

Determination of kinetic and equilibrium parameters of the batch adsorption of Ni(II) from aqueous solutions by Na-mordenite

Xue-Song Wang^{a,*}, Juan Huang^a, Huai-Qiong Hu^a, Jing Wang^a, Yong Qin^b

^a Department of Chemical Engineering, Huaihai Institute of Technology, Lianyungang, Jiangsu 222005, China

^b School of Resources and Geo-Science, China University of Mining and Technology, Xuzhou, Jiangsu 221008, China

Received 8 May 2006; received in revised form 23 June 2006; accepted 19 August 2006

Available online 25 August 2006

Abstract

The potential to remove nickel(II) ions from aqueous solutions using Na-mordenite, a common zeolite mineral, was thoroughly investigated. The effects of relevant parameters solution pH, adsorbent dose, ionic strength, and temperature on nickel(II) adsorption capacity were examined. The sorption data followed the Langmuir, Freundlich, Langmuir–Freundlich and Dubinin–Radushkevich (D–R) isotherms. The maximum sorption capacity was found to be 5.324 mg/g at pH 6, initial concentration of 40 mg/L and temperature of 20 °C. Thermodynamic parameters, viz. changes in standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) have also been evaluated and the results show that the sorption process was spontaneous and endothermic in nature. Dynamics of the sorption process were studied and the values of rate constant of adsorption, rate constant of intraparticle diffusion were calculated. The activation energy (E_a) was found to be 12.465 kJ/mol in the present study, indicating a chemical sorption process involving weak interactions between sorbent and sorbate. The sorption capacity increased with the increase of solution pH and the decrease of ionic strength and adsorbent dose. The nickel(II) ions sorption by the Na-mordenite is not completely attributable to ion exchange. Compared to the other adsorbents, the nickel(II) ions show a lower affinity towards the clay mineral adsorbents. © 2006 Elsevier B.V. All rights reserved.

Keywords: Adsorption; Nickel(II); Na-mordenite; Sorption mechanism; Wastewater treatment

1. Introduction

Nickel(II) may be found in wastewater discharges from mining, electroplating, pigments and ceramic industries, battery and accumulator manufacturing [1]. Nickel is toxic to a variety of aquatic organisms, even at very low concentration. The most common adverse health effect of nickel in humans is an allergic reaction; large amounts of nickel can cause lung and nasal sinus cancers. The EPA requires nickel in drinking water not to exceed 0.04 mg/L [2].

Conventional treatment technologies such as precipitation, ion exchange, and activated adsorption have been employed to remove nickel(II) ions from aqueous solution. However, these processes have significant disadvantages such as incomplete metal removal, particularly at low concentrations and high operational costs [3]. Cost-effective treatment technologies,

therefore, are needed to meet these requirements. Ion exchange process based on zeolites has been considered to be a cost-effective approach for waste decontamination. In the past few decades, both natural and synthetic zeolites have been studied for heavy metal removal [4]. However, nickel usually shows a low affinity towards some natural zeolites [5]. Moreover, removal of heavy metals from wastewaters by adsorption process is influenced by several factors, e.g., type of adsorbent and adsorptive material, solution pH, ionic strength, and temperature [6]. The basic objective of the present research was to study the adsorption mechanism of nickel(II) ions onto Na-mordenite (a common natural zeolite) and contribute to the understanding and modelling of the equilibrium of adsorption processes. The sorption capacity of nickel(II) was examined by varying experimental conditions, viz. solution pH, adsorbent dose, ionic strength, and contact time and reaction temperature. The experimental data were correlated to different kinetic and adsorption models and the corresponding parameters were determined. These parameters are considered fundamental for further studies involving the scale-up of the process for continuous studies.

* Corresponding author. Tel.: +86 518 5890786; fax: +86 518 5891791.
E-mail address: snowpine1969@yahoo.com.cn (X.-S. Wang).

2. Materials and methods

Naturally occurring mordenite was provided for study by China University of Mining and Technology. The mordenite was lightly ground and sieved. Fine particles with a diameter $<150\ \mu\text{m}$ were used to prepare the Na-mordenite. To prepare homoionic Na-mordenite, 30 g of mordenite was mixed with $500\ \text{cm}^3$ of 1 M NaCl. After 24 h end-over-end shaking, the mordenite suspension was centrifuged at 3000 rpm and the supernatant was replaced with fresh 1 M NaCl solution. This procedure was repeated three times, followed by a three-fold washing with $500\ \text{cm}^3$ deionized water. The Na-mordenite was dried at $60\ ^\circ\text{C}$ overnight and stored in polyethylene flask for further experiments.

The stock solutions of Ni^{2+} (2000 mg/L) were prepared in deionized water using nickel sulphate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) (analytical grade reagent). All working solutions were prepared by diluting the stock solution with deionized water.

Batch adsorption experiments were carried out by shaking 0.25 g of sorbent with $50\ \text{cm}^3$ aqueous solution of the desired concentration in a temperature-controlled water-batch shaker. The pH of solutions was adjusted to constant values using 0.1 M HCl or 0.1 M NaOH. Continuous mixing was provided during the experiments with a constant agitation speed of 200 rpm. Kinetic studies were carried out at constant pH 6 with initial concentration (40 mg/L) and adsorbent dose of 2 g/L at various temperatures (20, 30 and $40\ ^\circ\text{C}$). After shaking, the samples were withdrawn at suitable time intervals, filtered through a $0.45\ \mu\text{m}$ membrane filter and then analyzed for Ni^{2+} concentrations with atomic absorption spectrophotometer (AAS). For the isotherm studies, 0.25 g of Na-mordenite was put into $50\ \text{cm}^3$ solutions of various concentrations of Ni^{2+} (20–100 mg/L). The flasks were shaken for 120 min to reach equilibrium. A known volume of the solution was removed and filtered for Ni^{2+} analysis. Effect of pH on the adsorption of Ni^{2+} was studied by varying the pH from 2.0 to 6.0. The effect of temperature on adsorption equilibrium was studied by varying temperatures from 20 to $40\ ^\circ\text{C}$. Effect of sorbent dose on uptake of Ni^{2+} was investigated by varying the range of Na-mordenite doses from 1.0 to 5.0 g/L with an initial concentration 40 mg/L and agitation speed of 200 rpm. 0.1 and 0.01 M NaNO_3 were employed as background electrolyte to investigate the effect of ion strength on uptake of Ni^{2+} .

