Sorbent Characteristics of Montmorillonite for Ni^{2+} Removal from Aqueous Solution

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Abstract

Sorption of Ni^{2+} in aqueous solution was studied using montmorillonite. The experimental and equilibrium data fitted well to the Langmuir isotherm model. From the kinetics data for nickel sorption onto montmorillonite, the diffusion of Ni^{2+} inside the clay particles was the dorminant step controlling the sorption rate and as such more important for Ni^{2+} sorption than the external mass transfer. Ni^{2+} was sorbed due to strong interactions with the active sites of the sorbent and the sorption process tends to follow the pseudo second-order kinetics. Thermodynamic parameters ($\triangle G°$, $\triangle H°$, and $\triangle S°$) indicated a non spontaneous and endothermic adsorption process while the positive low value of the entropy change suggests low randomness of the solid/solution interface during the uptake of Ni^{2+} by montmorilionite. Heavy metals such as Ni^{2+} in aqueous bodies can effectively be sorbed by montmorillonite.

Keywords: Montmorillonite, Nickel, Kinetics, Adsorption isotherms

1. Introduction

Recovery of heavy metals from wastewaters and industrial wastes has become a very important environmental issue. Nickel has many useful applications in our life and equally harmful if discharged in appreciable quantities into natural water resources.[1] Ni^{2+} is present in the effluents of silver refineries, electroplating, zinc base casting and storage battery industries. The acceptable limit of Ni^{2+} in drinking water is 0.01 mg/L and 2.0 mg/L as industrial wastewater discharge. At higher concentrations, Ni^{2+} can cause cancer of the lungs, nose and bone. Dermatitis-Ni itch which may occur as a result of contact with coins and costume jewelries is one of the most frequent effects of exposure to Ni^{2+}. Ni carbonyl $[Ni(CO)_4]$ has been estimated as lethal in humans at atmospheric exposures of 30 ppm for 30 min.[3] Acute poisoning of Ni^{2+} causes headache, dizziness, nausea and vomiting, chest pain, tightness of the chest, dry cough and shortness of breath, rapid respiration, cyanosis and extreme weakness.[1,2] Hence, it is essential to remove Ni^{2+} from industrial wastewaters before it pollutes natural water sources. Conventional methods for removal of Ni^{2+} from wastewaters include chemical precipitation, ion exchange, adsorption unto activated carbon, filtration, chemical reduction, and electrodeposition.[4] Due to operational demerits and high cost of heavy metal treatment, some new technologies have been tried in recent times with less expensive adsorbents such as rice hull,[5] sphagnum peat[6] and *chlorella vulgaris*.[7] The adsorption of Cd^{2+}, Zn^{2+}, Pb^{2+} onto natural clays have been studied and owing to the crystalchemical features of montmorillonite, heavy metal retention by this mineral can occur by adsorption and/or cation exchange reaction. The ability of montmorillonite, to adsorb heavy metal ions from water is significant for the removal of toxic pollutants from the environment.

Sorption characteristics of Ni^{2+} onto montmorillonite and evaluation of the clay's potentialities as sorbent material for removal of Ni^{2+} from aqueous solution is the focus of this study. From batch adsorption studies, effects of pH, clay dosage, and concentration on Ni^{2+} adsorption unto montmorillonite were investigated. Equilibrium studies relating to kinetics, adsorption isotherms and thermodynamics were as well experimentally conducted.

2. Experimental Methods

2.1. Adsorbent

Analytical grade of montmorillonite was purchased from Aldrich Chemicals. Clay fraction passed through a 150 μm sieve

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was used as received, unwashed powder. Its surface area as determined by the EGME method[8] was found to be 699 m^2/g and from an extraction method with ammonium acetate, a CEC of 89 meq/100g was obtained.

2.2. Adsorbate

Stock solution of 1000 mg/L of Ni^{2+} was prepared by dissolving 4.960 g of ultra pure Ni(NO$_3$)$_2$. 6H$_2$O in a double distilled water, acidified with nitric acid to prevent hydrolysis. All the solutions were made with double distilled water.

