Application of thermodynamic characteristics to describe copper adsorption in some calcareous soils

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ABSTRACT

This work includes studying the thermodynamic parameters such as K^o, ΔG^o, ΔH^o, and ΔS^o determined in five calcareous soils at two different temperatures (298 ^oK and 318 ^oK) include Sharazor, Qaradagh, Bazian, Mawat, and Surdash differing in total calcium carbonate, organic matter, and cation exchange capacity of Sulaimani governorate in the Iraqi-Kurdistan region. One gram of soil samples equilibrated at (298 ^oK and 318 ^oK) with 50 ml of solution $CaCl_2$ (0.01*M*) containing a series of Cu concentrations (0, 2.5, 5, 10, 20, and 40) mg Cu L^{-1} as ($CuSO_4$). The values of the standard free energy (ΔG^o) were negative of the five soils ranging from (- 5.026 to - 4.009 kJ mol^{-1}) and (- 5.201 to - 4.075 kJ mol^{-1}) respectively at both 298 ^oK and 318 ^oK temperatures. Entropy values (ΔS°) were negative in Sharazor and Bazian soil, while, entropy values (ΔS°) were positive at both temperatures (298 ^oK and 318 ^oK) in Qaradagh, Mawat, and Surdash soil.

Keywords: Calcareous soils, thermodynamic parameters.

INTRODUCTION

Copper is an essential nutrient for plant (Lehman and Harter, 1984). Rashad et al. (2005) reported that a raw calcareous soil comprised of alginate biopolymer was used to study the adsorption of Cu^{2+} and Cd^{2+} from aqueous solutions on a composite surface at three temperatures: 30°C, 45°C, and 55°C. The adsorption of copper by calcareous soils was studied, and a supply parameter was calculated from the experimental data, integrating the quantity, intensity, and buffering capacity of copper. The uptake of copper by barley in these soils was significantly correlated with the supply parameter (Singh et al. 1990). Mehmedany et al. (2016) shows that alkaline calcareous soils in Duhok absorbed large amounts of copper, that copper adsorption increased as temperature increased, and that thermodynamic factors are useful in defining copper adsorption. Hosseinpur and Dandanmozd (2010) noticed that calcareous soils in western Iran had a high capacity for copper sorption. The measurement of thermodynamic parameters will facilitate determination of final metal state in soil system from initial state of non-equilibrium (Jurinak, and Bauer, 1956). These thermodynamic parameters include equilibrium constant, K^o, standard free energy (ΔG^o) standard enthalpy (ΔH^o), and standard entropy (ΔS^o). For instance,

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Adhikari et al. (2003) noted that the sorption process could be fully considered by determining the free energy change (ΔG^o) that conforms to transfer of elements into soil surface from bulk solution. They also indicated that understanding the difference in enthalpy (ΔH^o) and entropy (ΔS^o) can aid in determining the free change in energy and the disorder that happened during the sorption phase. Shariff (2011) determined that the values of the ΔG^o varied from -0.095 to -1.431 $kJ{\cdot}mol^{-1}$, and from -0.048 to -2.048 $kJ{\cdot}mol^{-1}$ for metolachlor and 2,4-D sequentially. The ΔH^o values metolachlor and 2, 4 – D ranged from -5.954 to -13.353 $kJ{\cdot}mol^{-1}$ and -16.998 to -42.127 $kJ{\cdot}mol^{-1}$ respectively. In agricultural soils, the value of ΔS^o ranged from -16.138 to -1.757 $J{\cdot}mol^{-1}{\cdot}K^{-1}$, and -16.292 to -61.292 $J{\cdot}mol^{-1}{\cdot}K^{-1}$ for metolachlor and 2,4-D respectively. Almalike et al. (2015) found that for the adsorption of the studied pesticides on the selected soil samples at 288.15, 298.15, and 309.15 ^oK, the ΔG^o values ranged from -10.296 to -0.179 kJ mol^{-1}.

The objective of this research was:

to investigate the thermodynamic characteristics of copper adsorption such as ^oK , ΔG^o , ΔH^o , and ΔS^o in some calcareous soil from Sulaimani governorate.