The amount of Ni^{2+} sorbed by Na-mordenite (q) in the sorption system was calculated using the mass balance:

$$q = \frac{V(C_i - C_e)}{M} \quad (1)$$

where V is the solution volume (mL), M the amount of sorbent (g), and C_i and C_e (mg/L) are the initial and equilibrium metal concentrations, respectively.

XRD measurement was done with Analytical X-ray spectrometer (D/Max-3B) using Cu $K\alpha$ radiations. Sears's method was chosen to estimate the surface area of the Na-mordenite and the copper bisethylenediamine complex method was used to determine the cation exchange capacity (CEC) of the Na-mordenite. The detailed procedures for the determinations of surface area and cation exchange capacity are referred to [7].

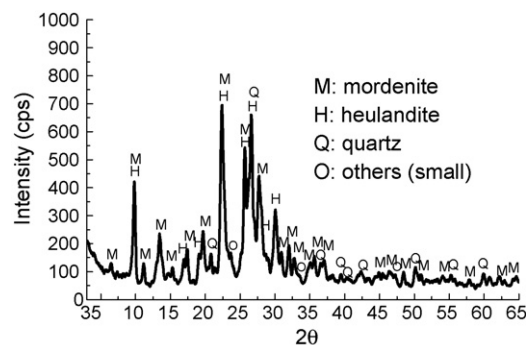


Fig. 1. XRD pattern for Na-mordenite.

3. Results and discussion

3.1. Adsorbent characterization

The XRD spectrum of the Na-mordenite is given in Fig. 1. The result indicates that the adsorbent used in this study consists mainly of mordenite. The surface area of a porous material is one of the most useful micro-structural parameters for defining its properties. It is the total internal boundary between the solid phase and the pore system [7]. The specific surface area of Na-mordenite was $7.0\ \text{m}^2/\text{g}$. The CEC is the number of equivalents of exchangeable charge per mass of adsorbent. In this work, the value of Na-mordenite CEC was found to 14.2 meq/100 g. These values (specific surface area and CEC) are comparable to those of kaolinite with the similar determination methods [7].

3.2. Adsorption isotherms

Analysis of equilibrium data is important for developing an equation that can be used to compare different materials under different operational conditions and to design and optimize an operating procedure [1]. The Langmuir, Freundlich and Langmuir–Freundlich isotherms are commonly used for wastewater treatment applications.

The Langmuir equation was developed by Irving Langmuir in 1916 to describe the adsorption of gas molecules on a planar surface [8]. The Langmuir model suggests, as a hypothesis, that uptake occurs on a homogenous surface by monolayer sorption without interaction between sorbed molecules. This Langmuir equation has the form:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (2)$$

where q_e is the amount adsorbed at equilibrium (mg/g), C_e the equilibrium concentration (mg/L), b a constant related to the energy or net enthalpy of adsorption (L/mg), and q_m is the maximum adsorption capacity (mg/g). The Langmuir equation can be described by the linearized form as follows:

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

By plotting (C_e/q_e) versus C_e , q_m and b can be determined if a straight line is obtained.

Table 1
Langmuir, Freundlich and Langmuir–Freundlich adsorption constants as well as free energy change associated with adsorption of nickel(II) onto Na-mordenite at various temperatures

Temperature (°C)	Freundlich			Langmuir			Langmuir–Freundlich			ΔG° (kJ/mol)
	K_F ((mg/g)/(mg/L) ^{1/n})	n	R	q_m (mg/g)	b (L/mg)	R	K_{LF} (L/mg)	n_1	R	
20	1.31	3.429	0.9928	5.324	0.07687	0.9899	1.244	0.2286	0.9902	−8.353
30	3.08	8.258	0.9927	5.364	0.2999	0.9967	1.428	0.04622	0.9916	−20.803
40	3.78	11.681	0.9930	5.516	0.8572	0.9977	2.448	0.04976	0.9901	−30.397

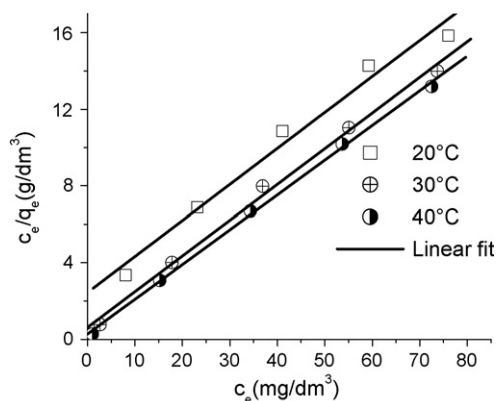


Fig. 2. Langmuir isotherms of nickel(II) at various temperatures.

The Langmuir plots for nickel isothermal adsorption data at various temperatures are shown in Fig. 2. It demonstrates that the Langmuir adsorptive isothermal equation fits the experimental data very well. The calculated constants q_m and b together with correlation coefficients are given in Table 1. The values of q_m increased with the rise of temperatures, indicating the sorption process is endothermic in nature. The constant, b , represents the affinity between the adsorbent and sorbate [9]. The values of b increased with increasing temperature as well.