2.3. Adsorption Studies

Batch adsorption studies were conducted. Adsorption kinetics were carried out using 50 mL of metal ion solution containing the desired concentration (50-300 mg/L) at a pH of 5.5 with 1 g of adsorbent in 100 mL conical flasks agitated at 200 rpm inside a rotary shaker (25±1℃). Samples were separated by fast filtration and analyzed by Flame atomic absorption spectrometer. Studies on adsorption kinetics were carried out using different initial Ni^{2+} concentrations with 1g of adsorbent dosage in 50 mL solution. 0.1 N of HCl and 0.1 N of NaOH were used to adjust the pH. The effect of hydrogen ion concentration was examined from solutions at pH ranging from 2.3 to 9.2, Ni^{2+} removal was studied in the range of 2.5-9.0.

3. Result and Discussion

3.1. Effects of pH

Fig. 1 summarizes the sorption of Ni^{2+} onto montmorillonite particles at various pH values. The maximum removal was achieved at pH values around 7-9 due to the nature of the chemical interactions of the metal ion with the montmorillonite surface. At pH above 9, Ni^{2+} precipitates. Montmorillonite surface contains several different active sites[4] and metal ion removal depends on these active sites as well as on the nature of the metal ions in the solution. Greater number of negatively charged groups on montmorillonite favours electrostatic interactions between cationic species, and this negative charge may be responsible for metal binding. However, as the pH is lowered, hydrogen ions compete with metal ions for the sorption sites in the sorbent; the overall surface charge on the particles becomes positive and hinds the binding of positively charged metal ions (Ni^{2+}). Hydrogen ion concentration affects not only active sites dissociation, but also the metal speciation. Hydrolysis products of metal cations can also be investigated as metal cations at around pH 5 would be expected to interact with the negatively charged binding sites of montmorillonite.[9-12]

3.2. Clay Dosage

Fig. 2 shows the adsorption of Ni^{2+} as a function of clay dosage. Increase in montmorillonite dosage increased the adsorption of Ni^{2+}, this may be attributed to availability of more func-
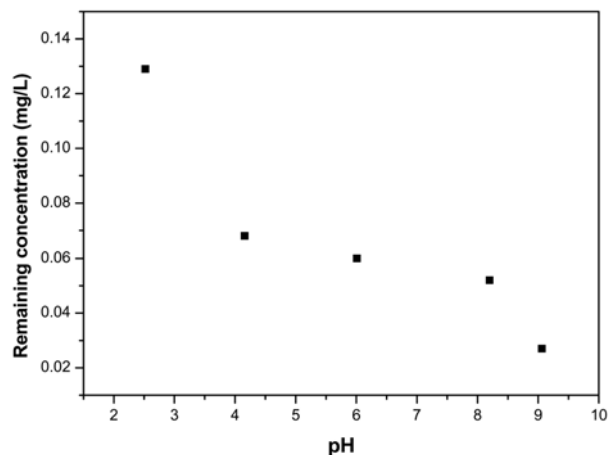

Fig. 1. Change in residual concentration of Ni^{2+} solution according to pH (amount of adsorbent: 1g; 25℃; 200 rpm; metal ion [Ni] = 100 mg/L).
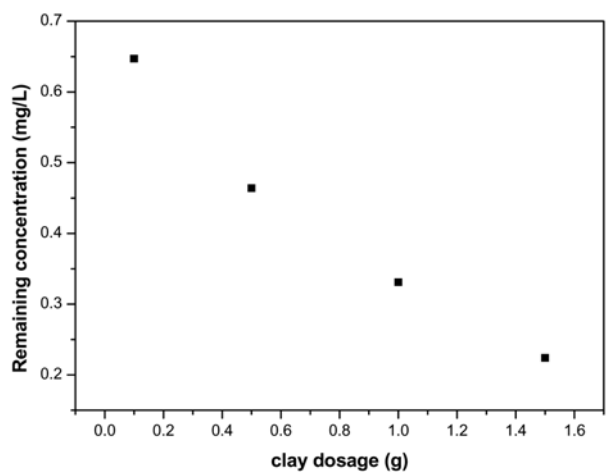

Fig. 2. Variation of the adsorption of Ni^{2+} onto montmorillonite according to sorbent dosage (25℃; 200 rpm; pH~5.5; metal ion [Ni] = 100 mg/L).

tional groups as well as active sites for adsorption. Large number of sites were available for each fixed concentration of sorbate hence the increase in extent of adsorption.

