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Equilibrium, kinetic, and thermodynamic studies on nickel removal from aqueous solutions using Ca-bentonite

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ABSTRACT

Sorption using natural materials such as clay minerals is generally regarded as a suitable method for wastewater treatment. Equilibrium nickel (Ni) sorption on Ca-bentonite was determined in solutions with initial Ni concentrations ranging from 0–100 mg L^{-1}. The effect of contact time and temperature on Ni sorption was also investigated. The equilibrium capacity of the bentonite for Ni removal was 2.93, 3.91, and 6.00 mg g^{-1} at 278, 298, and 318 K, respectively, showing sorption enhancement with rising temperature. The results obtained from the kinetic tests indicated that major Ni removal occurred within the first 2 h, but the equilibrium condition was not attained before 24 h. Negative changes in Gibbs free energy (ΔG°) of sorption indicated that Ni sorption on Ca-bentonite was a spontaneous reaction. The positive values of both ΔH° and ΔS° suggest the endothermic nature of the Ni sorption and increased randomness at the solid–solution interface during the Ni chemisorption on the Ca-bentonite, respectively. In conclusion, Ca-bentonite is a potential sorbent for removal of Ni from wastewaters with the most favorable removal behavior at higher temperatures.

Keywords: Ni; Adsorption; Clay minerals; Isotherm; Water decontamination

1. Introduction

Release of heavy metals into the environment as a result of human activities has posed a great hazard to plant, animal, and human health. As one of the most widely used heavy metals in the world, nickel (Ni) is released into the environment from paint industry, metal finishing, mineral processing, silver refineries, hydrometallurgical industry, leather tanning, electroplating, zinc base casting, storage battery industries, and steam-electric power plants [1]. Although Ni is a necessary nutrient element for many organisms, it may be toxic in large doses. Acute and chronic toxicity of Ni to humans has been well documented. Nickel is toxic to the kidneys, cardiovascular, respiratory, and reproductive systems [2]. Therefore, removal of Ni from water and wastewaters is highly warranted.

A number of methods are available for the removal of metal ions from water including ion exchange [3], reverse osmosis [4], chemical precipitation [5], and adsorption [6]. Among these techniques, adsorption is a simple and widely used method. In recent years, much attention has been given to low-cost and high-efficiency adsorbents such as organic wastes [7,8], fly ashes [9,10], and clay minerals [11–13] for removal of metal ions from waters and numerous

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equilibrium- and kinetic-based studies have been performed providing useful information about the capacity and affinity, and rate of metal sorption by these materials, respectively.

One of the most important environmental factors affecting sorption reactions is temperature. A large amount of studies have assessed the effect of temperature on metal sorption [14–16]. Increase of adsorption capacity with temperature reflects endothermic and strong chemical interactions between adsorbent and metal ions [17]. For sorbents with internal porosity, decreasing solvent viscosity and increasing solute motion at higher temperature also allow the uptake of soluble species into the pores more easily, causing adsorption capacity to increase as temperature rises [17]. On the other hand, when adsorption capacity decreases with temperature, the process is claimed to be exothermic and suggests weak adsorption interaction between surface and the metal ion, which supports physisorption [18].

Bentonite, an essentially impure clay consisting mostly of smectites, has attracted a great interest in environmental pollution control and wastewater purification activities because of its outstanding properties, such as great specific surface area and cation-exchange capacity, and excellent physical and chemical stability. Moreover, its natural abundance and low cost make bentonite a good sorbent for environmental purposes. It is well documented that bentonite is an efficient adsorbent for heavy metals, such as Pb, Cd, Cu, and Zn [19–21], and hazardous isotopes, such as Cs and Sr [22,23].

Several studies have been performed on the interactions of Ni with Na-motmorillonite [24,25] or Na-bentonite [26,27] samples from various deposits around the world; however, sorption of Ni on Ca-bentonite has been less investigated [28]. The purpose of this research was, therefore, to find out the equilibrium, kinetic, and thermodynamic parameters of Ni sorption on Ca-bentonite as a material serving for the removal of Ni from contaminated waters.