The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant, separation factor or equilibrium parameter, R_L , which is defined by:

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

where b is the Langmuir constant and C_i is the initial metal ion concentration (mg/L). R_L value indicates the type of isotherm. According to McKay et al. [10], R_L values between 0 and 1 suggest favorable adsorption. R_L values for nickel(II) at various temperatures were found to be between 0 and 1 (Table 2) indicating favorable adsorption.

Table 2
 R_L values for the adsorption of nickel(II) onto Na-mordenite at various temperatures

Temperature (°C)	Initial concentration				
	20 mg/L	40 mg/L	60 mg/L	80 mg/L	100 mg/L
20	0.394	0.245	0.178	0.139	0.115
30	0.143	0.076	0.053	0.040	0.032
40	0.055	0.028	0.019	0.014	0.011

The Freundlich isotherm based on sorption on a heterogeneous surface is as follows [11]:

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

where q_e is the amount adsorbed at equilibrium (mg/g) and C_e is the equilibrium concentration (mg/L). K_F and n are equilibrium constants indicative of adsorption capacity and adsorption intensity, respectively. The linearized form of Freundlich sorption isotherm is:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (6)$$

Freundlich plots for the nickel(II) adsorption at various temperatures are given in Fig. 3. It illustrates that adsorption of nickel(II) ions onto Na-mordenite obeys the Freundlich isothermal model as well. The corresponding Freundlich isotherm constants K_F and n together with the correlation coefficients (R) are also listed in Table 1. Values of K_F derived from the Freundlich theory are an indicator of the adsorption capacity of a given adsorbent [12]. The results obtained in the present study indicate the adsorption capacities towards nickel(II) ions onto Na-mordenite increased with increasing temperatures. The exponent n was greater than unity at various temperatures in Table 1 indicates a favorable adsorption processes [12].

Thermodynamic parameters including the standard enthalpy change (ΔH°), the Gibbs free energy change (ΔG°), and the entropy change (ΔS°) for the adsorption of nickel(II) onto Na-mordenite has also been calculated using the following equation [13,8]:

$$\Delta G^\circ = -nRT \quad (7)$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (8)$$

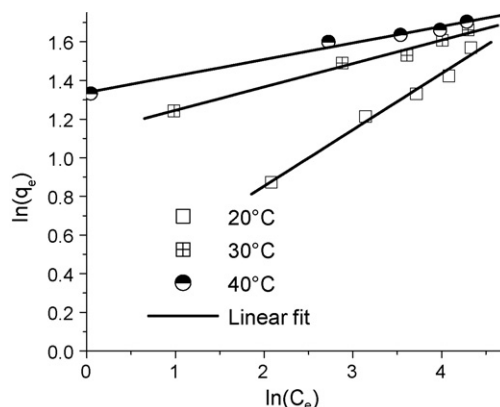
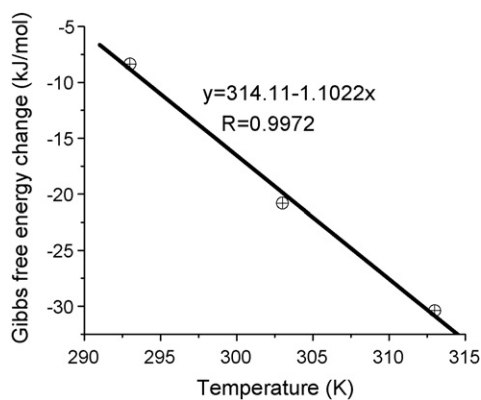


Fig. 3. Freundlich isotherms of nickel(II) at various temperatures.

Fig. 4. Plot of ΔG° versus T .

where n represents the Freundlich constant, R the gas law constant ($J/(\text{mol K})$) and T is the absolute temperature (K). The values of ΔG° at various temperatures are listed in Table 1. The values of ΔH° and ΔS° can be obtained from the intercept and slope of the plot of ΔG° versus T (Fig. 4). The values of these two parameters, ΔH° , and ΔS° are found to be 314.1 kJ/mol and 1.10 kJ/mol K . It is obvious from these values that the negative values of free energy change (ΔG°) were an indication of spontaneous nature of the adsorption process. The positive value of standard enthalpy change (ΔH°) indicated the endothermic nature of the adsorption process and the positive values of ΔS° suggested the increasing randomness at the solid/solution interface at various temperatures.

The Langmuir–Freundlich isotherm equation is characterized by the heterogeneity factor, n_1 , and it can be employed to describe the heterogeneity system [14]. The Langmuir–Freundlich isotherm can be expressed as:

$$q_e = \frac{K_{\text{LF}} C_e^{n_1}}{1 + a_{\text{LF}} C_e^{n_1}} \quad (9)$$

where K_{LF} is the Langmuir–Freundlich constant (L/mg). a_{LF} is the affinity coefficient (L/mg) and n_1 is the heterogeneity coefficient. The Langmuir–Freundlich isotherm equation is linearized as follows:

$$\ln \left[\frac{1}{q_e} - \frac{a_{\text{LF}}}{K_{\text{LF}}} \right] = \ln K_{\text{LF}} - n_1 \ln C_e \quad (10)$$

In this study, we tested the Langmuir–Freundlich model in its non-linearized form as expressed in Eq. (9), and shown in Fig. 5. The parameters and correlation coefficients extracted from these plots are also summarized in Table 1. The values of K_{LF} increased with the increasing temperatures. This model confirm the heterogeneity of sorbent surface since $0 < n_1 < 1$ at various temperatures.