MATERIALS AND METHODS

Soil samples were taken from soil surface at a depth of 0-30 cm in some calcareous soils in Sulaimani governorate in Kurdistan Region of Iraq, including Sharazor, Qaradagh, Bazian, Mawat, and Surdash. The study area is located between longitudes 35 ° 15 to 27 N; latitudes 45 07 to 37 E as shown in Fig.1. All five soils were classified as Argixerolls, Rendolls, Pelloxererts, Rendolls, and Argixerolls according to Soil Survey Staff 2004. Before analysis process and Cu adsorption studies, soil samples are air-dried, crushed, and sieved through a 2-mm sieve. Some of basic physicochemical properties of the soil studied include particle size distribution, pH, EC, percentage of organic matter, percentage of Calcium carbonate, and CEC determined according to the soil analysis methods as outlined by Page et al. 1982 and Rayan J. et al. 2001, available Cu content in the soil was determined using the (0.005 *M* + 0.1 *M* TEA + 0.01 *M* $CaCl_2$) procedure (Lindsay and Norvell,1978.)

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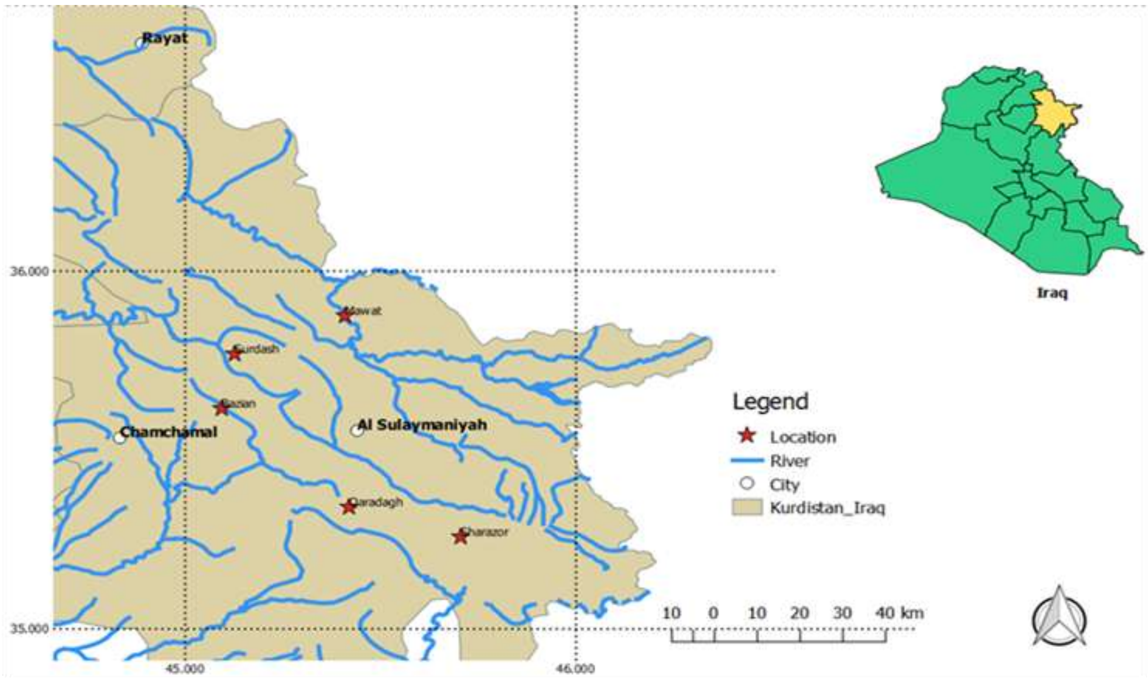

Fig. 1. The location of the studied area

Adsorption thermodynamics:

The adsorption isotherms of the Copper metal by the soil carried out using a batch method. One gram of each soil sample, in duplicate, was placed in plastic bottles (100 ml) and equilibrated with 50 ml of solution $CaCl_2$ (0.01*M*) as a background electrolyte to keep the ionic strength almost constant, containing a series of Cu concentrations (0, 2.5, 5, 10, 20, and 40) mg Cu L^{-1} in the form of ($CuSO_4$). Two drops of toluene added to each suspension to inhibit microbial activity. The suspension shaken for 30 minute and then kept it overnight for attaining equilibrium at two different temperatures (298°K and 318°K). The soil suspension immediately filtered through Whatman paper No.42, then the concentration of Cu determined in a solution using Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES). The amount of Cu adsorbed by the sample determined by subtracting the equilibrium Cu concentration in the solution from the added Cu.