2. Material and methods

2.1. Materials

The bentonite sample was obtained from Mehredjan mine, Isfahan province, Iran. The Mehredjan bentonite is a clay deposit composed of Ca-smectite (montmorillonite), quartz, crystobalite, calcite, and albite [29]. The mineral sample was powdered in a mortar and sieved using a No. 270 mesh (0.05 mm) sieve. Chemical composition of the bentonite sample was obtained using X-ray fluorescence (XRF) spectroscopy (Table 1). The cation-exchange capacity (CEC) of the bentonite is 66 $\text{cmol}_c\ \text{kg}^{-1}$ as determined by ammonium acetate method [30]. The bentonite sample was treated with 0.5 M $CaCl_2$ and then, washed with distilled water until no chloride was detected in supernatant with 0.01 M $AgNO_3$; centrifuged at 3,500 rpm for 20 min, dried, and ground to pass a 50-μm sieve.

A stock solution containing 1,000 mg of Ni per liter was prepared by dissolving an appropriate amount of $NiCl_2{\cdot}6H_2O$ in 0.01 M $CaCl_2{\cdot}2H_2O$ solution (all from Merck). A range of Ni concentrations from 5 to 100 mg L^{-1} were prepared from the stock solution for isotherm experiment. All chemicals were of reagent grade and were used without further purification.

2.2. Equilibrium studies

All the experiments were carried out using batch technique in 50-mL polyethylene centrifuge tubes in triplicates. An amount of 0.3 g Ca-bentonite was placed into each centrifuge tube and 30 mL of Ni solutions having concentrations of 5, 10, 20, 40, 60, 80, and 100 mg L^{-1} was added. The tubes were placed on a shaker and agitated at 298 K at a fixed agitation speed of 175 rpm. After 24 h of shaking, the solid and liquid phases were separated by centrifugation at 2,500 rpm for 10 min. Sorption of Ni on the tube wall was negligible according to the test of Ni sorption in the absence of Ca-bentonite. The concentration of Ni in the supernatant was determined by an atomic absorption spectrometer (Perkin–Elmer 3030). The amount of Ni adsorbed on Ca-bentonite was calculated from the difference between the initial and the equilibrium concentrations using Eq. (1):

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{1}$$

Table 1
X-ray fluorescence (XRF) and loss on ignition (LOI) analyses of Mehredjan bentonite

Constituent	Percentage
SiO_2	66.37
Al_2O_3	13.24
MgO	2.37
Fe_2O_3	2.04
CaO	1.79
Na_2O	1.69
K_2O	0.51
TiO_2	0.132
LOI	10.83

where C_0 and C_e are the initial and the equilibrium Ni concentrations (mg L^{-1}), V is the volume of the solution (L) and W is the amount of adsorbent used (g).

The Ni sorption percentage was calculated from Eq. (2), respectively, as follow:

$$\%\ \text{Ads} = \frac{C_0 - C_e}{C_0} \times 100 \tag{2}$$

Langmuir, Freundlich, and Temkin isotherm models (Table 2) were applied to describe the sorption data. Separation factor (R_L) was calculated based on the further analysis of Langmuir equation, using Eq. (3):

$$R_L = \frac{1}{1 + K_L C_0} \tag{3}$$

where C_0 (mg L^{-1}) is the initial concentration of the adsorbate and K_L is the Langmuir affinity constant. The R_L parameter is considered as a reliable indicator of the adsorption desire. The nature of the adsorption process may be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$) [31,32].

2.3. Kinetic experiments

The amount of Ni adsorbed onto Ca-bentonite was studied as a function of time in batch experiments. Based on isotherm experiments and sorption capacity of the Ca-bentonite, 30 mL solution with an initial concentration of 100 mg Ni L^{-1} was mixed with 0.3 g Ca-bentonite and shaken at 175 rpm. The agitation time was varied from 0.5 to 24 h. The suspensions were then centrifuged and the concentration of Ni in the supernatants was determined by AAS.

