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RESEARCH ARTICLE

KINETIC AND THERMODYNAMIC STUDIES OF THE ADSORPTION OF NICKEL (II) IONS FROM AQUEOUS SOLUTIONS BY SMECTITE CLAY FROM SABGA-CAMEROON

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ABSTRACT

The adsorption of Ni (II) ions from aqueous solution on smectite from Sabga (Sa0) has been investigated. The influences of the initial concentration, C_0 , temperature, T °C, and contact time, t , on the adsorption performances have been experimentally verified by a batch method. These results have showed that the amount of Ni (II) ions adsorbed increases with increased contact time, t , and that equilibrium adsorption is reached in 15 minutes. The experimental results obtained are described by Langmuir, Freundlich and Dubinin-Kaganer-Radushkevich (D-K-R) isotherm models. The Langmuir adsorption isotherm described the adsorption data very well at all studied temperatures. The maximum adsorption capacity; Q_0 , determined from the Langmuir adsorption isotherm studies was found to be 6.68 mg/g at 328 °K. Pseudo-first order, pseudo-second order, the mass transfer, Elovich and the intraparticle diffusion kinetic models were used to describe the kinetic data obtained. The experimental data fitted well to the pseudo-second order kinetic model, which indicates that chemical adsorption is the rate-limiting step. Thermodynamic parameters, such as ΔG° , ΔH° , and ΔS° were also calculated using adsorption equilibrium constant obtained from the Langmuir isotherm studies. These results suggest that the adsorption of nickel (II) ions on smectite is a spontaneous and endothermic process.

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INTRODUCTION

Heavy metals can pose health hazards to man and aquatic lives, if their concentrations exceed acceptable limits. Even concentrations below these are potentially toxic in the long run, because heavy metals are known to accumulate within biological systems and are non-biodegradable (Medhat and Shaker, 2007). Nickel is toxic and relatively widespread in the environment. It is used in a wide variety of industries such as plating and cadmium-nickel battery, phosphate fertilizers, mining, pigments, stabilizers and alloys, and find its way to the aquatic environment through waste water discharge (Surinder *et al.*, 2008). Nickel is a potent carcinogen. The contactness of nickel with skin results in painful disease, nickel itch, which is followed by sudden death. Acute poisoning of nickel causes chest pain, tightness of the chest, shortness of breath etc. The toxic nature of nickel to fish, lentil plants, crops and algae was also reported (Edwin, 2008). Decontamination of surface and underground water supplies is a major concern and conventional methods such as: Chemical precipitation, Membrane Filtration (Reverse Osmosis and Electro dialysis), Electrolytic processes, Biosorption and Adsorption can be used for decontamination of effluents. These techniques which have been mentioned above, with the exception of adsorption are expensive and also have

disadvantages such as incomplete metal removal, high reagent, energy requirements and generation of toxic sludge or other waste products that require proper disposal (Joanna *et al.*, 2008). Due to the problems mentioned above this research has been interested in using Adsorption since it is cheaper, making use of low cost and local Adsorbents, which are adapted in efficiently removing heavy metal ions found in low concentrations in solution. Research work on the adsorption of heavy metals has been carried by many students in the Physical and Theoretical Chemistry Laboratory, Faculty of Science, University of Yaoundé I (Yaoundé-Cameroon); however these studies were not directed towards elucidating the effect of temperature on the adsorption phenomena. It should be noted that the quantity of metal sorbed by a given adsorbent is a complex function of surface properties, environmental and solution parameters. In order to elucidate sorption processes, surface chemists have paid much attention to surface properties, but the potential influence of solution parameters can not be ignored. The goal in this work is to point out three main factors that affect metal sorption and to indicate the impact of these factors on metal sorption and also to valorize local materials which are clays. These three factors are contact time, metal-ion concentration and the temperature of solution. Also some research work has been carried out to study the influence of temperature in the adsorption of nickel and other metals (Ömer *et al.*, 2003; Huang-Shen and Jeng-Jong, 2009; Pankaj *et al.*, 2009). In conclusion the temperature is the important parameters in the processes of

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adsorption Hence in this work the adsorption of Nickel (II) ions onto a Cameroon smectite Clay, with respect to the changing of temperature; concentration and contact time will be investigated. This smectite clay was chosen in this study because it is relatively cheap compared to commercial adsorbents like activated carbon.