Normalized standard deviation was used to quantify the noise produced between the experimental and predicted data and to determine the best fitting model(s) since all correlation coefficients obtained from the Langmuir, Freundlich and Langmuir–Freundlich equations were quite high (Table 1). The

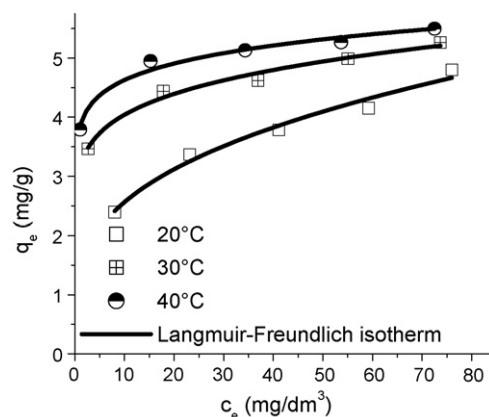


Fig. 5. Langmuir–Freundlich isotherms of nickel(II) at various temperatures.

normalized standard deviation (Δq , %) is given by [15]:

$$\Delta q = 100 \sqrt{\frac{\sum ((q_{\text{exp}} - q_{\text{cal}})/q_{\text{exp}})^2}{N - 1}} \quad (11)$$

where q_{exp} is the experimental nickel ion uptake, q_{cal} the calculated amount of nickel ions adsorbed and N is the number of data points. The Δq values summarized in Table 3 indicate that the Freundlich and Langmuir–Freundlich equations provide the best correlation between experimental and predicted data.

The experimental data were also fitted to Dubinin–Radushkevich (D–R) isotherm to evaluate the nature of sorption. This model envisages about the heterogeneity of the surface energies and can be written in the following linear form [16]:

$$\ln q_e = \ln X_m - \beta F^2 \quad (12)$$

$$F = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (13)$$

where q_e is the amount of sorbate sorbed by the Na-mordenite (mol/g), X_m the maximum sorption capacity of sorbent (mol/g) under investigation, β a constant (kJ^2/mol^2) related to energy, F the polanyi potential, R the gas law constant ($J/(\text{mol K})$), T the absolute temperature (K), and C_e is the concentrations at equilibrium (mol/L). The constant (β) was obtained from the slope of the plot of $\ln(q_e)$ versus F^2 .

The plots of $\ln(q_e)$ against F^2 are linear with high correlation coefficients at various temperatures (Fig. 6 and Table 4). This shows that the D–R sorption isotherm is applicable and reliable for this adsorption system studied.

Table 3
The Δq values for various isotherm equations at different temperatures

Temperature ($^\circ\text{C}$)	Δq (%)		
	Langmuir	Freundlich	Langmuir–Freundlich
20	9.106	3.1409	1.3859
30	15.9505	1.9555	1.9368
40	15.8574	1.8989	1.9511

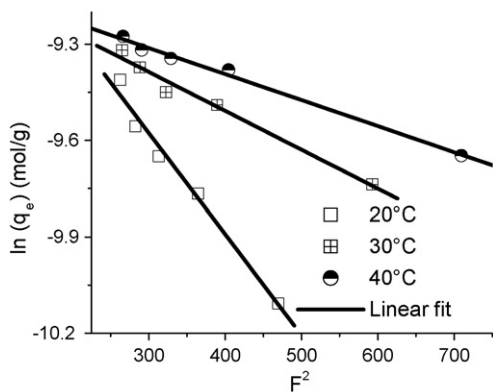


Fig. 6. D–R sorption isotherm of nickel ions onto Na-mordenite at various temperatures.

The values of sorption energy (E_s) (kJ/mol) can be correlated to β by using the following relationship [16]:

$$E_s = \frac{1}{\sqrt{-2\beta}} \quad (14)$$

If the magnitude of E_s is between 8 and 16 kJ/mol, the adsorption process proceeds by ion exchange, while for values of $E_s < 8$ kJ/mol, the adsorption process is of a physical nature [15]. The values of sorption energy (E_s) are presented in Table 4. The result shows that the interaction between nickel(II) ions and the Na-mordenite proceeded principally by ion exchange at temperature of 20 °C while at temperatures of 30 and 40 °C, the nickel sorption by the Na-mordenite may not to be completely attributable to ion-exchange, but also have other interactions (for example surface precipitation and/or co-precipitation). These processes such as ion-exchange and surface precipitation and/or co-precipitation are facilitated by the hydrolysis of the Ni^{2+} ions, which is favoured at the elevated temperature. As a result, various hydrolysis products interact progressively with the microporous solid, which can also act as a forceful cation exchanger. The positively charged solvated species, such as $[\text{Ni}(\text{H}_2\text{O})_n]^{2+}$ and $[\text{NiOH}]^+$, are sorbed primarily through ion-exchange replacing initial extra-framework Na^+ ions, whereas mononuclear and/or polynuclear insoluble hydroxide species can also be bonded to the material by surface precipitation. These results are in agreement with those obtained in the study of interactions between nickel(II) ions and HEU-type zeolites, which are defined as the zeolite mineral series having the distinctive framework topology of heulandite and the ratio $\text{Si}/\text{Al} < 4$ [17].

Table 4
Values of β and E together with correlation coefficients at various temperatures

Temperature (°C)	R	β (kJ ² /mol ²)	E_s (kJ/mol)
20	0.9916	−0.00315	12.598
30	0.9906	−0.00121	20.327
40	0.9964	−0.00081	24.821

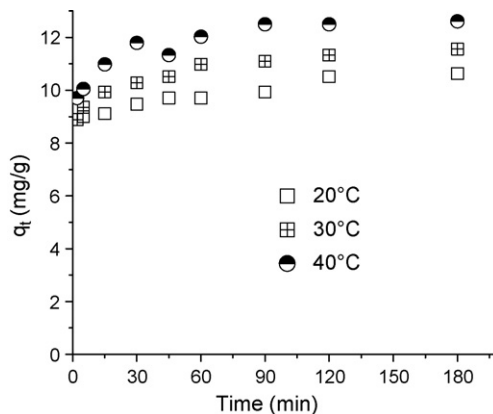


Fig. 7. Variation of Ni(II) sorption capacity against time at various temperatures (adsorption dose, 2 g/L; initial concentration, 40 mg/L; pH 6).