Thermodynamic parameters determined by the variance of the constant of thermodynamic equilibrium, K^o, calculated by the following method described by Biggar and Cheung, 1973. The value of K^o can be described as K^o = as/ae = γsCs/ γeCe for adsorption reaction. Where the adsorbed metal activity is denoted as, and ae is a metal activity in the solution of equilibrium. Cs, in

contact with the adsorbent surface, is milligrams of metal adsorbed per liter of the solution, and Ce, in equilibrium solution, is milligrams of solute per liter of the solution. The activity coefficient of the sorbed metal is γs and γe is the activity coefficient of the metal in the solution of equilibrium. Since the unity reaches a small concentration activity coefficient, and then the above equation is reduced to $K^o = Cs/Ce$. Plotting ln (Cs/Ce) vs Cs and extrapolating to zero Cs is used to obtain the K^o values.

The standard free energy (' ΔG^o) was measured as follows:

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

The standard enthalpy (ΔH^o) acquired from the Vant Hoff equation's integrated form: $\ln K_2/K_1 = \Delta H^o/R[1/T_1 - 1/T_2]$

The standard entropy (ΔS^o) is measured as $\Delta S^o = (\Delta H^o - \Delta G^o) / T$.

RESULTS AND DISCUSSION

Chemical and physical characteristics of the soil

Serval chemical and physical properties of the soils presented in Table 1. The CEC values ranged from 26.93 to 41.57 cmolc kg^{-1}, while the extractable Cu by DTPA ranged from 0.12 to 0.51 mg kg^{-1}. Texture classes of studied soils ranged from loam to Silty clay, indicating that the texture of these soils ranged from fine to moderately textured soils, and that soils were slightly to moderately alkaline, with values ranging from 7.48 to 7.9. Electrical conductivity (EC) of soil samples ranged from 0. 4 to 0.9 dS m^{-1}, indicating that soils investigated are non-saline. This could be attributed to the relatively higher precipitation and topographic variance of these areas. All soil termed as calcareous soil due to Calcium carbonate content was between (25 – 430 gm kg^{-1}). Organic matter ranged between 9 to 25 g kg $^{-1}$.

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Soil No.	pH	EC (dS m^{-1})	$T.CaCO_3$ (g kg^{-1})	O.M (g kg^{-1})	Sand	Silt	Clay	Textural class	DTPA Cu mg kg^{-1}	CEC $cmol_c$ kg^{-1}
					g kg^{-1}					
Sharazor	7.49	0.60	180	25	37.20	475.10	487.70	Silty clay	0.51	41.15
Qaradagh	7.65	0.70	25	17	383.50	370.30	246.20	loam	0.47	26.93
Bazian	7.78	0.60	100	15	55.80	430.50	513.70	Silty clay	0.20	41.57
Mawat	7.48	0.9	25	16	161.90	434.20	403.90	Silty clay	0.38	39.42
Surdash	7.90	0.40	430	9	91.60	490.40	418.00	Silty clay	0.12	36.39

Table (1) Some chemical and physical properties in the studied soils.