3.3. Adsorption Kinetics (effect of contact time and initial metal ion concentration)

Solute uptake rate, governing residence time of sorption reactions is one of the important characteristics in defining sorption efficiency. The effect of agitation time and initial Ni^{2+} concentration on adsorption is presented in Fig. 3 with the equilibrium time selected as the agitation time for the batch experiments. The progressive increase in adsorption and consequently the attainment of equilibrium adsorption may be due to limited mass transfer of the adsorbate molecules from the bulk liquid to the external surface of montmorillonite initially, and subsequently by slower internal mass transfer within the montmorillonite particles. Similar trends were also observed for polyvinyl alcohol adsorption onto montmorillonite.[13] Sorption kinetic was analyzed employing two models, first, using Lagergren equation, which allows the estimation of the adsorption rate k_l (min^{-1}) according to[14]:
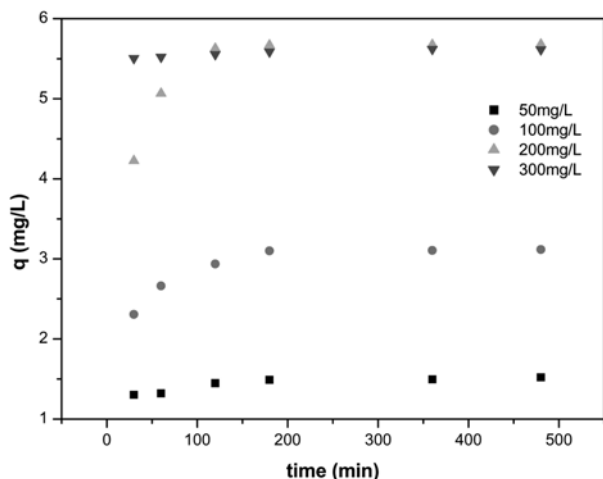
Fig. 3. Changes in residual concentration of Ni²⁺ according to adsorption time for various Ni²⁺ concentrations.

$$\log (q_e - q) = \log q_e - \left(\frac{k_1 t}{2.303} \right) \tag{1}$$

where, q is the amount adsorbed at any time t (mg/g), q_e is the amount adsorbed at equilibrium time (mg/g), k_1 is the adsorption rate constant (min⁻¹). Linear plots of $\log (q_e - q)$ versus t (plot not shown) shows a poor applicability of Lagergren equation for montmorillonite, the k_1 values at different initial metal ion concentrations were calculated from slope of the plots and presented in Table 1.

The pseudo-second-order model was equally applied using[14]:

$$\frac{t}{q} = \frac{1}{(k_2 q_e)^2} + \frac{t}{q_e} \tag{2}$$

where t (min) is the contact time, q (mg/g) and q_e (mg/g) the amount of metal ions sorbed at any time t and at equilibrium and k_2 (g/mg/min) is the pseudo-second-order rate constant. The second-order sorption rate constant k_2 and q_e values were determined from the slopes and intercepts of the plots and were presented in Table 1. The correlation coefficients (R^2), shown in Table 1, are indications of the strength of the linear relationship, showing R^2 values greater than 0.98. Theoretical q_e values agree well with the experimental q_e values, suggesting that the sorption of Ni²⁺ onto montmorillonite tends to follow the second-order kinetics. Therefore, the rate-limiting step may be chemical sorption or chemisorption through sharing or exchange of elec-

trons between sorbent and adsorbate. Previous authors have reported that the sorption kinetics of Ni²⁺ follows a pseudo-second-order reaction rate.[14] It was also noted that the pseudo-second-order rate constant (k_2), decreased with increase in Ni²⁺ concentration. As shown in Table 1, the value of k_2 reduced from 0.305 to 0.175 g/mg/min as the initial montmorillonite concentration increased from 50 to 300 mg/L. This varying trend of pseudo- second order rate constant resulting from the model fitting was in good agreement with the experimental Ni²⁺ adsorption kinetics, in which the time required for the equilibrium adsorption monotonically increased with increase in initial Ni²⁺ concentration (Fig. 3).

