

Influence of Temperature Regime on Nickel Kinetics in Two Alluvial Soils from Arid Region

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ABSTRACT

The effect of soil temperature on Nickel (Ni^{2+}) adsorption/desorption using a kinetics approach was studied in two Egyptian surface alluvial soil samples (0-30 cm) varying in their clay content and other related properties and collected from El-Menoufya Governorate, Egypt. The kinetics of Ni^{2+} adsorption, as well as desorption, were determined at three temperature regimes i.e. 5, 28, and 50°C for each soil using the batch technique. The calculated values of energies of activation for adsorption (K_a) ranged between 5.21 - 5.34 for Soil 1 (S_1) and 5.32 - 6.23 kcal mol⁻¹ for Soil 2 (S_2), respectively. The respective values of E_d were 2.44 - 3.71 and 2.42 - 3.57 kcal mol⁻¹. Results also showed that the E_d values were greater than the E_a values in both soils; implying further energy has been required to desorb Ni^{2+} than to release for both soils. Thermodynamic variables have been calculated by Gibbs' and Eyring's equations. The free energy of Ni^{2+} adsorption (ΔG°) were negative values (ranging between - 0.234 and - 0.411 in S_1 and from - 0.357 to - 0.436 in S_2 cal mol⁻¹), meaning decrease in ΔG values with increasing the temperature. For Ni^{2+} desorption (ΔG_d), The free energy of activation values was higher than those for Ni^{2+} adsorption (ΔG_a), suggesting that it is necessary to release Ni^{2+} more free energy than to adsorb it. The good agreement of calculated ΔG° from Gibbs' theory reaction denoting that the thermodynamic constants could be determined using the kinetic parameters. The enthalpy (ΔH) parameter numerical values were exothermic and showed a greater binding of Ni^{2+} ions in S_2 than in S_1 according to the distinction between external surfaces to interlayer surfaces charge ratio. The enthalpy of activation (ΔH) values in both soils were - 2.127 and - 0.497 cal mol⁻¹ in S_1 and S_2 respectively, proposing the heat energy needed to overcome the Ni^{2+} desorption in S_2 as compared to S_1 .

Keywords: Alluvial soils, Thermodynamics, Kinetics, Nickel.

INTRODUCTION

Soil contamination by inorganic pollutants like Ni^{2+} was originally noticed in soils, but in modern time it has become a significant problem due to increasing anthropogenic activities. Nickel is an important animal nutrient and important element for plants in trace concentration (Marschner, 1995 and Kabata-Pendias,

2011). Unlike other heavy metals, Nickel is safe for human consumption up to 8 mg could be consumed on a daily basis without any health risks. Nickel is an essential element as trace quantities for human life as a part of vitamin B-12, it also used as a treatment for anaemia, because it causes red blood cells production. The nickel in the soil as a pollutant is low compared to other heavy metals, but when Ni^{2+} combines with Cu or Zn, increase its toxicity through synergistic mechanism (Saber et al., 2012). Exposure to high levels of Ni can cause health hazards where its effects on the lungs and wheezing have been found in workers who breathed significant levels of Ni by the air. However, as with other inorganic pollutants, increasing Ni accumulation in soil ecosystems can have negative effects on the cultivated plants, animals and microorganisms, which increase the risky effects of Ni in soils (Thakali et al., 2006 and Antoniadis et al., 2017a, b). The natural geochemical processes like increasingly frequent anthropogenic activities, including industrial operations (mining, smelting, electroplating, stealing), weathering of rocks, metallic products (alloy, textile, pigment, motor vehicles, chemical, aircraft paint), high application of fertilizers and pesticides, waste combustion and sewage sludge spreading in agriculture have a significantly increased the Ni contamination in soil (Gimeno-García et al., 1996; Kopittke et al., 2007; Rajkumar and Freitas, 2008b). Recently, due to its concentration of more than 26,000 mg kg⁻¹ in heavy metals polluted soils and 0.2 mg L⁻¹ in contaminated waters, Ni becomes a severe issue; these values are much greater than those observed in cleaned areas (Ma and Hooda, 2010). Increasing of Ni concentrations in soils as a possibly pollutant can induce negative effects on soil function examples beside significant mobility-related environmental issues and transfer to the food chains. Pollution of soils by Ni could, therefore, be a worldwide environmental problem and protection issues should be applied in the environment (Kabata Pendias, 2011 and Yusuf et al., 2011). The impact of temperature on soil pollutant reaction rates is well recognized and important in understanding the pollutant distribution mechanisms. Although there is voluminous literature of