3.3. Effect of agitation time

The distribution of sorbate between sorbent and solution is influenced by agitation time. The effect of shaking time on sorption at various temperatures was studied between 0 and 180 min. The results are presented in Fig. 7. In general, a two-stage kinetic behavior is observed: rapid initial sorption in a contact time of 30 min, followed by a second stage with a much lower sorption rate. According to these results, the 120 min agitation time was considered to be sufficient for the sorption of Ni(II) onto Na-mordenite and was used for all the rest of the batch experiments. Fig. 7 also shows that the amount of Ni(II) uptake per unit weight of Na-mordenite increased with increasing temperature.

3.4. Dynamic modelling

In order to investigate the mechanism of adsorption, the following kinetic models are generally used to test experimental data.

The pseudo-first-order rate Lagergren model [3,16] is:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (15)$$

where q_t (mg/g) is the amount of adsorbed metal ion on the adsorbent at time t (min), q_e (mg/g) the amount adsorbed at equilibrium and k_1 is the rate constant of first-order adsorption. After integration between boundary conditions ($t=0$ to t and $q_t=0$ to q_e), Eq. (12) becomes:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (16)$$

where q_e and k_1 can be determined from the intercept and slope of the plot, respectively.

The pseudo-second-order model [19] is based on the sorption capacity of the solid phase and is written as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (17)$$

where k_2 (g/(mg min)) is the rate constant of second-order model, q_e (mg/g) the amount of metal ions adsorbed at equilibrium and q_t (mg/g) is the amount of soluted sorbate on the

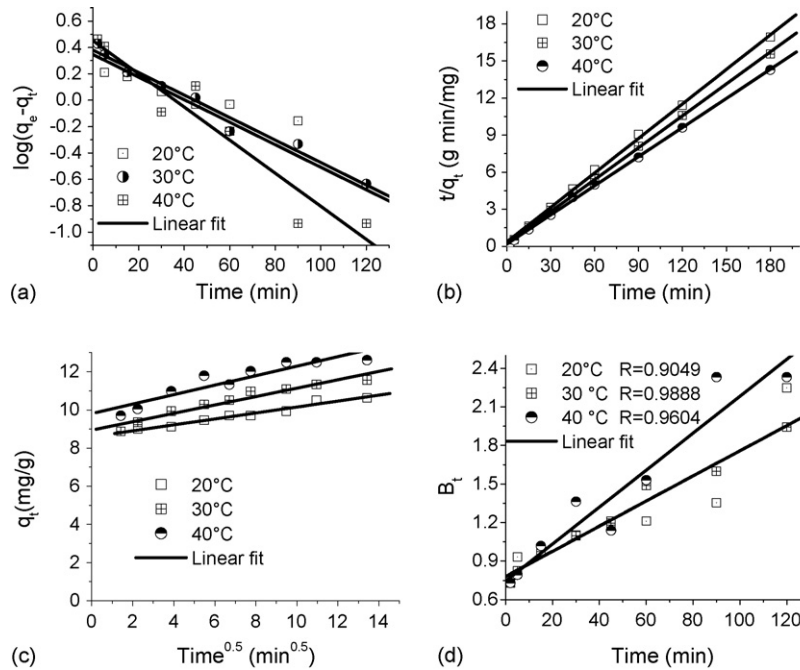


Fig. 8. Kinetic models: (a) pseudo-first-order model, (b) pseudo-second-order model, (c) intraparticle diffusion model, and (d) Reichenberg model for the adsorption of nickel ions onto Na-mordenite at various temperatures (adsorbent dose, 2 g/L; initial concentration, 40 mg/L; initial pH 6).

surface of the sorbent at any time t (min). For boundary conditions ($t=0$ to t and $q_t=0$ to q_e), Eq. (14) becomes:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (18)$$

The plot of t/q_t versus t should give a straight line if pseudo-second-order kinetic model is applicable and q_e and k_2 can be determined from the slope and intercept of the plot, respectively.

The intraparticle diffusion model [18] is characterized by a linear relationship between the amounts adsorbed (q_t) and the square root of the time and is expressed as:

$$q_t = k_p t^{0.5} \quad (19)$$

where q_t (mg/g) is the amount of metal ions adsorbed at time t (min) and k_p is the initial rate of the intraparticle diffusion (mg/(g min^{0.5})).

The applicability of the three models mentioned above was checked by attempting to obtain a linear fit of the experimental data by the appropriate equations (Fig. 8(a)–(c)). The corresponding parameters of the different kinetic models were determined by linear regression. Table 5 lists the results obtained from experimental data, which indicate that the pseudo-second-order kinetic equation provided the best model for describing the adsorption of the nickel(II) ions onto the Na-mordenite.

The Reichenberg equation was also applied to check that sorption proceeds via external diffusion or intraparticle diffusion mechanism [16]. Reichenberg equation can be expressed in the following form:

$$X = \left(1 - \frac{6}{\pi^2}\right) e^{-B_t} \quad (20)$$

where $X = q_t/q_e$ and B_t is a mathematical function of X which can be calculated from each value of X as:

$$B_t = -0.4977 \ln(1 - X) \quad (21)$$

Plots of B_t versus t are also shown in Fig. 8(d), which are straight lines. Fig. 8(d) shows that intraparticle diffusion is the rate controlling step with a small fraction of the sorption that occurs through external diffusion (film diffusion) because the plots do not pass through the origin.