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Adsorption thermodynamics

Standard thermodynamic parameters (ΔG^o), enthalpy change (ΔH^o), and entropy change ($\Delta S°$) were calculated to determine the practical application of the adsorption method (Liu, and Liu, 2008). The calculated thermodynamic parameter values at both temperatures of 298 ^oK and 318 ^oK are shown in (Table 2). At temperature 298 ^oK, the values of the thermodynamic equilibrium constant (K^0) of the soils ranged from 5,043 to 7,605; the highest value of (K^0) was observed in Surdash soil, while the lowest value was reported in Qaradagh soil, as shown in (Table 2). On the other hand, soil (K^0) values at a temperature of 318 ^oK ranged from 4,671 to 7,15. On Surdash soil, the highest value of (K^0) was recorded. Similarly, the lowest value was observed in the soil of Qaradagh at a temperature of 318 ^oK. Standard free energy (ΔG^0) values of the soils at temperature 298 ^oK ranged from - 5,026 to - 4,010 (kJ mol^{-1}). On the other hand, at temperature 318 ^oK, the (ΔG^o) values of the soil ranged from - 5.201 to - 4.075 (kJ mol^{-1}). Values of (ΔG^o) at different temperatures of 298 ^oK and 318 ^oK for all five soils do not vary significantly. The ΔG^o values for Cu were negative at both temperatures of 298 ^oK and 318 ^oK in all five soils. These negative values refer that the sorption mechanism is spontaneous. Therefore, the negative (ΔG^o) determines the amount of energy needed before reaching equilibrium; thus, a more negative (ΔG^o) value implies more Cu sorption at different temperatures (298 ^oK and 318 ^oK) in Surdash soil. These results are in line with the findings of (Adhikari, and Singh, 2003). The effects of altering the soils' enthalpy (Δ H^o) at both temperatures (298 ^oK and 318 ^oK). ranged from (- 8.641 to -2.430 kJ mol^{-1}) . A negative value (ΔH^o) confirms that the sorption is the exothermic process. Similarly, Das et al., (2014) found that the mechanism of adsorption was spontaneous, feasible, and exothermic. On the other hand, in the Sharazor and Bazian soil, the values of entropy ($\Delta S°$) were negative, which heat flows out to the surrounding in the system. Although the value of entropy ($\Delta S°$) was positive, the heat flows at both temperatures (298 ^oK and 318 ^oK) from the surrounding in the system in Qaradagh, Mawat, and Surdash soil. Positive values of (ΔS^o) also suggested an improvement in randomness at the solid/liquid interface during the sorption process for Qaradagh, Mawat and Surdash soil whereas low values of (ΔS^o) indicated that no significant change in entropy happened in Mawat soil. These results are in accordance with Dawodu and Akpomie (2014). The negative value of (ΔS^o) indicates that enthalpy is guided by the adsorption mechanism or that the system is becoming more orderly as found in the Sharazor and Bazian soil. The decrease in the degree of randomness causes the adsorption potential of the ion on the sorbent to increase (Abou-Mesalam,2003).

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Table 2. Adsorption of thermodynamic parameters of Cu at two different temperatures (298 ^{o}K and 318 ^{o}K) in studied soil.

Soil No.	K^{o}		ΔG^{o} (kJ mol^{-1})		ΔH^{o} (kJ mol^{-1})	ΔS^{o} (J mol^{-1} K^{-1})	
	Temperature ^{o}K		Temperature ^{o}K			Temperature ^{o}K	
	298	318	298	318		298	318
Sharazor	6.377	5.121	- 4.590	- 4.318	- 8.641	- 14.000	- 14.000
Qaradagh	5.043	4.671	- 4.010	- 4.075	-3.014	3.300	3.300
Bazian	5.545	4.968	- 4.244	- 4.238	-4.329	- 0.030	- 0.300
Mawat	5.413	5.016	- 4.184	- 4.264	-3.001	3.900	3.900
Surdash	7.605	7.150	- 5.026	- 5.201	-2.430	8.700	8.700

CONCLUSIONS

In all the five soils at both temperatures 298 ^{o}K and 318 ^{o}K, the ΔG^{o} values for Cu were negative,

as these results suggest that the sorption process is spontaneous. The value of (ΔH^{o}) of the studied soils was negative; this indicated that the sorption is the exothermic process. The values of entropy ($\Delta S°$) were negative in the Sharazor and Bazian soil. While the entropy values ($\Delta S°$) were positive at both temperatures (298 ^{o}K and 318 ^{o}K) in Qaradagh, Mawat, and Surdash soil.

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