MATERIAL AND METHODS

Adsorbents

The adsorption of nickel ions from aqueous solution has been carried out by using smectite clay (Sa0) from Sabga in the North West region of Cameroon with geographical coordinates: latitude 6° N and longitude 10°19' E. The characteristics of smectite clay (Sa0) samples have been reported in an earlier work (Tonle *et al.*, 2003)[9]. The smectite material was sieved and fraction finer than 80 µm grain size was used. The specific surface area is 86m²/g. The adsorbents were primarily heated in an oven at 110°C for 168 hours and cooled in a desiccator before use in the adsorption process (thermal activation).

Kinetic Batch Adsorption Experiments

Batch adsorption experiments were carried out at ambient temperature. The effect of contact time of the adsorbents is studied by using the kinetics and equilibrium models.

Effect of Agitation Time

In order to determine the effect of the agitation time, 0.3 g of the adsorbent was stirred with a 30 mL solution (pH=6,2) of Nickel (II) ion of initial concentration 50 mg/L at different time intervals. At the end of each time, the solution was filtered rapidly and the Nickel (II) ion content of the filtrate determined. The Nickel (II) ion titration was carried out by using an atomic absorption spectrophotometer (AAS) model 210 Buck Scientific at the wavelength 232 nm.

Batch Equilibrium Experiments

For each run the adsorbent is mixed with 30 mL solution of nickel ion at different initial concentrations (20–140 mg/L) and different temperatures (288-328 K). The suspensions were stirred for 15 minutes by using a magnetic stirrer. The amount of Ni²⁺ adsorbed at equilibrium, Q_e (mg/g) was calculated using equation:

$$Q_e = (C_0 - C_e)V / m \quad (1)$$

Where C₀ and C_e are Ni²⁺ ion concentrations initially and at equilibrium respectively, V the volume of the solution (L) and m the adsorbent mass. The equilibrium data were then fitted by using the Langmuir, the Freundlich and Dubinin-Kaganer-Radushkevich adsorption isotherm models.

Langmuir Adsorption Isotherm Studies

The Langmuir adsorption equation is one of the most common isotherm equations for modelling equilibrium data in solid - liquid systems. This equation is valid for monolayer adsorption onto a surface with a finite number of identical

sites which are homogeneously distributed over the adsorbent surface. The general form of the Langmuir equation is (Sukdeb *et al.*, 2006):

$$Q_e = Q_m \frac{bC_e}{1 + bC_e} \quad (2)$$

where C_e is the equilibrium concentration of Ni²⁺ ion (mg/L), Q_e is the amount of Ni²⁺ ion adsorbed per unit mass of the adsorbent, b is the Langmuir adsorption constant (L/mg) and Q_m is the maximum amount of per unit mass of adsorbent to form a complete monolayer on the surface (mg/L). The linear form of this equation is as follows:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{bQ_m} \quad (3)$$

The effect of isotherm shape can be used to predict whether an adsorption system is “favorable” or “unfavorable.” the essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_L, which is defined by the following relationship:

$$R_L = \frac{1}{1 + bC_0} \quad (4)$$

The value of R_L indicates the type of the isotherm to be either unfavorable (R_L >1), favorable (0 < R_L < 1) or irreversible (R_L=0) (Sevil and Bilge, 2007).

Freundlich Adsorption Isotherm Studies

Freundlich equation is an empirical equation based on the adsorption on a heterogeneous surface (Chabani *et al.*, 2007):

$$Q_e = K_f C_e^{1/n} \quad (5)$$

Where, C_e is the equilibrium concentration of Ni²⁺ ion (mg/L), Q_e is the amount of Ni²⁺ ion bound to per gram of the adsorbent at equilibrium (mg/g), k_f and n are the Freundlich constants related to sorption capacity and sorption intensity of the sorbent respectively. The linear form of the Freundlich isotherm equation is:

$$\ln Q_e = \ln K_f + \left(\frac{1}{n}\right) \ln C_e \quad (6)$$

Dubinin-Kaganer-Radushkevich (D-K-R) Isotherm Studies

Langmuir and Freundlich isotherms are insufficient to explain the physical and chemical characteristics of adsorption. D-K-R isotherm is commonly used to describe the sorption isotherms of single solute systems. The D-K-R isotherm, apart from being analogue of Langmuir isotherm, is more general than Langmuir isotherm as it rejects the homogeneous surface or constant adsorption potential. The D-K-R isotherm is expressed as (Achanai *et al.*, 2008):

$$Q_e = Q_{\max} \exp \left(\frac{\left(RT \ln \left(1 + \frac{1}{C_e} \right) \right)^2}{-2E_a} \right) \quad (7)$$

E_a : is the main energy of adsorption and gives information about the physical and chemical features of adsorption. The linear form of the D-K-R isotherm equation is:

$$\ln Q_e = \ln Q_{\max} - \beta \varepsilon^2 \quad (8)$$

where $\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right)$ is called the Polanyi Potential.