Table 5 also indicates that the values of k_2 increase with increase in temperature. The increase in rate of adsorption with increasing temperature is described by the Arrhenius equation:

$$\ln k_2 = \ln A_0 - \frac{E_a}{RT} \quad (22)$$

where A_0 is the temperature independent factor called “frequency factor”, E_a the activation energy (kJ/mol), R the gas law

Table 5
Kinetic parameters for the adsorption of Ni(II) onto Na-mordenite (adsorbent dose, 2 g/L; initial concentration, 40 mg/L; initial pH 6)

Temperature (°C)	k_1 (min ⁻¹)	R_1	k_2 (g/(mg min))	R_2	K_p (mg/(g min ^{0.5}))	R_p
20	0.0196	0.9049	0.02389	0.9993	0.1559	0.9809
30	0.0196	0.9888	0.03121	0.9997	0.2198	0.9683
40	0.0354	0.9604	0.03306	0.9997	0.2482	0.9299

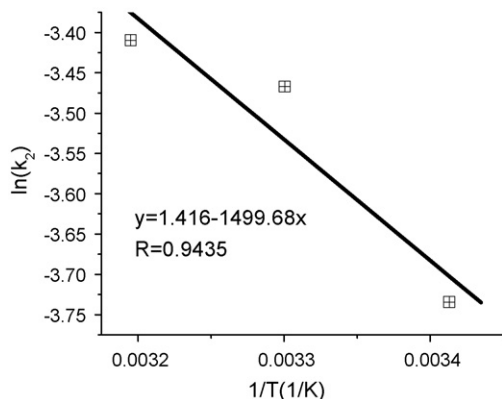


Fig. 9. Plot of $\ln k_2$ versus $1/T$.

constant (8.314 J/(mol K)), and T is the absolute temperature (K).

A linear relationship was obtained between $\ln k_2$ and $1/T$ (Fig. 9). The values of A_0 and E_a were calculated from the intercept and slope of the $\ln k_2$ versus $1/T$ plot and were found to be 4.12 g/(mg min) and 12.46 kJ/mol, respectively. The value of 12.46 kJ/mol in the present study indicates a chemical sorption process involving weak interactions between sorbent and sorbate [20]. The relatively low E_a value suggests that the adsorption has a low potential energy barrier.

3.5. Influence of solution pH

The experimental results obtained for nickel(II) ions uptake by Na-mordenite under different initial pH conditions are shown in Fig. 10. The nickel(II) ions uptake was sensitive to pH variation over the examined range of 2–6. At low pH values, the surface of sorbent would be also surrounded by H^+ ions, which decrease the nickel ion interaction with binding sites of the Na-mordenite by greater repulsive forces.

The percentage removal of nickel(II) ion was obtained by calculation using the following equation:

$$\text{removal (\%)} = \frac{C_i - C_e}{C_i} \times 100 \quad (23)$$

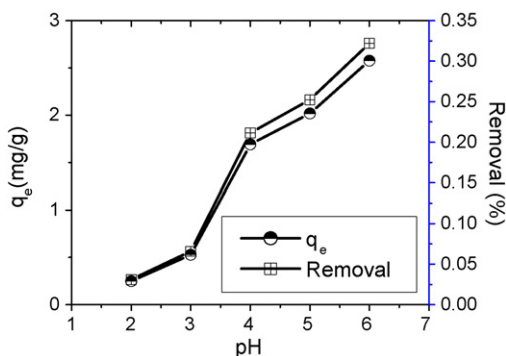


Fig. 10. Effect of solution pH on uptake of nickel(II) ions on Na-mordenite (sorbent dose, 2 g/L; initial concentration, 40 mg/L; agitation speed, 200 rpm).

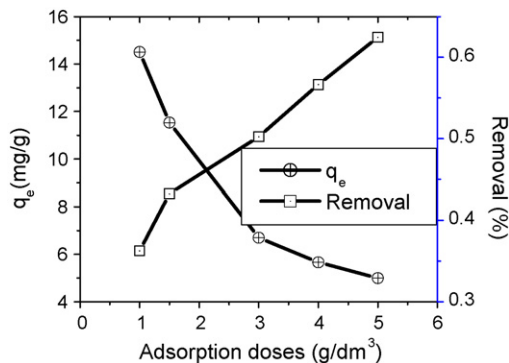


Fig. 11. Effect of sorbent dose on uptake of nickel(II) ions on Na-mordenite (initial solution pH 6; initial concentration, 40 mg/L; agitation speed, 200 rpm).

where C_i and C_e (mg/L) represent the initial concentration and equilibrium concentration, respectively. The nickel ion removal against pH of solution is also shown in Fig. 10. At pH 2, the maximum Ni(II) removal efficiency was only 3.10%, whereas at pH 6 the removal efficiency increased to 32.2%. Further increase in pH was not attempted because of the possibility of precipitation of the nickel ions at $pH > 6$.

3.6. Influence of adsorption dose

The effects of adsorbent dose on the uptake and removal of nickel(II) ions are illustrated in Fig. 11. As the sorbent dose was increased from 1.0 to 5.0 g/L, the equilibrium sorption capacity, q_e , decreased from 14.51 to 4.99 mg/g. However, the nickel ion removal efficiency, increased from 36.27% to 62.46% with increase in sorbent dose of from 1.0 to 5.0 g/L. A similar trend for the sorption of nickel onto peat was also reported [21]. Evidently, the equilibrium sorption capacity and percentage removal are sensitive to the variation of sorbent dose.

