

Thermodynamics of Cobalt Exchange in Soil Using Kinetic Approach

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Abstract: Thermodynamics of Cobalt (Co) exchange using a kinetics approach was investigated in alluvial soil samples from two surface soil samples (0-30 cm) of Egyptian soils selected from Nile Delta mainly varied in clay content and other related properties. Kinetics of adsorption and desorption were determined at temperatures of 5, 25 and 50°C on each soil using an Electrical Stirred Flow Unit (ESFU). Energies of activation for adsorption and for desorption (E_a and E_d , respectively) ranged from 3.74 to 5.63 kcal mol⁻¹. The E_d values were higher than the E_a values, indicating that more energy was needed to desorb Co than to adsorb Co. Thermodynamic and pseudo thermodynamic parameters were determined using Gibbs' and Eyring's reaction rate theories. The free energy for Co exchange (ΔG°) values was negative (ranging from 1,155 to 1,294 cal mol⁻¹) and increased with increasing temperature. The free energy of activation values was higher for Co desorption (ΔG_d) than for Co adsorption (ΔG_a), suggesting a greater free energy requirement to desorb Co. The excellent agreement between ΔG° calculated from Gibbs' theory and from Eyring's reaction rate theory indicated that pure thermodynamic parameters could be calculated using a chemical kinetics approach. The enthalpy (ΔE°) values were exothermic and indicated stronger binding of Co²⁺ ions in the S1 than in the S2. The latter was related to the difference in external surface-to-interlayer surface-charge ratio in the studied soils. The enthalpy of activation (ΔH) values in both soils were higher for desorption (ΔH_d), than for adsorption (ΔH_a), suggesting the heat energy required to overcome the Co desorption barrier was greater than for that of Co adsorption.

Key words: Kinetics • Cobalt • Enthalpy • Entropy • Ionic diffusion

INTRODUCTION

Cobalt is an element that occurs naturally in many different chemical forms throughout our environment. Small amounts of cobalt are essential for good health. It is a natural earth element and is present in trace amounts in soil, plants and in our diets. In agricultural point of view, Co is considered a beneficial element for higher plants in spite of the absence of evidence for direct role in their metabolism. It is an essential element for the synthesis of vitamin B₁₂, which is required for human and animal nutrition [1, 2]. Unlike other heavy metals, cobalt is safer for human consumption up to 8 mg can be consumed on a daily basis without health hazards.

Cobalt is essential in trace amounts for human life. It is part of vitamin B-12 and plays a key role in the body's synthesis of this essential vitamin. Cobalt has also been used as a treatment for anemia, because it causes red blood cells to be produced. The toxicity of cobalt is quite low compared to many other metals in soil. Exposure to very high levels of cobalt can cause health effects. Effects on the lungs, including asthma, pneumonia and wheezing, have been found in workers who breathed high levels of cobalt in the air.

The effect of temperature on reaction rates is well known and important in understanding reaction mechanisms. Svante Arrhenius, a Swedish physical chemist who received the 1903 Nobel Prize for chemistry,

noted that for most reactions, the increase in rate with increasing temperature is nonlinear. Although there are voluminous literature describe Co reactions in soils or its essentiality to higher plants, no available data regarded thermodynamic quantities (enthalpy and entropy) the effect of temperature on Co desorption from soils. The aim of this work is to study the effect of different temperatures on Co desorption from soils.

MATERIALS AND METHODS

In previous study of Nadia *et al.*, [3], it was found that Co adsorption and desorption in soils conformed to first-order kinetics. Using an Electrical Stirred flow unit (ESFU), the apparent adsorption and desorption rate coefficients (k_a' and k_d' , respectively) can be determined from first-order kinetic equations as derived below.

Apparent adsorption rate coefficient (k_a')

Apparent adsorption rate calculated according to the following equation:

$$\text{Log} (1 - K_t/K_\infty) = k_a' t,$$

where:

K_t , = Amount of Co on the soil at time t and
 K_∞ , = Amount of Co on the soil at equilibrium.