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Ni reactions in soils, no available data regarding the thermodynamic parameters (enthalpy and entropy) and their effects on Ni adsorption in soils of arid regions. The aim of this study is to investigate the effect of different temperatures regime on Ni kinetics in alluvial soils of the arid region.

MATERIALS AND METHODS

Location and characteristics of soil

Two surface alluvial soil samples (S_1 & S_2) were collected from west east middle Delta (El-Menoufya Governorate). The collected samples varied in their clay contents. The studied soils were analyzed to their physicochemical and mineralogical properties according to standard methods described by Sparks, (1995) and reported in Table (1). Soil samples were air dried and crushed to pass through a 2-mm sieve and prepared for application of the different treatments.

Kinetics of Ni adsorption for the studied soils as influenced by temperature regimes:

Kinetic experiments for Ni sorption and desorption were carried out using Batch method, explanation of the technique was documented by Nadia Gad et al. (2013). Soil samples were shaken in a water bath at $5 \pm 1^\circ\text{C}$, $28 \pm 1^\circ\text{C}$, and $50 \pm 1^\circ\text{C}$ for 48 hours. The equilibration period was 48 hours for adsorption and desorption of Ni by the selected soils assigned on the basis of previous experiments with shaking period of 12, 24, 36, 48 hours. According to the literature, the equilibrium for nickel adsorption is reached within 24 hours (Cavallaro and McBride, 1978). After the equilibrium period, the soil samples were centrifuged at 15000 rpm for 10 minutes and Ni was determined by using an ICP. A volume of deionized water equal to that of the adsorption solution was added to the remaining solid and samples were shaken for 48 hours at $5 \pm 1^\circ\text{C}$, $28 \pm 1^\circ\text{C}$, and $50 \pm 1^\circ\text{C}$. After centrifugation Ni desorbed was also measured using ICP. It should be noted that the pH reached at the equilibrium for the adsorption varied from 4.9 to 5.6, while for the adsorption, it was the same for all samples. Adsorption and desorption rate constants were calculated using the first-order equations. The first-order kinetic model provided, in terms of R^2 and standard error (SE), the best fits of the data and apparent rate constants, k_a , were calculated. Energies of activation values for adsorption and desorption were calculated by the Arrhenius and van't Hoff equations. The ΔG , ΔH , and ΔS for Ni exchange were calculated using Eyring's absolute reaction rate theory as mention by Nadia Gad et al., (2013). The adsorption of Ni and desorption from used soils were confirmed to the first-order kinetic model. The rate coefficients of Ni adsorption and desorption (k_a' and k_d' , respectively) will be calculated

from the first-order kinetic model as derived below.

Apparent Adsorption Rate Coefficient (k_a')

Adsorption rate was calculated according to the following equation:

$$\log(1 - K/K_\infty) = k_a' \cdot t$$

Where:

K = amount of Ni adsorbed on the soil at equilibrium (mg / kg).