The kinetic parameters of Ni sorption on bentonite were determined with different kinetic models including pseudo-first-order, pseudo-second-order, intra-particle diffusion, and Elovich equations (Table 3).

2.4. Thermodynamic studies

Thermodynamic parameters, including Gibbs free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) are useful for the evaluation of the sorption process. ΔG° values were calculated from the following equation:

$$\Delta G^\circ = -RT \ln K_L \tag{4}$$

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the temperature (K), and K_L is the Langmuir constant. The K_L is dependent on temperature letting us to estimate the thermodynamic parameters based on Eqs. (5) and (6):

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{5}$$

$$\ln K_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{6}$$

Therefore, thermodynamic parameters, ΔH° and ΔS°, were calculated from the slope and intercept of the plot of ln K_L vs. $1/T$, respectively [33–35].

2.4. Curve fitting and data analysis

Fitting of isotherm, kinetic, and thermodynamic equations to the Ni sorption data was carried out using linear and non-linear regression analyses of statistical package GraphPad Prism (version 5.00 for Windows, GraphPad Software, San Diego, California, USA).

3. Results and discussion

3.1. Effect of initial Ni concentration on sorption efficiency

The Ni adsorption efficiency decreases with increase of initial Ni concentration. Increase in the Ni concentration from 5 to 100 mg L^{-1} resulted in

Table 2
Isothermal equations used to fit the equilibrium Ni sorption data

Isotherm	Equation	Nomenclature
Langmuir	$q_e = \frac{q_{max} K_L C_e}{1+K_L C_e}$	q_e is the equilibrium Ni concentration adsorbed on the adsorbent (mg g^{-1}), C_e is the equilibrium Ni concentration in solution (mg L^{-1}), q_{max} is the sorption capacity of the sorbent (mg g^{-1}) and K_L is the Langmuir constant (L mg^{-1}) related to the sorption energy
Freundlich	$q_e = K_F C_e^N$	K_F (mol^{1-n} L^n g^{-1}) represents the sorption capacity when metal ion equilibrium concentration equals to 1, and N represents the sorption strength (The smaller values of N, the stronger the sorption bond will be for that specific adsorbate)
Temkin	$q_e = \frac{RT}{b} \ln(K_T C_e)$	K_T is equilibrium binding constant (L g^{-1}), b is related to heat of adsorption (J mol^{-1}), R is the gas constant (8.314×10^{-3} kJ K^{-1} mol^{-1}) and T is the absolute temperature (K)

Table 3
Linearized kinetic models tested to describe time-dependent Ni sorption data

Kinetic model	Equation	Nomenclature
Pseudo-first order	$\ln(q_e - q_t) = \ln q_e - k_1 t$	q_e and q_t (mg g^{-1}) are the amounts of the metal ions sorbed at equilibrium and at any time, respectively; and k_1 (h^{-1}) is the rate constant of the pseudo-first order model
Pseudo-second order	$t/q_t = 1/(k_2 q_e^2) + t/q_e$	k_2 (g mg^{-1} h^{-1}) is the rate constant of the pseudo-second order equation; q_e (mg g^{-1}) is the equilibrium sorption capacity; and q_t (mg g $^{-1}$) is the amount of Ni sorption at time t (h)
Intra-particle diffusion	$q_t = K_{\text{dif}} t^{\frac{1}{2}} + C$	q_t (mg g^{-1}) is the amount of sorption at time t (h). C is intercept and gives information about the boundary layer thickness and K_{dif} (mg g^{-1} h$^{-1/2}$) is intra-particle diffusion rate constant
Elovich	$q_t = \frac{1}{\beta}\ln(\alpha\beta) + (\frac{1}{\beta})\ln t$	q_t (mg g^{-1}) is the amount of sorption at time t, and α (mg g^{-1} h^{-1}) and β (g h^{-1}) are model constants