Separating variables

$$D (k_a'/k_\infty) / 1 - (k_t/k_\infty) = k_a' dt$$

Integration of the form $\int dx/1+x = \ln(1+x)$ yields:

$$\ln (1 - K_t/K_\infty) = -k_a' t.$$

Expressed in terms of base 10 logarithms gives:

$$\log(1 - K_t/K_\infty) = -k_a' t,$$

where k_a' = product of A : and K_∞ divided by 2.303

Apparent Desorption Rate Coefficient (k_d'): For the solid surface phase,

$$d(K_t/K_\infty)/dt = -k_d'(K_t),$$

where

K_0 = Amount of Co on the exchange sites of the soil at zero time,

K_t = Amount of Co on the exchange sites of the soil at time t,

t = Time and

k = Absolute velocity constant.

On integration with boundary conditions,

$$t = 0, K_t/K_0 = 1; t = \infty, K_t/K_0 = 0 \text{ and}$$

$$\log (K_t/K_0) = -k_d' t$$

Calculation of thermodynamic parameters of Co exchange from Gibbs theory

The variation between the adsorbed and desorbed of Co was controlled by several factors manage the availability of this ion, indicating partial reversibility, subsequently the following relationship could be written:

$$k_a'/k_d' = K$$

where K is the apparent equilibrium constant.

The free energy for Co exchange (ΔG°) can be obtained, $\Delta G^\circ = -RT \ln K$ or

$$\Delta G^\circ = -RT \ln (k_a'/k_d')$$

Using the Arrhenius and van't Hoff equations Denbigh [4], energies of activation for K adsorption and for Co desorption (E_a and E_d , respectively) can be determined as shown below:

$$d \ln k_a'/dt = E_a/RT^2$$

and for the desorption kinetic reaction

$$d \ln k_d'/dt = E_d/RT^2$$

substituting,

$$d \ln k_a'/dt - d \ln k_d'/dt = d \ln K'/dT$$

and from the van't Hoff equation, the enthalpy for Co exchange (ΔH°) can be determined:

Table 1: Some physical and chemical characteristics of the studied soils.

Soil No.	Dep. (cm)	EC dS. m ⁻¹	pH	OM (%)	Clay Cont. %	Amors. Fe ₂ O ₃ ppm	Total CaCO ₃ %	Av. Co Ppm	S. area m ² /g
S ₁	0-30	0.4	7.51	0.98	38.5	518	3.31	10.44	145
S ₂	0-30	0.6	8.22	1.24	53.6	1103	4.5	14.77	210

$$d \ln K'/dT = \Delta H^\circ/RT^2, \text{ or}$$

$$E_a - E_d = \Delta H^\circ.$$

From the third law of thermodynamics, the entropy for Co exchange (ΔS°) can be found,

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

Soils: Two soil samples from the top 0-30 cm layer (A horizon) were collected from the alluvial soil of Nile Delta. Samples varied in their clay content used in this study were analyzed to their physicochemical and mineralogical properties by standard methods described by Sparks [5] are reported in Table 1. Soil samples were air dried and crushed to pass a 2-mm sieve in and prepared for the application of different treatments.

Calculation of pseudo thermodynamic parameters for Co exchange using Eyring's reaction rate theory.

The transition-state theory for absolute reaction rates can be used as a model to substantiate the thermodynamic parameters calculated by Gibbs' theory. In terms of absolute rate theory, pseudo thermodynamic parameters can be expressed as Moore [6, 7].

$$\Delta S^\circ = \Delta H^\circ - T\Delta S^\circ = -RT \ln K_c$$

or

$$K_c = \exp(-\Delta G/RT) = \exp(-\Delta H/RT + \Delta S/R)$$

where

ΔG = Free energy of activation,

ΔH = Enthalpy of activation,

ΔS = Entropy of activation

R = Universal gas constant,

T = Absolute temperature and

K_c = Equilibrium constant of activation

The relationship:

$$K'_a = K^*T/h \exp(\Delta S_a/R) \exp(-\Delta H/RT)$$

where:

K*: Boltzmann's constant,

H: Planck's constant and

Subscript a: adsorption reaction.

The equation would enable the calculation of AS_{0t}, since ΔS_a is found from the following relationship:

$$\Delta h_a = E_a - RT$$

The AG_a may be calculated using this expression:

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

Analogous expressions can be obtained for the reverse reaction through the use of k'd and E_d calculated for the desorption process.