k_a' = adsorption of Ni at time t divided by 2.303

Desorption Rate Coefficient (k_d')

$$\log(K_t/k_0) = k_d' \cdot t$$

Where

K_t = amount of Ni desorption at time t (mg/kg)

k_d' = desorption rate coefficient

Thermodynamic parameters

Calculation of thermodynamic parameters of Ni exchange was done by Gibbs and Eyring's reaction rate equations. The variation between the adsorbed and desorbed of Ni was controlled by several factors that limited the availability of this pollutant, indicating partial reversibility, subsequently the following relationship and could be written according to Nadia Gad et al., 2013 as:

$$K_a/k_d' = K$$

Where K is the apparent equilibrium constant

Free energy of activation ΔG

The free energy for Ni exchange (ΔG^0) can be obtained,

$$\Delta G^0 = -RT \ln K$$

Or

$$\Delta G^0 + -RT \ln(k_a'/k_d')$$

The entropy for Ni exchange (ΔS^0) could be determined by the relation mentioned in the work of Nadia Gad et al., 2013 as:

$$\Delta S^0 = (\Delta H^\circ - \Delta G^\circ)/T$$

Where

ΔH = enthalpy of activation,

ΔS = entropy of activation

T = absolute temperature, and

Since ΔH_a is found from the following relationship:

$$\Delta H_a = E_a - RT$$

The ΔG_a can be measured using this formula:

$$\Delta G_a = \Delta H_a - T \Delta S$$

Analogous expressions for the reverse reaction can be achieved by using k_d' and E_d estimated for the desorption process.

Table 1. Some physicochemical characterization of used soils according to Standard Methods of Sparks (1995)

Soil No.	Depth (cm)	EC dSm ⁻¹	pH	OM (%)	Clay Cont. %	Amorphous Fe ₂ O ₃ ppm	Total CaCO ₃ %	Available Ni ppm	Surface area m ² /g
Soil 1 (S ₁)	0 – 30	0.5	7.94	1.39	28.5	0.39	3.31	1.44	131
Soil 2 (S ₂)	0 – 30	0.8	8.12	1.72	41.6	0.22	4.5	1.77	200

RESULTS AND DISCUSSION

Kinetics of Ni adsorption and desorption from used soils as influenced by temperature regime:

The kinetics of Ni adsorption and desorption from the used soils confirmed to first-order kinetic model at various temperatures tested by having high R² and low SE. The linear straight-line of Ni sorption in the soil 1 (S₁) and soil 2 (S₂) samples indicates to existence of the kinetic first-order model Figure (1).

Also, the kinetic results confirmed that Modified Freundlich and parabolic diffusion models gave high conformity to describe the kinetic data of the studied soils with linear relationships existing in both the adsorption and desorption experiments (Data not shown).

The low Ni exchange rate is associated the existence of clay mineral amounts in the used soils as shown in the soil characterizations represent in Table (1), showing a diffusion mechanism is controlled exchange (Sparks, *et al.*, 1980; Nadia Gad and Zaghoul, 2007).

Effect of temperature regime applied on Ni adsorption and desorption Rate Coefficients:

Results in figure (2A) represent the impact of temperature regime on the rate of Ni adsorption and desorption. Data imply that increasing of temperature from 5°C to 28°C led to increasing the rate of adsorption from 5.14 to 5.21 and from 5.32 to 5.78 mg kg⁻¹ hr⁻¹ in S₁ and S₂, respectively. Increasing the temperature to 50°C gave the highest values for both soils reached to 5.34 and 6.23 mg kg⁻¹ hr⁻¹ in S₁ and S₂ respectively. Increasing of the rate of adsorption in S₂

compared to S₁ mainly due to increasing the clay content in S₂ and S₁ (41.6 and 28.5%) respectively. Also, increasing of OM in S₂ compared to S₁ could be playing an important role in Ni retention in S₂. Figure (2B) represents the rate of Ni desorption as affected by the same temperature regime. Results showed that the rate of desorption slightly varied between the two studied soils. Increasing the temperature regime from 5 to 28°C and 50°C, increased the rate of desorption from 2.44 to 3.07, 3.7 mg kg⁻¹ hr⁻¹ and from 2.41 to 3.04 and 3.57 mg kg⁻¹ hr⁻¹. Hysteresis phenomena in natural clays have a significant impact on inorganic pollutants for both transport and bioavailability. Sorption and desorption of Ni in selected soils were significantly observed as depicted in figures 2A and 2B. Hysteresis is a condition in which the adsorption and desorption isotherms do not overlap (Strawn and Sparks, 1999).