Kinetic Adsorption Experiments

Kinetic adsorption experiments were conducted using a series of 30 mL solutions containing fixed amount of adsorbent and nickel ions (50ppm). The solutions were vigorously agitated with a magnetic stirrer for increasing time intervals. At the end of each run, the solution is filtered and the Ni^{2+} ion concentration in the filtrate is determined. Kinetics models have been used to fit experimental data.

The Pseudo-First Order Model

The pseudo-first order equation of Lagergren is generally expressed as follows (Demirbas et al, 2007):

$$\frac{dQ_t}{dt} = k_1(Q_e - Q_t) \quad (9)$$

Where Q_e and Q_t are the sorption capacity at equilibrium and at time t respectively (mg.g^{-1}) and K_1 is the rate constant of pseudo-first order sorption (L.min^{-1}). After integration and applying boundary conditions, $t = 0$ to $t = t$ and $Q_t = 0$ to $Q_t = Q_t$ the integrated form of equation is:

$$\ln \left(\frac{Q_e - Q_t}{Q_e} \right) = k_1 t \quad \text{or} \quad \ln C_t = -k_1 t + \ln C_o \quad \text{after reduction}$$

The Pseudo-Second Order Model

If the rate of the sorption is a second order mechanism, the pseudo-second order chemisorption kinetic rate equation is expressed as (Augustine et al., 2007):

$$\frac{dQ_t}{dt} = k_2(Q_e - Q_t)^2 \quad (10)$$

Where k_2 is the rate constant of pseudo-second order sorption ($\text{g.mg}^{-1}.\text{min}^{-1}$). The integrated and rearranged form of equation is:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}$$

The Elovich equation

The Elovich equation is general expressed as follows (Zora and Snezana, 2006):

$$\frac{dQ_t}{dt} = \alpha e^{-\beta Q_t} \quad (11)$$

where α is the initial sorption rate (mg.l.g.min^{-1}) and β is the desorption constant (g.mg^{-1}) during any one experiment. The integrated and simplified equation is:

$$Q_t = \frac{\ln(\alpha\beta)}{\beta} + \frac{\ln t}{\beta}$$

The intraparticle diffusion model

The linear form of this equation is expressed as follows (Zora and Snezana, 2006):

$$\ln P = \ln k_{id} + a \ln t \quad (12)$$

Where P is the percent removal of mercuric ions at time t , K_{id} is the intraparticle diffusion rate constant and a is a gradient whose value depends on the adsorption mechanism.

Mass Transfer Equation

The mass transfer equation is generally expressed as (Augustine et al., 2007):

$$C_o - C_t = D e^{k_o t} \quad (13)$$

Where C_o is the initial metal ion concentration (mg.dm^{-3}), C_t is the metal ion concentration at time t , t is the shaking time (min), D is a fitting parameter, K_o is the adsorption constant which is related to the mass transfer adsorption coefficient, where M is the mass of the adsorbent (g). A linearised form of equation is:

$$\ln(C_o - C_t) = \ln D + K_o t$$

RESULTS

Effect of Agitation Time

Adsorption experiments were carried out on given solutions of Ni(II) ions of initial concentration 50 ppm for time interval between 5 to 60 mins with $\text{pH}=6.2$. The experimental results obtained for the adsorption of nickel ions during varying contact times are show in figure 1. Ni^{2+} ion uptake increases with increasing agitation time within 15 minutes and then it becomes nearly constant.