RESULTS AND DISCUSSION

Kinetics of Co Adsorption and Desorption from Used

Soils: Kinetic experiments for Co sorption and desorption were carried out using Electrical stirred Flow unit (ESFU) method Zaghoul [8]. Solution samples were taken at different periods ranged from 1min to 48 hrs. and then analyzed for their Co concentration. Worth to mention that Kinetics of Co adsorption was measured using duplicate 10 g samples of the soil used. The kinetic experiments were conducted at three-soil temperature 5, 25 and 50°C, supposed that soil systems under Egyptian conditions undergo to these temperatures through the different soil seasons. Apparent adsorption and desorption rate coefficients were determined using the first-order equations elucidated earlier. Energies of activation for adsorption and for desorption were determined from the Arrhenius and van't Hoff equations. The ΔG , ΔH and ΔS° values for Co exchange were determined as outlined previously. The ΔG , ΔH and ΔS for Co exchange were determined from Eyring's absolute reaction rate theory Laidler [9].

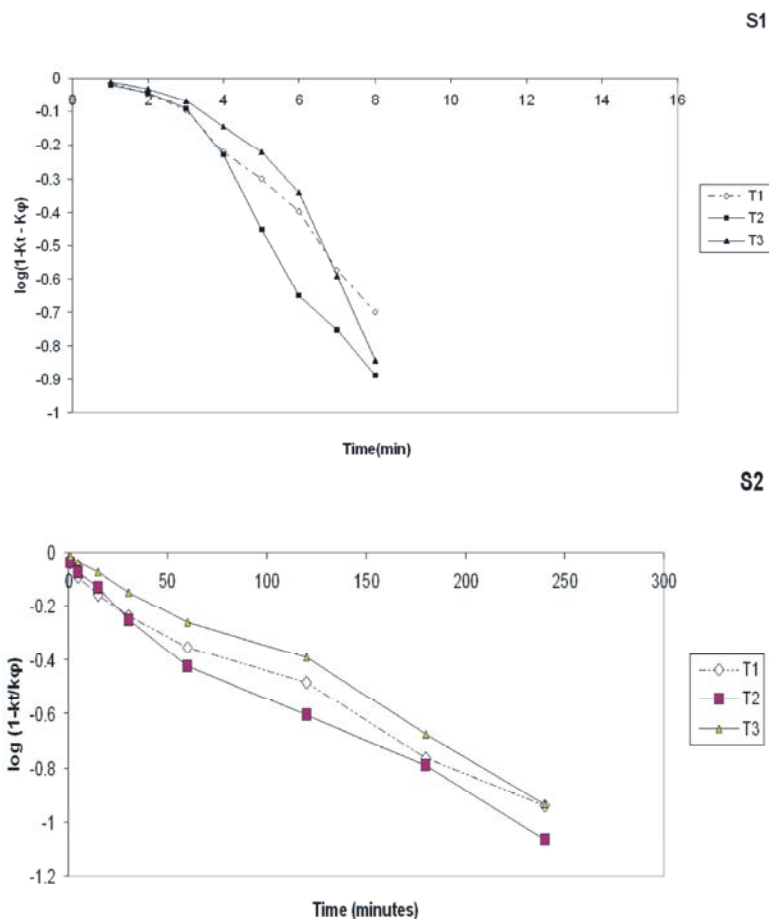


Fig. 1: Log (1 -K/K⁰) vs. time at 5, 25 and 50°C for the alluvial soil samples

As previously mentioned, the kinetics of Co adsorption and desorption in the used soils conformed to first-order kinetics at different temperatures tested by having high R² and low SE. The linear relationship for Co adsorption in the soil 1 (S1) and soil 2 (S2) indicating first-order kinetics is shown in Fig. 1. Although not shown, the data also conformed to the MFE and parabolic diffusion law in the used soil with linear relationships occurring for both the adsorption and desorption processes. The low rate of Co exchange is related to the presence of type of clay minerals in the soil (Table 2) which demonstrate diffusion-controlled exchange Sparks *et al.* [10].

