Delta G^\circ_{ads} - \Delta G^\circ_{des} \quad \text{Equation 12}$$

where ΔG°_{exc} denotes the Gibbs free energy of ion-exchange reaction, ΔG°_{ads} is the Gibbs free energy of adsorption of Ni²⁺ onto clinoptilolite and ΔG°_{des} is the Gibbs free energy of desorption of exchangeable ions in the clinoptilolite (Na⁺, K⁺ and Ca²⁺). R is the universal gas constant (8.314 J/mol.K) and T is the temperature in Kelvin.

The ΔS° and ΔH° values were obtained from the slope and intercept of the Van't Hoff plots (plots of the natural logarithm of equilibrium constant of the reaction versus the reciprocal of temperature in Kelvin).

$$\ln K_{eq} = \Delta S^\circ/R - (\Delta H^\circ/R)1/T \quad \text{Equation 13}$$

The enthalpy of the reaction can be found from the gradient of the plot, which equals $-\Delta H^\circ/R$, and the entropy is the intercept, $\Delta S^\circ/R$. Table 3 reports the thermodynamic values at different temperatures.

The equilibrium constants K_{eq} derived from this study were quite high compared to those reported by Argun²⁷ despite using the same type of zeolite. Argun reported very low K_{eq} values of 3.28, 2.97 and 2.65 at 293.15 K, 313.15 K and 333.15 K, respectively, using Turkish natural clinoptilolite from the Langmuir isotherm constants to approximate the equilibrium constant, whereas, in this study, we found K_{eq} to be 23.69 at 298.15 K, which increased as temperature was increased (Table 3). A re-evaluation of the isotherm data in Argun's²⁷ study (after 3-h contact time instead of 60 min as in the original paper) at 293.15 K and at an

initial concentration of Ni²⁺ of 25 mg/L for 1 g of clinoptilolite yielded a K_{eq} of 18 for the natural-Ni²⁺ system, which is very close to the values obtained in this study. The recalculated ΔG° value at 293.15 K is -7.04 kJ/mol (from -2.89 kJ/mol). Our results demonstrate that the reliance on linearised Langmuir equations potentially limits the ability to model sorption data accurately.

The thermodynamic quantities reported in Table 3 are in accordance with the selectivity series depicted from the isotherm plots. The Gibbs free energy of natural and pretreated clinoptilolite were evaluated, and the spontaneity of adsorption is seen to follow the series Na⁺-form > natural-form > K⁺-form > Ca²⁺-form. In all cases, the free energy (ΔG°) of the Ni²⁺ sorption was negative, suggesting that the spontaneity of the process increased with increasing temperature. The values of the ΔG° also confirm that the maximum adsorption is obtained with the Na⁺-exchanged clinoptilolite followed by the natural, K⁺ and Ca²⁺ forms.

The ΔH° was positive in all forms of clinoptilolite and ranged from 18.72 kJ/mol to 42.05 kJ/mol (Table 1), which indicates that the sorption reaction is endothermic for Ni²⁺. These values were calculated from plots of $\ln K_{eq}$ versus 1/T. The linear nature of the plot indicates that the mechanism of adsorption is not changed as temperature is changed. But the amount of adsorption is changed because the supply of thermal energy is different. The endothermic nature of the adsorption processes shows that these processes are not energetically stable.³⁰ If the values of ΔH° for Ni²⁺ adsorption had been within the range of 8.4–12.6 kJ/mol, then one could propose that the adsorption process was ionic in nature.¹⁵ However, the values obtained in this study were greater than 12.6 kJ/mol, which indicates that the mechanism for the adsorption of these ions in zeolites is not ion exchange.

The Ni²⁺-Na⁺ system

The ion-exchange isotherms shown in Figure 1 demonstrate the extreme selectivity of Na⁺-clinoptilolite for the incoming Ni²⁺ cations, which is confirmed by the high values of the equilibrium constant ($K_{eq} > 1$) in Table 3 and the corresponding negative values of the free energies of exchange. The data also indicate that the value of K_{eq} increases with increasing temperature from 298.15 K to 348.15 K in all forms of the zeolite.