Hysteresis phenomena were explained by many authors with different mechanisms including variability of the binding mechanism with time, chemical precipitation, micro-porous deformation and holding, movement and incorporation of the solute into the soil matrix (Weber & Huang, 1998, McBride, 2000 and Sander *et al.*, 2005). Pseudo-hysteresis phenomenon is associated to slow desorption kinetics, fail to reach the equilibrium before the starting of the desorption (McBride, 2000). One possible reason for slow desorption is that chemical adsorption processes generally need a much greater activation energy in the direction of desorption than adsorption, to separate the energetically very suitable bonds of the sorbate with the surface (McBride, 2000 and Apple & Ma, 2002).

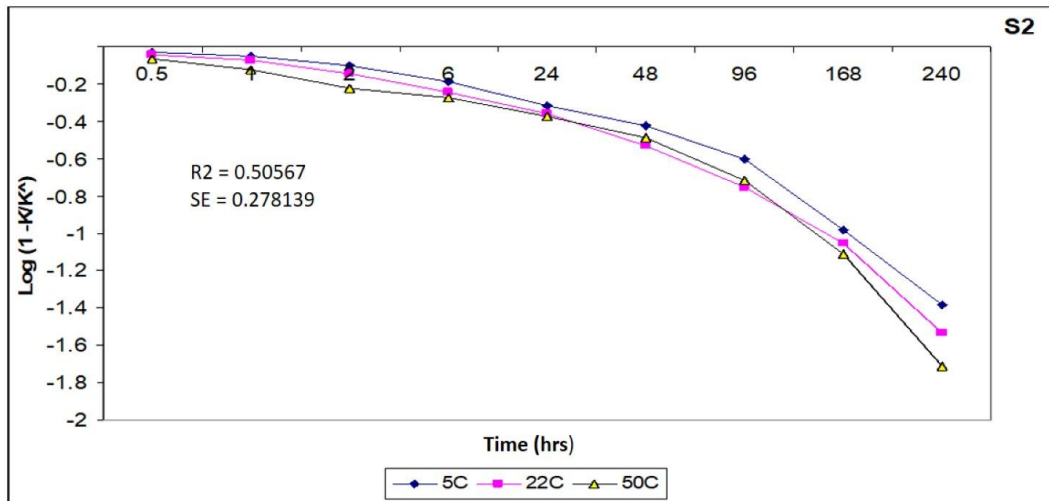
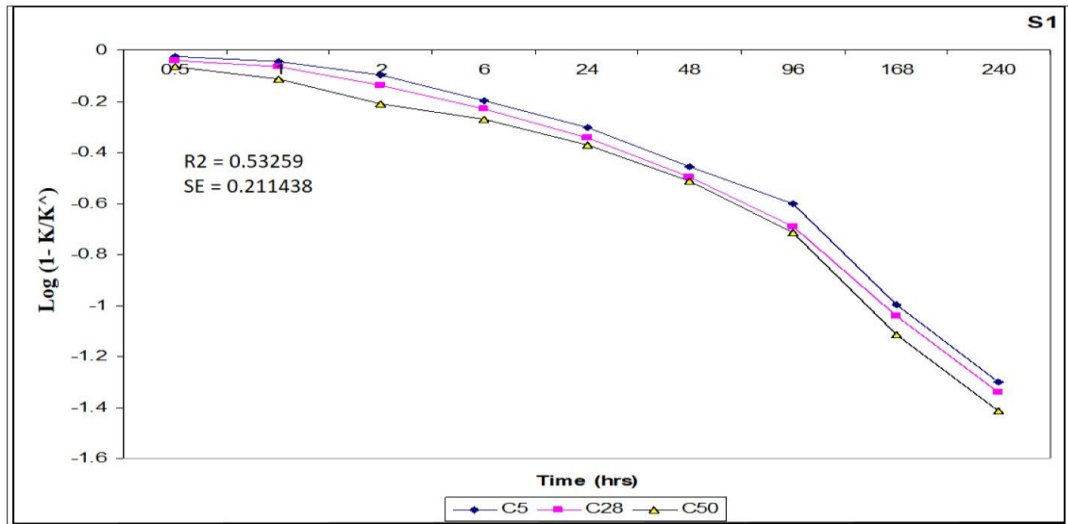
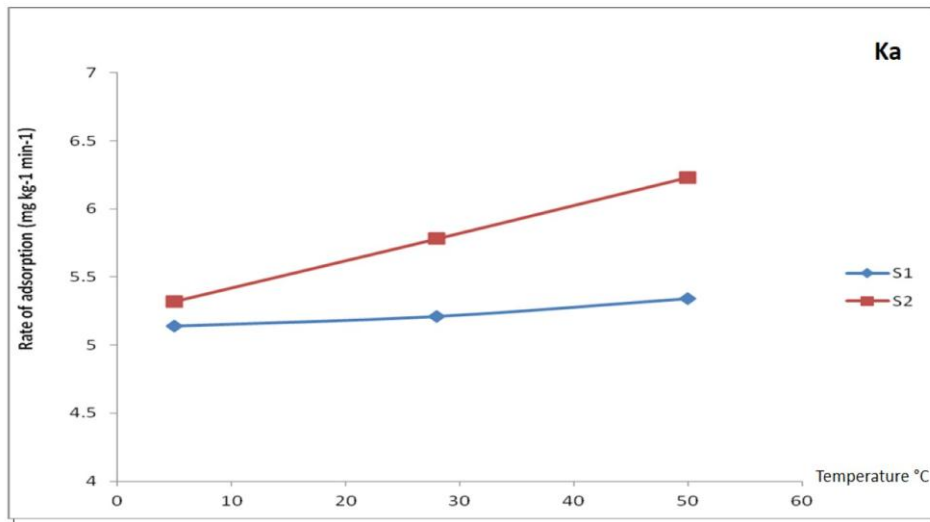