decrease in the percentage of Ni removal from 90 to 35.4%, but increase in adsorption capacity from 0.45 to 3.54 mg g^{-1} (Fig. 1). At low Ni concentrations, the number of available adsorption sites are very high comparatively to that of Ni ions and a higher proportion of Ni is removed from the solution. As initial metal concentration increases, the driving force for the migration of the metal ions from the bulk solution to the mineral surface increases and more surface sites become occupied resulting in approaching the sorption to its capacity above a certain concentration of Ni. At the low Ni concentrations surface complexation presumably is the main sorption mechanism. With increasing Ni concentration and surface coverage, aggregation and precipitation reactions on the mineral surface become the main sorption mechanism [19,36].

3.2. Ni sorption isotherms

Fig. 2 shows sorption isotherms of Ni on bentonite at different temperatures. These curves were found to be convex upward throughout and were designated as favorable type [37]. Langmuir, Freundlich, and Temkin models fitted the sorption isotherms of Ni on Ca-bentonite well (Table 4).

Using the Langmuir model, maximum sorption capacity ($q_{\max}$) of the Ca-bentonite for Ni was estimated to be 2.93, 3.91, and 6 mg g^{-1} at 278, 298, and 318 K, respectively. This increase in the sorption capacity with the rise in temperature may be attributed to increase in the kinetic energy of mineral particles which promote the collision frequency between the sorbent and sorbate, increase in number of available active sites on the sorbent surface at higher temperatures due to bond rupture of surface functional groups, and increase in the diffusive mobility of Ni ions towards the clay surface sites [16,38,39]. Sheikhhosseini et al. [40], working with Ni concentration comparable to those used in this study, reported that Ni sorption capacity of Ca-palygorskite and Ca-sepiolite minerals at 298 K was 2.41 and 4.81 mg g^{-1}, respectively, showing that the capacity of Ca-bentonite for Ni removal is greater than that of Ca-palygorskite, but is lower than that of Ca-sepiolite. They also

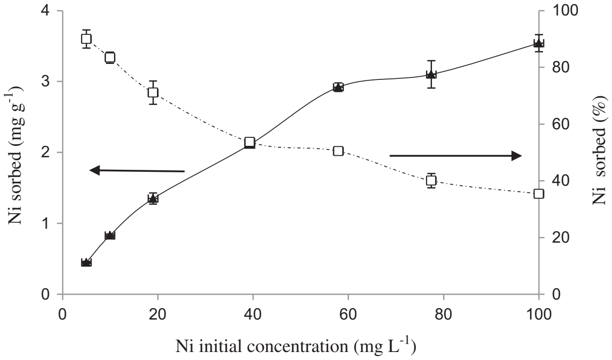

Fig. 1. Effect of initial Ni concentration on sorption content and percentage of Ni by Ca-bentonite at 298 K.

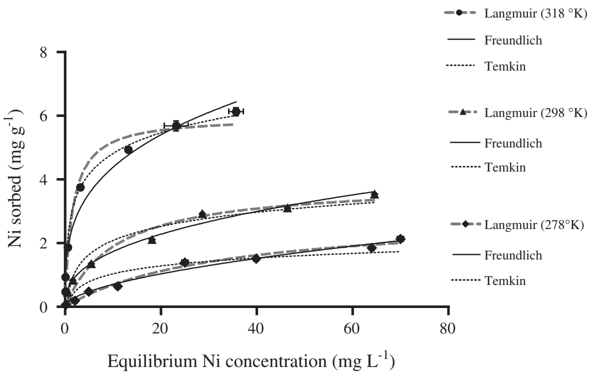

Fig. 2. Sorption isotherms of Ni on Ca-bentonite at 278, 298 and 318 K.