Apparent Adsorption and Desorption Rate Coefficients of Used Model: As shown in Table 2, the k_a and k_d values increased with increasing temperature as predicted from Bronsted's reaction rate theory Adamson [11] and from the Arrhenius equation. According to hysteresis phenomena, the k_d values were lower than the k_a values,

indicating that the desorption rate was lower than the adsorption rate for both soil used. Desorption would be slower than adsorption because of the partial collapse of the clay minerals upon Co adsorption. The rate coefficients were also lower in the S1 than S2, possibly due to higher clay content in S2. The larger quantity of clay could promote increased diffusion and intraparticle transport Sparks *et al.* [12].

Energies of Activation E_a and E_d for Co Adsorption and for Desorption: The energy of activation measures the magnitude of the forces to be overcome during the process of ionic exchange [9, 4]. Energies of activation vary inversely with the rate of exchange [13]. The energies of activation (Table 2) for desorption (E_d) were greater than those for adsorption (E_a). This indicates that the energy needed to desorb Co is greater than that to adsorb Co, which is probably due to the partial collapse of the clay minerals upon Co adsorption. The low E_a and E_d values i.e. 3.243 to 4.503 kcal mol⁻¹ suggested that

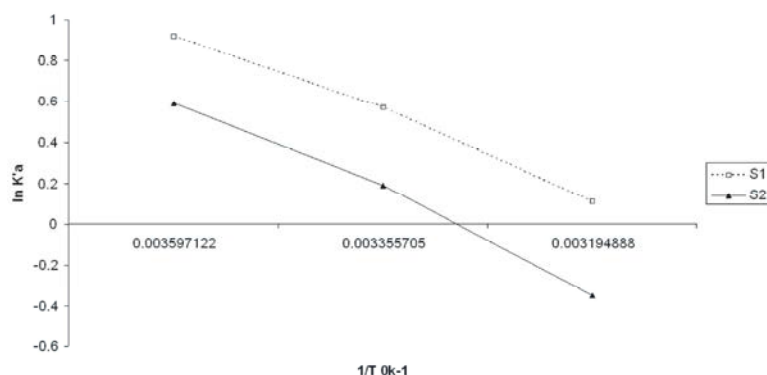


Fig. 2: Plot of k'a versus 1/T for the studied soil samples

Table 2: Apparent rate coefficients (ka and kd) at 3°C, energies of activation (Ea and Ed) and thermodynamic parameters using a kinetics approach for Co exchange in two alluvial soils

Temperature °C	Ka Hour ⁻¹	Kd	Ea Kcal mol ⁻¹	Ed	ΔG Cal mol ⁻¹	ΔH	ΔS Cal mol ⁻¹ °k ⁻¹
				S1			
5	1.09	0.111		-1.253		-0.254	
25	1.88	0.221	3.243	4.503	-1.249	-1.26	-0.354
50	2.48	0.347		-1.223		-1.138	
				S2			
5	1.18	0.147		-1.142		-1.523	
25	1.98	0.252	3.385	4.951	-1.22	-1.565	-1.16
50	2.78	0.399		-1.207		-1.109	

diffusion-controlled exchange [14-16]. The magnitude of the Ed values is similar to that found by authors [14, 15], which used a film-diffusion experiment to study the kinetics of K release from vermiculite.

Thermodynamic Parameters of Co Exchange in Soil Systems:

The ΔG values for Co exchange were negative and increased with increasing temperature as shown in Table 2 and they are comparable to those found by authors [15, 16]. The more negative values for ΔG in the S2 than in the S1 would indicate that the driving force for the overall process was greater in the high clay content soil as shown in table 1 [17, 18], causing Co reactions to occur more easily with less diffusional resistance.