Figure 1. Kinetics of Ni adsorption for the selected soil samples as described by 1st order kinetic models at different temperature regime studied where K, reflects the Ni quantity on the soil exchange sites after time t of adsorption, and K₀ indicates the quantity of Ni on the exchange sites at equilibrium.

A



B

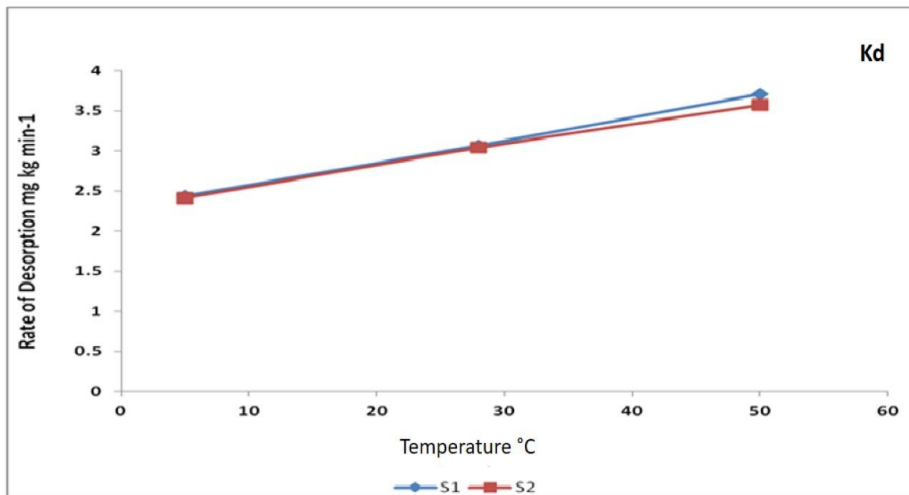
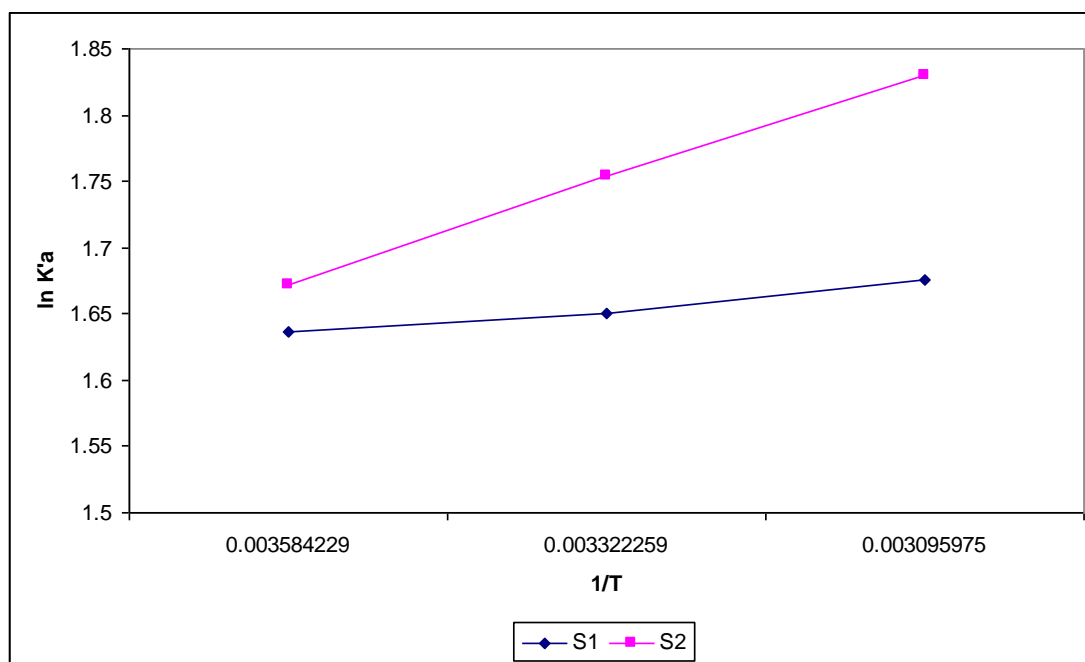


Fig.2. Impact of temperature regime of the rate of Ni adsorption (K_a) and desorption (K_d) in the two studied soil samples

Table 2. Rate parameters (k_a and k_d) of Ni at three temperature regimes, energies of activation (E_a and E_d), and thermodynamic parameters using 1st order kinetic model exchange in two alluvial soils

Temperature °C	K_a	K_d	E_a	E_d	ΔG	ΔH	ΔS
	mg kg ⁻¹ hr ⁻¹		Kcal mol ⁻¹		Cal mol ⁻¹		Cal mol ⁻¹ k ⁻¹
			S1				
5	5.14	2.441			-0.411		-6.17
28	5.21	3.072			-0.316	-2.127	-6.02
50	5.34	3.709			-0.234		-5.86
			0.393	2.52			
			S2				
5	5.32	2.415			-0.436		-0.219
28	5.78	3.041			-0.384	-0.497	-0.316
50	6.23	3.572			-0.357		-0.433
			1.811	2.308			

**Fig. 3. The relation of k'_a versus $1/T$ for the two studied soil samples**

The scale of the E_d values is similar to those found by Mortland and Ellis, 1959 and Zaghoul, 2002, worth to mention that the same trend was observed in S_2 .