3.7. Influence of ionic strength

Ionic strength has a key impact on the uptake of the nickel(II) ion uptake onto Na-mordenite (Fig. 12 and Table 6). In the presence of 0.01 and 0.1 M $NaNO_3$, the maximum uptake capacities

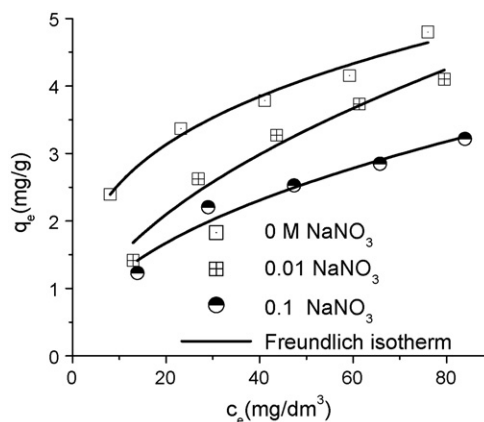


Fig. 12. Freundlich isotherms in the absence and the presence of $NaNO_3$ electrolytes of different concentrations at pH 6 and 293 K.

Table 6

Freundlich isothermal constants along with coefficients of determination (R^2) in the absence and the presence of NaNO_3 electrolytes of different concentrations at pH 6 and 293 K

	R^2	$K_F ((\text{mg/g})/(\text{mg/L})^{1/n})$	n
0.0 M NaNO_3	0.9788	1.293	3.3886
0.01 M NaNO_3	0.9678	0.4547	1.9608
0.1 M NaNO_3	0.9627	0.4197	2.1651

(q_m) of the nickel(II) ions were decreased with the increase in the ionic strength. This can be explained in terms of two aspects. Firstly, competition of Na^+ ions with the nickel(II) ions for sorption sites of Na-mordenite resulted in the observed decrease in the maximum uptake capacities with increasing electrolyte NaNO_3 concentration. Secondly, adsorption is sensitive to the change in ionic strength if electrostatic attraction is a significant mechanism. Thus the results show electrostatic attraction plays an important role in the adsorption of nickel(II) ions onto Na-mordenite [22]. At high ionic strength, the increased amount of NaNO_3 can help to swamp the surface of the sorbent, which decrease nickel ion's access to the surface sites. When solid adsorbent is in contact with sorbate species in solution, they are bound to be surrounded by an electrical diffused double layer, the thickness of which is significantly expanded by the presence of electrolyte. Such expansion inhibits the sorbent particles and nickel(II) ions from approaching each other more closely and, through the decreased electrostatic attraction, results in the decreased uptake of nickel(II) ions [20].

The distribution coefficient, K_D (L/g), has been used to indicate the adsorption affinity of a solid sorbent towards a solute [4]. In this study, K_D is written as:

$$K_D = \frac{C_i - C_e}{C_e} \frac{V}{M} \quad (24)$$

where C_i and C_e (mg/L) represent the initial concentration and equilibrium concentration, respectively, and V/M (L/g) is the ratio of the solution volume over the mass of sorbent, namely the batch factor.

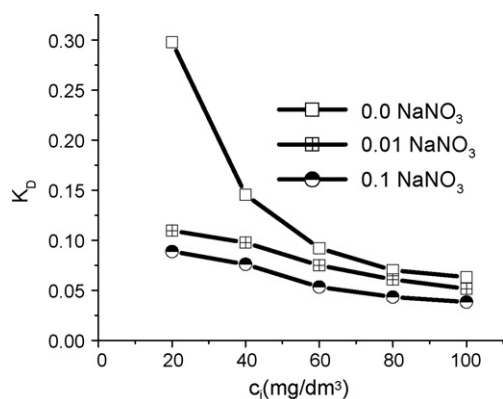


Fig. 13. Distribution coefficients (K_D) of nickel(II) as a function of initial concentration C_i in the absence and presence of NaNO_3 electrolyte of different concentrations at pH 6 and 293 K.

Table 7

Comparison of uptake capacity for nickel(II) with various adsorbents

Adsorbent	Maximum uptake capacity, q_m (mg/g)	References
Ballclay	0.41	[6]
Clinoptilolite	0.9	[5]
Kaolinite	1.669	[23]
Chabazite	4.5	[5]
Na-mordenite	5.32	This work
Eerbeek sludge	12.02	[24]
Nedanco sludge	13.33	[24]
Coir pith	15.95	[1]
Brown seaweed (<i>Sargassum wightii</i>)	18.58	[9]
Waste Fe(III)/Cr(III) hydroxide	21.0	[25]

Fig. 13 illustrates the effects of initial concentration and background electrolyte on the distribution coefficients (K_D). The distribution coefficients of nickel(II) ions were decreased to varying degree with the increase of initial nickel(II) ions concentration. On the other hand, the distribution coefficients decreased in the presence of background electrolyte. Such a decrease is very remarkable with the increase of the NaNO_3 concentration.

3.8. Comparison with other adsorbents

The maximum uptake capacities (q_m) for nickel(II) of Na-mordenite and other adsorbents reported in the literature are given in Table 7. The uptake values obtained in this study are comparable with those values obtained from the clay mineral adsorbents, whereas, on the whole, nickel(II) ions usually show a lower affinity towards these clay minerals studied compared to the other adsorbents.

4. Conclusions

Na-mordenite was found to be an effective sorbent for the removal of nickel(II) ions from wastewater compared to the other clay mineral adsorbents. It was noted that an increase in the temperature and a decrease with sorbent dose and ionic strength resulted in a higher nickel loading per unit weight of the sorbent. The sorption of nickel(II) ions onto Na-mordenite was found to be pH dependent. The sorption of nickel(II) ions onto Na-mordenite is of its spontaneous and endothermic nature. Adsorption data indicate the applicability of pseudo-second order kinetics. These results show that the nickel(II) sorption by the Na-mordenite is not completely attributable to the ion exchange.