Table 4
The parameters of the fitted Langmuir, Freundlich and Temkin isotherms to Ni sorption on Ca-bentonite at different temperatures

		Langmuir constants			Freundlich constants					Temkin constants		
T (K)	$q_{\max}$	K_L	R^2	SE	K_F	N	R^2	SE	b	K_T	R^2	SE
278	2.93	0.03	0.97	0.11	0.19	0.55	0.97	0.12	6.17	1.76	0.83	0.31
298	3.91	0.09	0.96	0.26	0.69	0.39	0.98	0.15	3.55	2.54	0.94	0.29
318	6.00	0.63	0.97	0.39	2.18	0.30	0.96	0.46	2.40	16.46	0.99	0.23

showed that the $q_{\max}$ values of both Ca-palygorskite and Ca-sepiolite clays increased with increasing temperature.

The Freundlich K_F value, that is a sorption capacity factor, showed a similar trend with temperature observed for the Langmuir $q_{\max}$ and increased from 0.19 at 278 K to 2.18 at 318 K.

The sorption affinity parameter (K_L) values derived from the fitted Langmuir equation were 0.03, 0.09, and 0.63 L kg^{-1} at 278, 298, and 318 K, respectively, (Table 4) suggesting a greater affinity of Ni ions to the mineral surface at the higher temperatures. The values of Freundlich N parameter decreased from 0.55 at 278 K to 0.30 at 318 K (Table 4), which indicate that Ni forms stronger bonds with the surface sites at higher temperatures as the smaller Freundlich exponents show the stronger adsorption bonds [41]. The Temkin constants, K_T were found to be 1.76, 2.54, and 16.46 L g^{-1} for 278, 298, and 318 K, respectively (Table 4) confirming that Ni-binding affinity increased with rising temperature as raveled by the Langmuir K_L and Freundlich N values. Thamilarasu et al. [42] also showed that K_T values for Ni sorption by activated carbon increased from 1.304 at 303 K to 1.690 and 2.354 at 313 and 323 K, respectively.

The variation of the separation factor (R_L) with the initial concentration of the solution is shown in Fig. 3. The R_L values were found to vary between 0.87 to 0.26 at 278 K, 0.684 to 0.098 at 298 K, and 0.249 to 0.016 at 318 K, suggesting that the sorption of Ni from aqueous solutions by Ca-bentonite is a favorable reaction especially at higher temperatures [31,32].

3.3. Nickel sorption kinetics

Sorption of Ni on Ca-bentonite was a bi-phasic process with an initial rapid step followed by a slower one approaching a pseudo-equilibrium condition (Fig. 4). The fast initial sorption may be attributed to the availability of a large number of bare sorption sites at the initial stage. As the sites are being gradually filled, sorption becomes slower and the kinetics become more dependent on the rate at which the Ni ions are transported from the bulk phase to the actual sorption sites [43]. Furthermore, while the superficial sites are occupied within the first few minutes of contact between the solid and solute, sorption in interlayer spaces of Ca-bentonite may be diffusion-controlled and time dependent [43,44]. Although Ni sorption on Ca-bentonite increased with time, the substantial amount of Ni ions was sorbed within the first 90 min. Liu and Zhou [6] reported the same results regarding adsorption kinetic of Ni on Na-bentonite. Eick et al. [45] also reported an initial fast and a final slow step for Ni sorption reaction on kaolinite. They suggested that the fast stage may be the result of chemical sorption, while the slow stage is the consequence of nucleation and precipitation on the mineral surface.