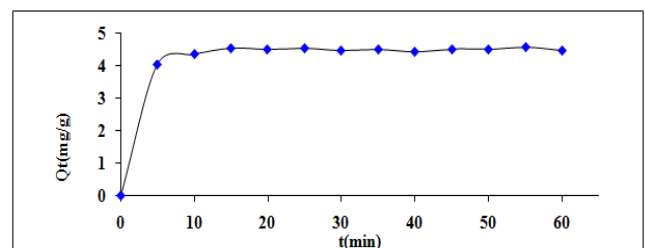


Figure. 1: Effect of Agitation Time on the Adsorption of Nickel(II) Ions on Sa0 at 25°C

Kinetic Modelling of Ni²⁺ Ion Adsorption

The kinetics of the adsorption of nickel ions has been studied using five kinetics models. In order to obtain parameters related to each kinetic model, experimental data have been tested with linear forms of these models. The straight-line plots are presented on figures 2 to 6. Parameters are given in table 1. These results show that the adsorption of Nickel ion on smectite is better described by the pseudo-second order model with a correlation coefficient greater than 0.9990. This suggests that chemisorption is the rate-limiting step. Other sorption studies done in Physical and Theoretical Chemistry Laboratory, Faculty of Science, University of Yaoundé I, on Colbat; Aluminium, Chromium, Lead, Cadmium and Mercury have shown the same results for the clay.

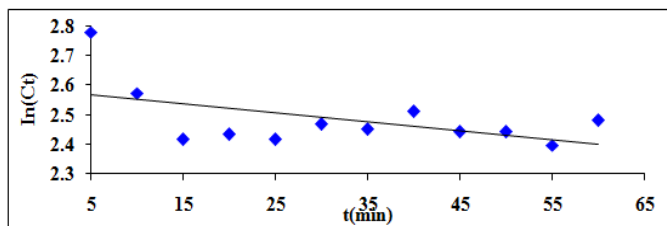


Figure 2: Linearized Pseudo-First Order Plots

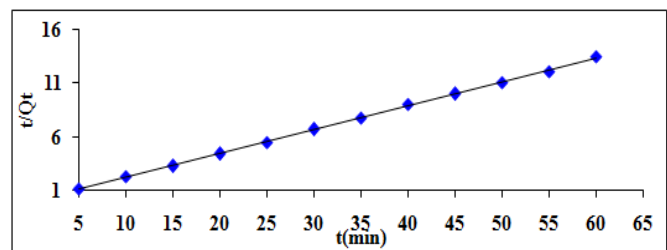


Figure 3: Linearized Pseudo-Second Order Plots

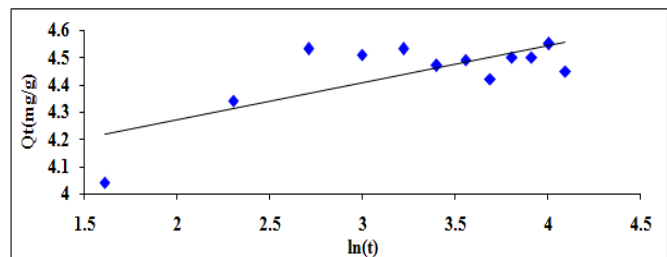


Figure 4: Linearized Elovich Plots

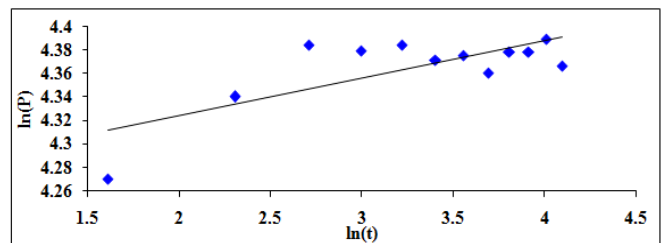


Figure 5: Linearized Intraparticle Diffusion Plots

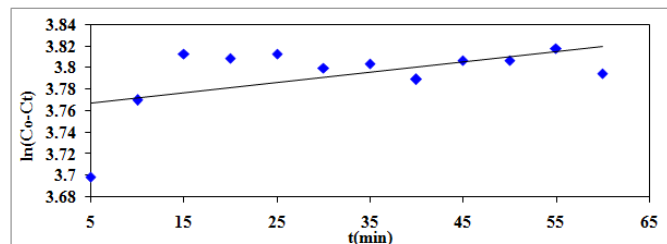


Figure 6: Linearized Mass Transfer Equation Plots

Table 1: Kinetic models parameters of adsorption on Sa0

Kinetic models	Constants	Values
Pseudo-First Order	$K_1 (10^{-3} \text{ min}^{-1})$	3,1
	R^2	0,279
Pseudo- Second Order	$K_2 (10^{-1} \text{ g.mg}^{-1}.\text{min}^{-1})$	9,354
	R^2	0,9995
	$B (\text{g.mg}^{-1})$	7,3368
Elovich	$\alpha (\text{mg.g}^{-1}.\text{min}^{-1})$	$7,4655.10^{11}$
	R^2	0,5451
Intraparticle Diffusion	K_{id}	70,7604
	a	0,0321
	R^2	0,5572
Mass Transfer	$K_o (\text{min}^{-1})$	0,001
	$\ln D$	3,7626
	R^2	0,2815