The enthalpy of exchange is positive for the Ni²⁺-Na⁺ clinoptilolite. This positive value is explained on the one hand by the substitution of Na⁺ cations by Ni²⁺ cations, which have a greater heat of hydration (-406 kJ/mol for Na⁺ and -2105 kJ/mol for Ni²⁺)³² in the aqueous phase, and on the other hand by the greater interaction energy of the Ni²⁺ cations with the exchange centres of clinoptilolite as a result of their similarity in size.

The K⁺-Ni²⁺ and natural-Ni²⁺ systems

The K⁺-Ni²⁺ and natural-Ni²⁺ systems presented highly selective convex isotherms when Ni²⁺ was adsorbed; this finding is confirmed by the high values of the exchange constant ($\sim K_{eq} > 16$ at 323.15 K). The enthalpies of exchange for both of these systems were positive and were almost of the same magnitude (18.75 kJ/mol for K⁺-Ni²⁺ and 22.38 kJ/mol for natural-Ni²⁺). This result suggests that K⁺ is common to both systems as an exchangeable ion.

Table 3: Values of various thermodynamic parameters for the adsorption of Ni (II) in solution onto natural and pretreated clinoptilolite

Form of zeolite	Thermodynamic parameters											
	K_{eq}					$\Delta G^\circ_{reaction}$ (kJ/mol)					ΔH° (kJ/mol)	ΔS° (kJ/mol.K)
	298.15 K	308.15 K	323.15 K	333.15 K	348.15 K	298.15 K	308.15 K	323.15 K	333.15 K	348.15 K		
Na form	29.60	44.21	53.85	83.75	144.48	-9.12	-10.54	-11.63	-13.49	-15.90	26.00	0.12
K form	8.73	11.26	16.45	21.73	24.47	-5.58	-6.46	-7.82	-8.90	-9.82	18.72	0.08
Ca form	0.35	0.989	1.34	2.2	9.01	3.10	0.53	-0.34	-3.94	-6.11	42.05	0.14
Natural form	23.69	24.53	39.87	60.45	76.73	-8.50	-9.70	-10.69	-12.20	-13.50	22.38	0.10

The Ca^{2+} - Ni^{2+} system

Distinct from the other systems, the Ni^{2+} - Ca^{2+} system yielded a concave isotherm, clear non-selectivity and the equilibrium constants (K_{eq}) were less than 1 at 298.15 K and 305.15 K (Table 3). The Gibbs free energy of exchange was positive at these temperatures, but a further increase in temperature resulted in the spontaneity of the reaction. The ΔG° values were positive at 298.15 K and 308.15 K (3.098 kJ/mol and 0.527 kJ/mol, respectively) and positive at temperatures greater than 323.15 K. Pabalan²² also reported a positive ΔG° value of 4.19 kJ/mol at 298.15 K for a system involving Ca^{2+} - Na^+ using American clinoptilolite.

The substitution of the doubly charged Ca^{2+} cations with doubly charged Ni^{2+} ions proved to be an endothermic exchange process (positive enthalpy). The entropy for the Ca^{2+} - Ni^{2+} exchange system was positive because in the aqueous phase the strongly hydrated doubly charged cations (Ca^{2+}) were substituted by the similarly hydrated Ni^{2+} cations.

Conclusion

Evaluation of the thermodynamic parameters K_{eq} , ΔG° , ΔH° and ΔS° provided insight into the mechanism of Ni^{2+} sorption by the zeolite. The results of this research showed that clinoptilolite is an effective low cost adsorbent for the removal of Ni^{2+} from aqueous solution. Pretreatment of the zeolite enhances the removal efficiency if monovalent ions are used, and selectivity depends on the type of the exchangeable ions on the zeolite. Treating the zeolite with CaCl_2 decreased the zeolite's ability to remove Ni^{2+} from aqueous solution. Ca^{2+} bind more strongly to the zeolite than sodium and potassium ions. The thermodynamic parameters revealed that Ni^{2+} sorption in clinoptilolite is spontaneous and endothermic. The surface area and pore volume data presented for the Na^+ and Ca^{2+} forms were within experimental error, while the K^+ form had a higher surface area and pore volume.

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Authors' contributions

J.G., B.T. and K.K. collected the data; L.L.J. supervised the work; J.G. wrote the first draft of the manuscript; and all authors contributed to revisions of the manuscript.

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