Fig. 5 represents the fitting curves resulting from the linearized-integral form of pseudo-first-order, pseudo-second-order, Elovich, and intraparticle diffusion kinetic models to the time-dependent Ni sorption data. The fitted constants obtained from the linear least square method are also presented in Table 5 along with the determination coefficients. Among the models tested, the pseudo-second-order kinetic model most properly described the Ni sorption data

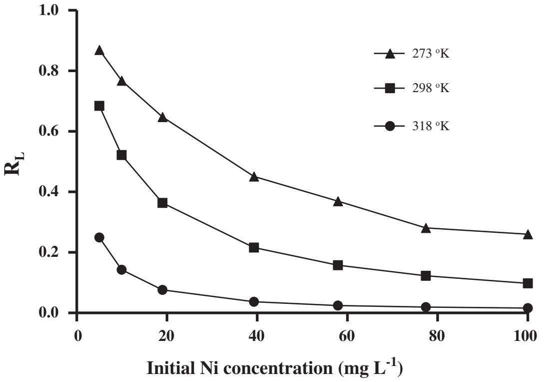

Fig. 3. Variation of separation factor (R_L) with initial Ni concentration at different temperatures.

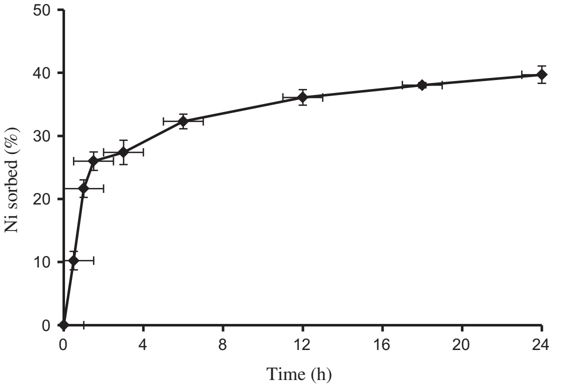

Fig. 4. Effect of contact time on Ni sorption percentage on Ca-bentonite.

($r^2 = 0.996$). The amounts of the Ni sorbed on the Ca-bentonite sample at equilibrium, estimated by the pseudo-second-order kinetic model ($q_{e2} = 4.03\,\mathrm{mg\,g^{-1}}$), was comparable to the maximum sorption ($q_{\max} = 3.91\,\mathrm{mg\,g^{-1}}$) obtained by the Langmuir model. The Pseudo-first-order model also adequately fitted to the Ni sorption data ($r^2 = 0.965$). However, it was observed that there were two linear portions in the pseudo-first-order model plot, indicating two different adsorption stages. It has been reported that in most cases the pseudo-first-order equation does not fit well for the whole range of contact time in sorption studies [46].

The intraparticle diffusion and Elovich models also significantly described the experimental data (Table 5). Fitting a single parabolic diffusion equation to the entire range of Ni sorption data yielded a relatively poor fit ($r^2 = 0.808$). In fact, the q_t vs. $t^{1/2}$ plot showed two distinct linear portions with r^2 values of 0.985 and 0.941, respectively (Fig. 5(d)), indicating that the intraparticle diffusion is not the rate-limiting step for the whole sorption reaction [47]. The initial portion of the plot may indicate the diffusion of Ni ions from the bulk solution into the boundary layer that surrounds the solid particles, whereas the second linear portion may be due to the ions' intraparticle diffusion reaching the active adsorption sites on the mineral's internal surfaces [47,48]. The slope of the second linear portion of the plot, defined as the intraparticle diffusion rate constant (k_{dif}), was $0.391\,\mathrm{mg\,g^{-1}\,h^{-1/2}}$ (Table 5).