Thermodynamic Parameters of Ni Exchange in soil systems:

The ΔG values for exchange of Ni were negative and increased with increasing the temperature as shown in table 2, they are similar with those discovered by Zaghoul, (2002) and Kuo, and Lotse, (1974). The more negative values for ΔG in S_2 than in the S_1 could be related to increasing of per cent of clay in the soil which gave driving force for the entire process in the high clay content soil as shown in Table (1). This driving force for all process makes Ni reaction easier with less diffuse

resistance. The ΔH values are shown in Table (2) express something about nickel's binding force to the soil. The reduced adverse value of ΔH in the S_2 than in the S_1 shows a greater binding of Ni^{2+} in S_2 relative to S_1 . The variance in the binding strength of Ni^{+2} ions in both soils may be linked directly to differences in the external surface to interlayer surface charge ratio associated with the increase of clay content and organic matter in this soil. Increasing the clay content in S_2 , indicating for the former a lower external surface to interlayer charge ratio. The rate coefficients of reactions and activation energies in Table (2) indicate that a partial collapse of the clay minerals is likely to occur in the S_2 soil in the presence of Ni^{2+} ions. The lowering ratio between the external surface and interlayer surface-

charge in the S_2 , greater binding of Ni^{2+} ions should be expected. This is illustrated by the decreasing of the exothermic ΔH_o value of the S_2 that Ni^{2+} exchange in the soils is an exothermic process, these results were in agreement with the results of Adamson (1973). Exothermic mechanisms are especially encountered in Ni exchange where electrostatic attraction forces are predominate (Filep and Khargitoan, 1977 and Kittrick, 1967). The ΔS° values in used soils (Table 2 & Figure 3) indicate greater (more favourable) entropy in the S_1 than in S_2 . Since there is a substantial difference in clay in both studied soils, there may be more external and internal sites for Ni^{2+} reactions occurring in the greater clay content. For adsorption, there would be more methods for Ni^{2+} ions to distribute themselves refer to more sites for Ni adsorption in S_2 . Thus the solid component of ΔS would enhance (Kuo and Lotse, 1974 and Diast and Talibudeen, 1967). Concerning desorption process, there would have been increasing of Ni desorption from the solid phase in S_1 to the solution phase compared to that in S_2 . This would likely from a higher rise in the solution component of ΔS° in the S_1 relative to S_2 . The parameter ΔG represent is the variation in free energy needed for Ni to pass the barrier of adsorption at an obvious rate of k'_a . This parameter reflects the variation in free energy required by the inverse reaction of desorption at the obvious rate of k'_d . The distinction between these two parameters produces ΔG , the thermodynamic parameter formed from the equation of Gibbs. Although data are not shown, the comparison of these values to those computed from the equation demonstrates great agreement, suggesting that thermodynamic parameters can be calculated using a kinetic strategy. Also, in table 2, the ΔG values reflect the difference in free energy between the activated complex and the reactants, all substances remained in their standard states (Glasstone, et al., 1941 and Laidler, 1965). It is the value of ΔG that assesses the reaction rate (Filep and Khargitoan, 1977). The ΔG values for desorption were greater than for adsorption, indicating that Ni desorption needs large free energy. This would be well associated with reduced k'_d values and greater E_d values (Table 2). Also, the values of ΔG for both adsorption and desorption were also slightly greater in the S_2 than in the S_1 indicating slow reactions occurrence, due to the more binding sites for Ni^{2+} in the S_2 .

The ΔH value measures the energy barrier that can be achieved by reacting the molecules (Glasstone et al., 1941). The ΔH values in the studied soils were lesser in adsorption than for desorption, implying that the heat energy needed to deal with the Ni^{2+} desorption barrier was higher than that for Ni adsorption. This was also shown in the magnitude of the values of E_a and E_d as

found in Table (2). The ΔH of adsorption reflects the change in heat energy required for Ni^{2+} to go from the solution phase to the solid phase, whereas ΔH of Ni^{2+} desorption is the heat energy needed for the inverse process. The differences between these two parameters represent ΔH° . The process of adsorption is an exothermic process which by it the heat is released, and the process of desorption is an endothermic reaction that by it the heat is adsorbed. This in agreement with Glasstone et al., (1941) conclusions that ion adsorption was obviously exothermic while desorption was always endothermic. Since the total ΔH° of the reaction is negative as shown in Table (2), Ni exchange is not an energy consuming mechanism. The entropy parameter is usually used to estimate the point of energy width (Jencks, 1969; Moreale and van Bladel, 1979). This parameter indicated that the molecules reaction must move as complexes with activation energy. Thus ΔS transmits if a specific reaction proceeds quickly or slowly than another reaction individually takes place. It should be mentioned that the kinetics of adsorption were quicker than the kinetics of desorption, a more highly ordered system could be acquired with adsorption than with desorption. This is observed in the slightly larger negative values of ΔS .