3.4. Adsorption Mechanisms

It is always important to predict the rate-limiting step in an adsorption process in order to understand the mechanism associated with the phenomena. For a solid liquid sorption process, the solute transfer may be characterized by an external mass transfer, intraparticle diffusion or by both transport phenomena. Three types of mechanisms are involved in adsorption process[15]: the film diffusion, which involves the movement of adsorbate molecules from the bulk of the solution towards the external surface of the adsorbent; the particle diffusion, where the adsorbate molecules move and being sorbed in the interior of the adsorbent particles; retention on active sites through sorption, complexation or intraparticle precipitation. Of the three steps, the third step is assumed to be very fast and hence considered negligible. Therefore for design purposes, it is required to clearly distinguish between film diffusion and particle diffusion in order to establish identify the slowest step in the adsorption process. Intraparticle diffusion is characterized by the relationship between specific sorption (q) and the square root of time[16] according to Equation 3

$$q = \frac{K_i}{m} t^{1/2} \tag{3}$$

where m is the mass of sorbent (g), q the amount of solute adsorbed at time t (mg/g) and K_i is the initial rate of intraparticle diffusion (mg/Lsec⁻¹ᐟ²). From Fig. 4, the rate constant of intraparticle diffusion K_i was determined by plotting q (mg/g) as a function of the square root of the time.[17]

Fig. 4 shows a non-linear distribution of points, with two separate portions of a curve and a linear plot for the sorption process and as such indicating the existence of intraparticle dif-

Table 1. Kinetic parameters for Ni²⁺ uptake by montmorillonite at different concentrations

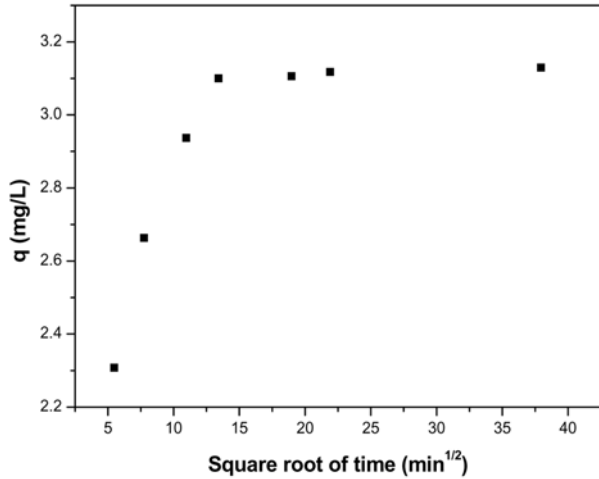| Adsorbate	Initial Con. (mg/L)	q_e Exp. (mg/g)	First - order kinetics			Second - order kinetics		
			k_1	q_e, cal. (mg/g)	R^2	k_2 (g/mg/min)	q_e, cal. (mg/g)	R^2
Ni²⁺	50	1.52	0.003	2.56	0.887	0.305	1.53	0.998
	100	3.11	0.0024	4.36	0.721	0.211	3.15	0.999
	200	5.68	0.0021	5.66	0.583	0.198	5.70	0.998
	300	5.61	0.0014	6.05	0.688	0.175	5.62	0.999

Fig. 4. Equilibrium sorption for Ni^{2+} onto montmorillonite as a function of time-rate constant of intraparticle diffusion determination (metal ion: 100 mg/L; clay dosage:1g ; pH ~ 5.5; T: 25 ± 1℃).
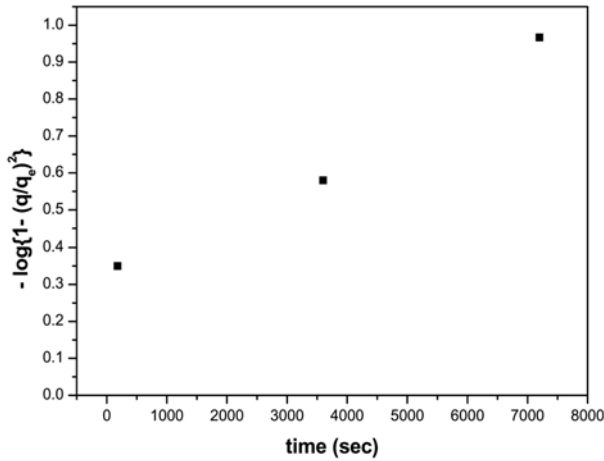

Fig. 5. Boyd plot for the adsorption of Ni^{2+} onto montmorillonite (metal ion: 100 mg/L; m: 1g; pH ~ 5.5; T: 25 ± 1℃).