The ΔH values represented in Table 2 convey something about the binding strength of Co²⁺ to the soil. The lower negative value of ΔH in the S2 than in the S1 indicates a stronger binding of Co²⁺ in S2 compared to S1. The difference in the binding strength of Co²⁺ ions in the two soils may be related to differences in the external surface to interlayer surface charge ratio related to the increase of clay content in this soil. Increasing the clay content in S2, suggesting a smaller external surface to interlayer charge ratio for the former. The rate coefficients and energies of activation (Table 2) suggest that in the

presence of Co²⁺ ions, a partial collapse of the clay minerals probably occurs in the S2 soil. Since the external surface-to interlayer surface-charge ratio is smaller in the S2, there should be a stronger binding of Co²⁺ ions. This is evidenced from the less exothermic ΔH° value in the S2. That Co²⁺ exchange is an exothermic process would conform to findings of others [19]. Exothermic processes are characteristic of reactions encountered in Co exchange where electrostatic attractive forces predominate [20, 21].

The ΔS° values of the used soils (Table 2 & Figure 2) show higher (more positive) entropy in the S1 than in S2. Since there is more clay in the former soil, there are more external and internal sites for Co reactions to occur. For adsorption, due to more sites for Co adsorption in the S2 there would be more ways for Co²⁺ ions to arrange themselves. Thus the solid component of ΔS would increase [16, 17]. In desorption, there would be more desorption of Co²⁺ ions from the solid to solution phases. This would probably result in a greater increase in the solution component of ΔS° in the S1 than in S2 of the alluvial soil since Co²⁺ increases the entropy of water.

The ΔG* value may be considered as the difference in free energy between the activated complex and the reactants from which it was formed, all substances being

in their standard states [6, 9]. It is the ΔG value, which determines the rate of the reaction [20]. The ΔG values were higher for desorption than for adsorption, suggesting a greater free energy requirement for Co desorption. This would correlate well with the lower k_d and higher E_d values (Table 2). The ΔG values for both adsorption and desorption were also slightly higher in the S2 than in the S1 suggesting slower reactions due to more binding sites for Co in the S2.

The ΔG at is the change in free energy required for K^* to cross the barrier of adsorption at an apparent rate of k_a . This parameter represents the change in free energy needed by the reverse reaction of desorption at the apparent rate of k_d . The difference between these two parameters yields ΔG , the thermodynamic parameter established from Gibbs' theory. Although data not shown, the comparison of these values to those calculated from the Equation, data shows excellent agreement, indicating that thermodynamic parameters can be calculated using a kinetics approach.

The ΔH value is a measure of the energy barrier that must be overcome by reacting molecules [22]. The ΔH values in both soils were higher for desorption than for adsorption, suggesting that the heat energy required to overcome the Co desorption barrier was greater than that for Co adsorption. This was also seen in the magnitude of the E_a and E_d values as represented in Table 2. The ΔH of adsorption represents the change in heat energy needed for Co^{2+} to go from the solution phase to the solid phase, whereas ΔH of Co desorption is the heat energy requirement for the reverse reaction. The difference in these two parameters represents ΔH° . The adsorption process is an exothermic process where by heat is liberated and desorption process is an endothermic reaction whereby heat is adsorbed. This concurs with findings of others soils that solute adsorption was clearly exothermic while desorption was often endothermic [22, 23]. Since the overall ΔH° of the reaction is negative as represented in table 2, Co exchange is not an energy consuming process. Jencks, [24] noted that entropy of activation could be regarded as a measure of the width of the "saddle point of energy" [23, 25] over which reactant molecules must pass as activated complexes. Thus ΔS conveys whether a particular reaction proceeds faster or slower than another individual reaction. It should be mention that the kinetics of adsorption were faster than the kinetics of desorption, a more highly ordered system would be obtained more rapidly with adsorption than with desorption. This is seen in the slightly larger negative values for ΔS .

CONCLUSIONS

Thermodynamics of Cobalt (Co) exchange using a kinetics approach was investigated in alluvial soil samples from two surface soil samples of Egyptian soils selected from Nile Delta mainly varied in clay content and other related properties at temperatures of 5, 25 and 50°C. The E_d values were higher than the E_a values, indicating that more energy was needed to desorb Co than to adsorb Co. The free energy for Co exchange (ΔG°) values was negative and increased with increasing temperature. The enthalpy of activation (ΔH) values in both soils were higher for desorption (ΔH_d), than for adsorption (ΔH_a), suggesting the heat energy required to overcome the Co desorption barrier was greater than for that of Co adsorption.

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