References

- [1] H. Parab, S. Joshi, N. Shenoy, A. Lali, U.S. Sarma, M. Sudersanan, Determination of kinetic and equilibrium of Co(II), Cr(III), and Ni(II) onto coir pith, *Process Biochem.* 41 (2006) 609–615.
- [2] P.X. Sheng, Y.P. Ting, J.P. Chen, L. Hong, Sorption of lead, copper, cadmium, zinc, and nickel by marine algal biomass: characterization of biosorptive capacity and investigation of mechanisms, *J. Colloid Interf. Sci.* 275 (2004) 131–141.
- [3] E.L. Cochrane, S. Lu, S.W. Gibb, I. Villaescusa, A comparison of low-cost biosorbents and commercial sorbents for the removal of copper from aqueous media, *J. Hazard. Mater.* 137 (1) (2006) 198–206.

- [4] L. Lv, G. Tsoi, X.S. Zhao, Uptake equilibrium and mechanism of heavy metal ions on microporous titanosilicate ETS-10, *Ind. Eng. Chem. Res.* 43 (2004) 7900–7906.
- [5] S.K. Ouki, M. Kavannah, Treatment of metals-contaminated wastewaters by use of natural zeolites, *Water Sci. Technol.* 39 (1999) 115–122.
- [6] V. Chantawong, N.W. Harvey, V.N. Bashkin, Comparison of heavy metal adsorption by Thai kaolin and ball clay, *Water Air Soil Pollut.* 148 (2003) 111–125.
- [7] K.G. Bhattacharyya, S.S. Gupta, Kaolinite, montmorillonite, and their modified derivatives as adsorbents for removal of Cu(II) from aqueous solution, *Sep. Purif. Technol.* 50 (3) (2006) 388–397.
- [8] I. Langmuir, The constitution and fundamental properties of solids and liquids, *J. Am. Chem. Soc.* 38 (1916) 2221–2295.
- [9] K. Vijayaraghavan, J.R. Jegan, K. Palanivelu, M. Velan, Nickel recovery from aqueous solution using crab shell particles, *Adsorpt. Sci. Technol.* 23 (2005) 303–311.
- [10] G. McKay, H.S. Blair, J.R. Garden, Adsorption of dyes on chitin. I. Equilibrium studies, *J. Appl. Polym. Sci.* 27 (1982) 3043–3057.
- [11] H.M.F. Freundlich, Über die adsorption in lösungen, *Z. Phys. Chem.* 57 (1906) 385–470.
- [12] Sun FY., J.L. Chen, A.M. Li, F.Q. Liu, Q.X. Zhang, Adsorption of phenol from aqueous solution by aminated hypercrosslinked polymers, *Adsorpt. Sci. Technol.* 23 (2005) 335–345.
- [13] F.Q. Liu, J.L. Chen, A.M. Li, Z.H. Fei, J.J. Ge, Q.X. Zhang, Equilibrium adsorption of single component and binary mixtures of aromatic compounds onto a polyfunctional hypercrosslinked polymeric adsorbent, *Adsorpt. Sci. Technol.* 22 (2004) 13–24.
- [14] K.K.H. Choy, G. McKay, Sorption of metal ions from aqueous solution using bone char, *Environ. Int.* 31 (2005) 845–854.
- [15] M.S. Onyango, Y. Kojima, A. Kumar, D. Kuchar, Uptake of fluoride by Al³⁺ pretreated low-silica synthetic zeolites: adsorption equilibrium and rate studies, *Sep. Sci. Technol.* 41 (2006) 683–704.
- [16] R. Ahmad, Sawdust: cost effective scavenger for the removal of chromium(III) ions from aqueous solutions, *Water Air Soil Pollut.* 163 (2005) 169–183.
- [17] A. Godelitsas, T. Armbruster, HEU-type zeolites modified by transition elements and lead, *Micropor. Mesopor. Mater.* 61 (2003) 3–24.
- [18] X.S. Wang, Y. Qin, Z.F. Li, Biosorption of zinc from aqueous solutions by rice bran: kinetics and equilibrium studies, *Sep. Sci. Technol.* 41 (2006) 747–756.
- [19] Y.S. Ho, G. McKay, Sorption of dyes and copper onto biosorbents, *Process Biochem.* 38 (2003) 1047–1061.
- [20] K.A. Krishnan, T.S. Anirudhan, Removal of cadmium(II) from aqueous solutions by steam-activated sulphurised carbon prepared from sugarcane bagasse pith: kinetics and equilibrium studies, *Water SA* 29 (2003) 147–156.
- [21] Y.S. Ho, D.A.J. Wase, C.F. Forster, Batch nickel removal from aqueous solution by sphagnum moss peat, *Water Res.* 29 (1995) 1327–1332.
- [22] Das, Bandyopadhyay, Removal of lead by vermiculate medium, *Appl. Clay Sci.* 6 (1991) 221–231.
- [23] O. Yavuz, Y. Altunkaynak, F. Guzel, Removal of copper, nickel, cobalt and manganese from aqueous solution by kaolinite, *Water Res.* 37 (2003) 948–952.
- [24] E.D. Van Hullebusch, A. Peerbolte, M.H. Zandvoort, P.N.L. Lens, Sorption of cobalt and nickel on anaerobic granular sludge: isotherms and sequential extraction, *Chemosphere* 58 (2005) 493–505.
- [25] C. Namasivayam, K. Ranganathan, Recycling of “waste” Fe(III)/Cr(III) hydroxide for the removal of nickel from wastewater: adsorption and equilibrium studies, *Waste Manage.* 14 (1994) 709–716.