Effect of Temperature

Adsorption isotherms

Equilibrium studies were conducted with 0.3 g of Sa0 at different temperatures from 288 K to 328 K with the same pH that above. These results are shown in figure

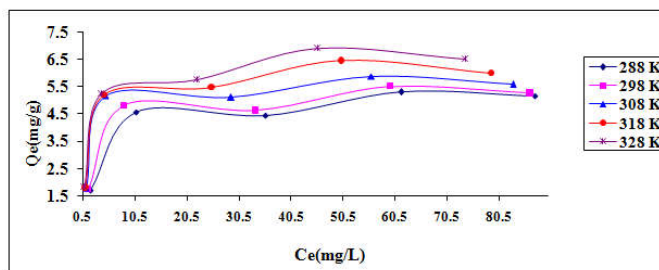


Figure 7: Adsorption isotherms at different temperatures

Adsorption isotherms on Sa0 is type I adsorption isotherm, characteristic of microporous adsorbent, chemical adsorption or physical adsorption limited to monolayer coverage. While adsorption process reaches equilibrium, the curve is not parallel to the concentrations-axis; this reveals that mesopores are also involved in the adsorption process. Data obtained from these studies have been tested with the Langmuir, Freundlich and Dubinin-Kanager-Raduskevich linearized equations. These results are summarized in table 2.

These results show that adsorption isotherms are in agreement with the Langmuir adsorption isotherm for both Sa0 with the values of r^2 in the range of 0,9943 to 0,9969. And the good value of r^2 for Dubinin-Kanager-Raduskevich isotherm allowed to said that it describe very well the nature of the adsorption of Ni²⁺ on smectite. The mean sorption energy (E) increase with the temperature and these small values between 0.7071 and 1.291 kJ/mol indicating that the adsorption of Nickel ions is more physical.

Influence of Temperature on Separation Factor

The values of R_L for different temperatures are given in Figure 2. Theses values indicate that adsorption is more favorable for the higher initial cobalt ion concentrations and solution temperatures than for the lower ones.

Table 2: Isotherm Parameters for Ni²⁺ Uptake from Aqueous Solution

T (°K)	Langmuir			Freundlich			D-K-R		
	b (L/mg)	Q _{max} (mg/g)	R ²	K _f (mg/g)	1/n	R ²	Q _{max} (mg/g)	E _a (kJ/mol)	R ²
288	0,255	5,4113	0,9949	1,703	0,276	0,8254	4,917	0,7071	0,9793
298	0,395	5,4555	0,9943	1,909	0,258	0,7757	5,114	0,8451	0,9828
308	0,57	5,767	0,9969	2,323	0,232	0,7107	5,5467	1,118	0,9896
318	0,579	6,2422	0,9958	2,342	0,258	0,7678	5,905	1,120	0,9868
328	0,586	6,68	0,9957	2,476	0,263	0,8058	6,217	1,291	0,9788

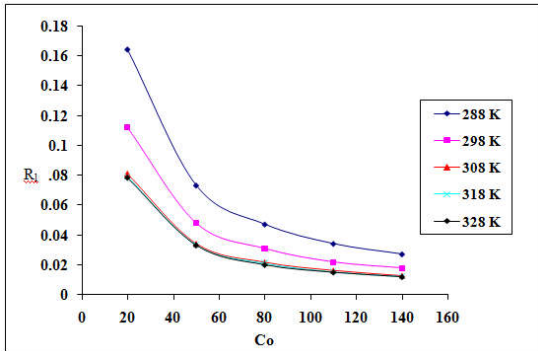


Figure 8: Plot of R_L against initial cobalt concentration in different temperatures

Influence of Temperature on Adsorption Percentage

The results are presented in figure 9. Nickel (II) ion adsorption percentage increases with Temperatures and it is higher for the smallest concentration. Increasing in adsorption percentage is due to the increase in available number of binding sites when the temperature begins higher. Maximum adsorption percentage is 95,79% at 328 K for 20ppm.