CONCLUSION

Temperature has a significant and often ignored parameter in the fate and transport of pollutants in the environmental soil ecosystems. Temperature trails are quite essential to establish complete functioning models that allow investigators to better identify the movement and bioavailability of pollutants in soils. For most reactions, increasing the rate with increasing temperature is nonlinear. Nickel sorption was examined on alluvial soils varied in their properties at temperature degrees 5, 28 and 50°C to calculate the first-order parameters and other thermodynamic parameters. The data in this work will be useful in developing inclusive models that describe sorption/desorption reactions affected by temperature and possible conditions of pollutant reactions in the alluvial soil environment.

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الملخص العربي

تأثير نظم درجات الحرارة على حركيات النيكل في أرضين طينيتين من مناطق جاف

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و Eyring ان الطاقة الحرة لتبادل النيكل ΔG كانت ذات قيم سلبية تراوحت ما بين -0.234 - 0.411 في الأرض رقم ١ بينما كانت -0.357 - 0.436 كالوري/مول في الأرض رقم ٢ مما اوضح انخفاض قيم ΔG مع زيادة درجات الحرارة . كذلك أوضحت النتائج أن قيم ΔG للانطلاق كانت اعلى من قيم ΔG للادمصاص مما يوضح ان هناك طاقة حرة مطلوبة للانطلاق اعلى من الطاقة الحرة لإدمصاص للعنصر الملوث تحت الدراسة. يمكن القول من خلال هذه الدراسة انه يمكن استخدام الدراسات الكينيتيكية للحصول على ثوابت الديناميكا الحرارية للعناصر الملوثة في الأراضي وهذا يتضح من القيم المتحصل عليها. اوضحت نتائج قيم الأنتالبي وهي -2.127 و -0.497 كالوري/مول للأرض ١ ورقم ٢ على التوالي ان هناك طاقة حرارية مطلوبة للتغلب على انطلاق النيكل للأرض تحت الدراسة. وبالتالي يتضح من هذه الدراسة أهمية دور الحرارة في التفاعلات الكيماوية المختلفة للعناصر الملوثة التي تضاف الى التربة.

اهتمت هذه الدراسة بتوضيح تفاعلات النيكل تحت تأثير درجات حرارة مختلفة باستخدام الدراسات الكينيتيكية على نوعين من الأراضي المصرية الطينية التي تم جمعها من اراضي دلتا النيل (المنوفية) مختلفة في محتواها من الطين والخواص الأخرى المرتبطة بهذا الاختلاف. أوضحت النتائج المتحصل عليها من الدراسات الكينيتيكية لادمصاص وأنطلاق النيكل من الأراضي تحت الدراسة عند 5 ، 28 ، 50 درجة مئوية أن ثابت الأدمصاص K_a تراوح ما بين 0.21 - 0.34 للأرض رقم ١ ومن 0.32 - 0.23 كيلوكالوري/مول للأرض رقم ٢ بالترتيب. في حين كان ثابت الأنطلاق K_d تراوحت قيمته ما بين 2.44 - 3.71 و 2.42 - 3.57 كيلوكالوري/مول للأرض رقم ١ والأرض رقم ٢ على الترتيب. أيضا أظهرت النتائج ان قيم طاقة الأنطلاق كانت اعلى من قيم طاقة الربط للأدمصاص مما يوضح أن انطلاق الملوث يحتاج الى طاقة أعلى من الطاقة اللازمة للأدمصاص بالأرض. أظهرت ثوابت الأنطلاق الحراري التي تم حسابها باستخدام نظريات Gibbs