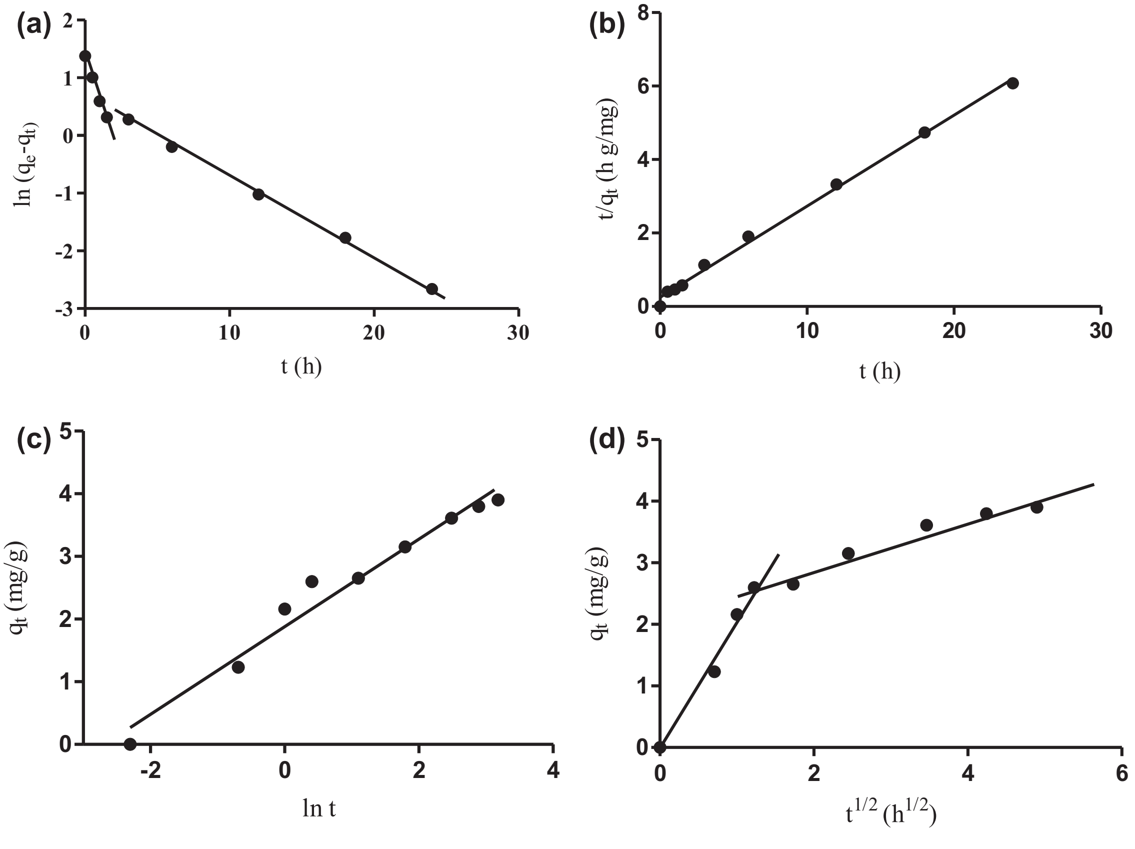

Fig. 5. Kinetic models fitted to the time-dependent Ni sorption data on Ca-bentonite: (a) pseudo-first order model, (b) pseudo-second order model, (c) Elovich model, and (d) intraparticle diffusion model.

Table 5
Constants of linear kinetic equations for Ni sorption onto Ca-bentonite

Pseudo-first order		Pseudo-second-order		Intraparticle diffusion^c		Elovich	
k_1	0.150	k_2	0.244	K_{dif}	0.391	α	10.26
q_{e1}	2.391	q_{e2}	4.035	C	2.11	β	1.43
R^{2a}	0.965	R^2	0.996	R^2	0.941	R^2	0.968
SE^b	0.265	SE	0.141	SE	0.603	SE	0.245

^{a}Determination coefficient. All R^2 values are significant at $p < 0.001$.
^{b}Standard error.
^{c}Related to the second linear portion of q_t vs. $t^{1/t}$ plot (Fig. 5(d)).

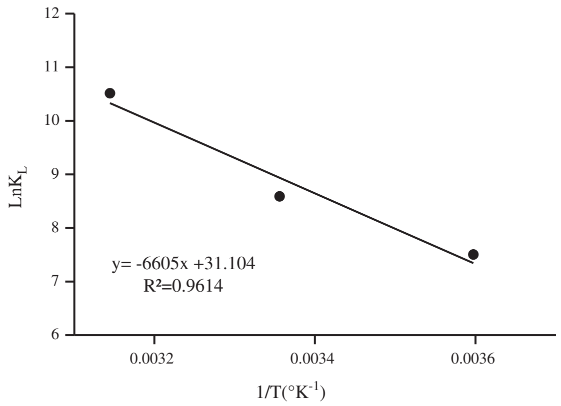

Fig. 6. Plot of ln K_L vs. $1/T$ for estimating of thermodynamic parameters of Ni sorption on Ca-bentonite.