fusion process. According to the intraparticle diffusion model, if a plot of the amount of sorbate adsorbed per unit weight of sorbent, q, versus square root of contact time gives a linear plot, it indicates that intraparticle/pore diffusion is the rate limiting step in the adsorption process. The plot obtained in Fig. 4 contrasted the prediction of the intraparticle diffusion model. This indicates that intraparticle/pore diffusion is not the singular rate limiting step in the adsorption process. The first part is attributed to boundary layer (film) diffusion, the second to the intraparticle diffusion and chemical reaction in the sorption process and as such indicating the existence of intraparticle diffusion process. Due to the step by step nature of this plot, the linear portion was linearized. The second linear portion indicates the existence of intraparticle diffusion in the process. The intraparticle diffusion coefficient D_i was determined by plotting $\log[1 - (q/q_e)^2]$ against time (Fig. 5), according to Urano and Tachikawa model.[18] If the plots are linear and pass through the origin, then the slowest (rate controlling) step in the adsorption process is the internal diffusion, and vice versa. From Fig. 5, it was observed that the plot was linear but do not pass through the origin.

3.5. Adsorption Isotherms

The Langmuir model was originally developed to represent chemisorption on a set of well-defined localized adsorption sites independent of surface coverage; having the same adsorption energy; and with no interaction between adsorbed molecules. This model, also called as the ideal localized monolayer model, is valid for monolayer sorption onto a surface with a finite number of identical sites[19] and is given by Equation 4

$$q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e} \tag{4}$$

where Q_o is a constant related to the area occupied by a monolayer of adsorbate, reflecting the maximum adsorption capacity (mg/g), C_e is the equilibrium liquid-phase concentration (mg/L), K_L is a direct measure of the intensity of adsorption (L/mg) and q_e is the amount adsorbed at equilibrium (mg/g).This equation can be linearized as follows[19]:

$$\frac{1}{q_e} = \left(\frac{1}{K_L Q_0}\right)\left(\frac{1}{C_e}\right) + \frac{1}{Q_0} \tag{5}$$

From the data of $1/q_e$ versus $1/C_e$, K_L and Q_o can be determined from the slope and intercept.

The Freundlich adsorption isotherm usually fits the experimental data over a wide range of concentrations. This empirical expression encompasses the surface heterogeneity and exponential distribution of the active sites and their energies. The widely used empirical Freundlich equation based on sorption on a heterogeneous surface[19] is given by Equation 6

$$q_e = K_F C_e^{1/n} \tag{6}$$

where K_F ((mg/g)(L/mg)$^{1/n}$) and n (dimensionless) are constants incorporating all factors affecting the adsorption process such as adsorption capacity and intensity, respectively. This equation can be linearized as follows[19]:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{7}$$

The values of n and K_F were calculated from the slope and intercept of the plot of $\log q_e$ versus $\log C_e$ .On the basis of correlation coefficient, R^2. Applicability of the isotherm equations was compared (Table 2). It was clear that the Langmuir model yields a better fit than the Freundlich model for the adsorption of Ni^{2+} onto montmorillonite.

Table 2. Freundlich and Langmuir parameters for Ni^{2+} sorption

Adsorbate	Freundlich isotherm			Langmuir isotherm		
Ni^{2+}	$1/n$	K_F ((mg/g)(L/mg)$^{1/n}$)	R^2	Q_o (mg/g)	K_L (L/mg)	R^2
	1.100	1.655	0.925	12.886	0.007	0.983

3.6. Thermodynamic Parameters

The thermodynamic parameters for the adsorption process, $\triangle H°$ and $\triangle S°$, were evaluated using the Van't Hoff equation:

$$\log K_{\mathrm{N}} = \frac{\Delta S^o}{2.303R} - \frac{\Delta H^o}{2.303RT} \qquad (8)$$

The values of $\log K_{\mathrm{N}}$ were defined as follow:

$$K_{\mathrm{N}} = \frac{f}{1-f} \qquad (9)$$

where $\triangle S°$ and $\triangle H°$ are entropy (kJ/mol K) and enthalpy (kJ/mol) change of adsorption, respectively, R is universal gas constant (8.314 J/mol K), and T is the absolute temperature (K). K_{N} is the equilibrium constant and f is uptake percentage of adsorbate at equilibrium. The values of $\triangle H°$ and $\triangle S°$ were calculated from the slope and intercept of linear regression of $\ln K_{\mathrm{N}}$ versus $(1/T)$. The values of $\triangle G°$ were estimated by Equation 10