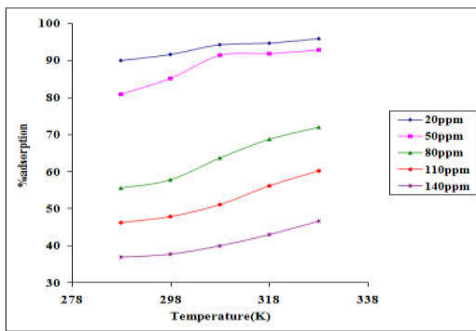


Figure 9: Influence of temperature on adsorption percentage

Thermodynamic Studies

Thermodynamic considerations of an adsorption process are necessary to conclude whether the process is spontaneous or not. The Gibbs free energy change, ΔG°, is an indication of the spontaneity of a chemical reaction and therefore is an important criterion for spontaneity. Both energy and entropy factors must be considered in order to determine the Gibbs free energy of the process. Reactions occur spontaneously at a given temperature if ΔG° is a negative quantity. The free

energy of an adsorption, considering the adsorption equilibrium constant *b* is given by the following equation:

$$\Delta G^\circ = -RT \ln b \tag{14}$$

Where ΔG° is the standard free energy change, J/mol; R is the universal gas constant, 8.314 J/mol K; and T is absolute temperature, K. The parameter ΔG° for the adsorption process using the *b* from the Langmuir isotherm is shown in Table.

The other useful relationships are ΔH° and ΔS° and they are given by:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{15}$$

Table 3. Variation of ΔG° with Temperature

ΔG° (kJ/mol)	-23,02	-24,903	-26,678	-27,586	-28,486
T(K)	288	298	308	318	328

A plot of ΔG° versus temperature, T, will be linear and the values of ΔH° and ΔS° are determined from the slope and intercept of the plot (Figure 10).

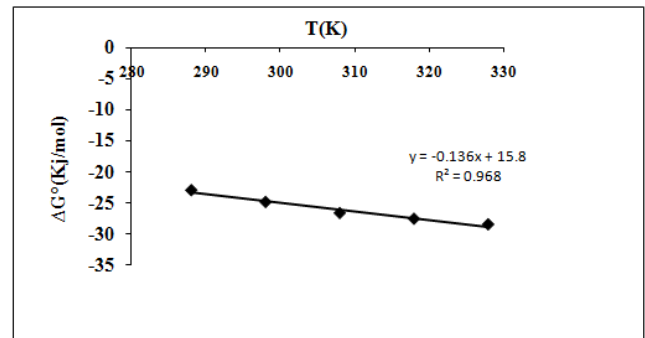


Figure 10: Plot of Gibbs Free Energy change, ΔG°, versus Temperatures, T (°K).

The values of ΔH° and ΔS° are found to be 15,8 kJ/mol and 0,1361 kJ/mol/K respectively. The values of ΔG° were found to decrease -23;02 to -28;486 kJ/mol using the equilibrium constant, *b*. The decrease in the negative value of ΔG° with an increase in temperature indicates that the adsorption process of nickel ions on smectite becomes more favorable at higher temperatures. The value of ΔH° was positive, indicating that the adsorption process was endothermic. The positive value of ΔS° reflects the affinity of the smectite for the nickel ions and suggests some structural changes in adsorbate and adsorbent.

Conclusion

Sa0 is able to adsorb nickel ions from aqueous solutions. The removal of nickel ions using Sa0 was a function of temperature. The adsorption capacity increased with increasing temperature. The Langmuir isotherm had a high coefficient of determination with experimental data. The thermodynamic parameter, ΔG° , could be calculated from the adsorption equilibrium constant obtained from the Langmuir isotherm. The value of ΔH° and ΔS° could be also obtained from the slope and intercept of the relationship between ΔG° and reaction temperature. The negative values of ΔG° indicate the spontaneous nature of adsorption with a high preference of nickel ions onto Sa0. The value of ΔH° was positive, which indicated that the adsorption reaction was endothermic. The positive value of ΔS° shows that increasing randomness at the solid/liquid interface during the adsorption of cobalt ions on Sa0. It is found that the pseudo-second order model is applicable for whole the range of contact time while not for the other models

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