3.4. Nickel sorption thermodynamics

Thermodynamics parameters calculated for Ni sorption reaction on Ca-bentonite, based on the linear regression equation between K_L and $1/T$ (Fig. 6) are shown in Table 6. The Gibbs free energy change (ΔG°) was negative showing that Ni sorption reaction on Ca-bentonite is thermodynamically feasible and spontaneous. The ΔG° value decreased from −17.34 to −27.80 kJ mol^{-1} as temperature rose from 278 to 318 K which indicates reaction spontaneity increases with increase in temperature leading to more efficient Ni sorption at higher temperatures [49].

The value of ΔH° was positive showing that the Ni sorption process on Ca-bentonite is endothermic. The positive ΔH° value may be explained by the fact that the hydration sphere of Ni^{2+} ions has to be destroyed before Ni adsorption take places on Ca-bentonite sites. The dehydration process needs energy and is favored at higher temperatures. This energy exceeds the exothermicity of Ni bounding to the solid surface [50]. Chang et al. [15] also reported that the removal of Ni from aqueous solutions by Na-rectorite was spontaneous and endothermic. Also, the magnitude of ΔH° gives an idea about the sorption mechanism. The standard enthalpy change for physical adsorption is usually less than 4.2 kJ mol^{-1} but that for chemical adsorption is more than 21 kJ mol^{-1} [51]. The ΔH° value of Ni sorption reaction on Ca-bentonite in the current study was 54.91 kJ mol^{-1} suggesting that adsorption of Ni ions on the Ca-bentonite is a chemical process (inner-sphere surface complexation). It may be due to the competition of Ca and Ni ions for the bentonite non-specific active cites. Considering the presence of 0.01 M Ca^{2+} in the background solutions, the possibility of non-specific outer-sphere adsorption of Ni^{2+} on the negatively charged sites on the mineral surfaces is weak.

The value of standard entropy change (ΔS°) for Ni sorption reaction on Ca-bentonite was 258.56 J mol^{-1} K^{-1}. The positive value of ΔS° suggests the increased randomness at the solid–solution interface during the adsorption of Ni on Ca-bentonite, because chemisorptions reactions are associated with decreasing the number of water molecules surrounding the sorptive ions via partial dehydration process which cause the degree of freedom of the water molecule to be increased [52,53]. Mishra and Tiwari [54] also reported a positive value of ΔS° (78.47 J mol^{-1} K^{-1}) for Ni sorption on synthetic zeolite, and concluded that partial dehydration of the metal ions occurred before adsorption.

4. Conclusion

Results of this study show that both sorption capacity and energy of Ca-bentonite towards Ni

Table 6
Thermodynamic parameters for Ni sorption on Ca-bentonite

T (K)	ln K_L	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})
278	7.51	−17.34	54.91	258.56
298	8.59	−21.29		
318	10.52	−27.80		

increases at higher temperatures; therefore, sorption of Ni from aqueous solutions by Ca-bentonite is much favorite at higher temperatures. Kinetically, Ni sorption on Ca-bentonite is relatively fast with the major part of the Ni sorption taking place within the first 90 min. The metal sorption is considered a diffusion process in which two stages were observed to take place. Calculated thermodynamic parameters (ΔG°, ΔH°, and ΔS°) values suggested that Ni sorption on Ca-bentonite is a spontaneous and endothermic chemical adsorption reaction. Overall, Mehredjan bentonite, as a quite economic and available sorbent, has prominent potential for a favorable removal of Ni from wastewaters.

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