$$\triangle G° = - RT \ln K_{\mathrm{N}} \qquad (10)$$

The plot shown in Fig. 6 for Ni^{2+} was linear at the range of temperature investigated. The calculated thermodynamic parameters such as $\triangle H°$, $\triangle S°$ and $\triangle G°$ are given in Table 3. The positive values of $\triangle G°$ indicate that the sorption of Ni^{2+} onto montmorillonite is not a spontaneous process. The change in enthalpy ($\triangle H°$) values is positive, showing that the sorption of Ni^{2+} is endothermic in nature, ions uptake increased with increase in temperature. The sorption of Ni^{2+} also requires a diffusion process, which is an endoth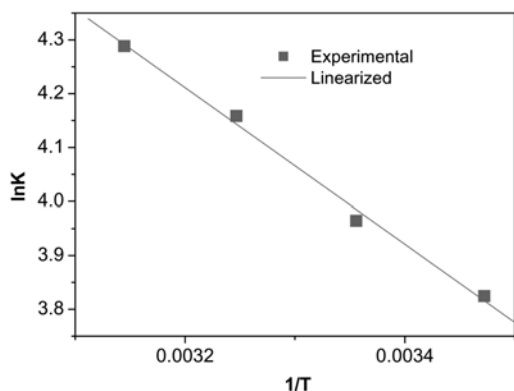ermic process; i.e., increase in temperature favors adsorbate transport within the particles of the adsorbent. The positive low values of $\triangle S°$ indicate low randomness at the solid/solution interface during the uptake of Ni^{2+} by montmorillonite.

4. Conclusion

Adsorption characteristics of Ni^{2+} onto montmorillonite and the potential use of montmorillonite as sorbent material for Ni^{2+} have been studied. Nickel as representative of heavy metals is chosen for this study as it is present in effluents of many industries. Ni^{2+} was sorbed due to strong interactions with the active sites of the sorbent. Montmorillonite was able to remove Ni^{2+} from aqueous solutions and the equilibrium experimental data fitted well to Langmuir than the Freundlich isotherm model. The pseudo first- order and pseudo-second-order models were employed to fit the adsorption kinetics and as such the adsorption of Ni^{2+} onto montmorillonite followed the pseudo-second-order kinetics. Diffusion of Ni^{2+} inside the clay particle was confirmed as the rate-controlling step and more important for Ni^{2+} adsorption rate than the external mass transfer. Thermodynamic parameters ($\triangle G°$, $\triangle H°$, and $\triangle S°$) were determined and their values indicated that the adsorption process was not spontaneous, but endothermic in nature, with a low positive value for the entropy change. This study shows that montmorillonite can be used as an effective and favorable adsorbent for the removal of Ni^{2+} and other heavy metals from aqueous solutions.

Nomenclature

C_e : equilibrium concentration of solution (mg/L)
$\triangle G°$: change in Gibb's free energy of adsorption (kJ/mol)
$\triangle H°$: change in enthalpy of adsorption (kJ/mol)
$\triangle S°$: change in entropy of adsorption (kJ/mol K)
K_F : Freundlich isotherm constant related to adsorption capacity $((mg/g)(L/mg)^{1/n})$
K_L : intensity of adsorption (L/mg)
m : clay mass (g)
n : Freundlich isotherm constant related to adsorption intensity
q : amount of heavy metal adsorbed at time t (mg/g)
q_e : amount of adsorbed heavy metal per unit clay mass (mg/g)
Q_o : maximum adsorption capacity (mg/g)
R^2 : correlation coefficient
R : gas constant (Jmol/K)
V : volume of solution (L)
K_{N} : Van't Hoff equilibrium constant
f : uptake percentage of adsorbate at equilibrium.
T : absolute temperature (K)
t : time (min)

Fig. 6. Plot of $\ln K$ vs $1/T$ for Ni^{2+} sorption unto montmorillonite.

Table 3. Thermodynamic parameters for Ni^{2+} uptake

Adsorbate	Temperature (K)	$\triangle G°$ (kJmol^{-1})	$\triangle H°$ (kJmol^{-1})	$\triangle S°$ (kJmol^{-1} K^{-1})
Ni2+	288	2.183		0.0944
	298	4.303		0.0825
	303	5.083	28.9	0.0773
	313	6.063		0.0718

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