Adsorption Behavior of Copper in Some Calcareous Soils from Duhok Governorate

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Abstract:

Soil samples were taken from the surface layer of eight locations (Smail Ava, Khanki, Khirshanya, Esyan, Mahed, Suwaratoka, Bamerny and Tirwanish) Duhok governorate -Iraqi Kurdistan region, to evaluate the adsorption and thermodynamic parameters of copper (K^o, ∆G^o, ∆H^o and ∆S^o) which were determined using adsorption data and Cu^{2+} in equilibrium solution at two different temperature. The results demonstrated that an concentration increasing in adsorbed $Cu^{2+}$with increasing added Cu^{2+} and temperature in all studied soils. The values of the thermodynamic equilibrium constant (K^o) and ∆G^o increased with increasing temperature from (25 to 48) °C. The values of ∆G^o of both temperatures (25°C and 48°C) were negative, ranged from (-16.505 to -17.346 and -18.658 to -21.519) kJ mol^{-1} respectively, these negative values designate that the adsorption process is spontaneous. Enthalpy (∆H^o) and entropy (∆S^o) of studied soils were positive and varied from (2.678 to 36.716) kJ mol^{-1} and (66.466 to 181.417) J mol^{-1}K^{-1}. The positive results of (∆H^o) showed that Cu^{2+} adsorption is an endothermic reaction. The results also revealed that alkaline calcareous soils in Duhok adsorbed high quantities of Cu^{2+} and thermodynamic parameters are helpful in describing Cu^{2+} adsorption. The high value of K^o, ∆G^o, ∆H^o and ∆S^o for copper at 25°C and 48°C were found in soil of Smail Ava location, but low value of ∆H^o and ∆S^o for copper initiate in soil of Suwaratoka location. The type of adsorption process in Khirshanya and Suwaratoka locations can be explained by ion exchange because the mean free energy of adsorption (E) value in both locations were less than 16 kJ mol^{-1}.

Keywords*: copper, adsorption, calcareous soils, thermodynamic parameters.*

Introduction:

Copper is an essential micronutrient and little amounts of Cu^{2+} are necessary for crop growth. However, high concentrations of copper will produce toxicity effects (Xiong et al., 2005). In soil solution total concentration of copper is normally low (0.01-0.6) µmol L^{-1}, due to coppers have high affinity to soil colloids (inorganic and organic). Generally the availability of Cu^{2+} in calcareous soils is low (Mocqluot et al., 1996). The role of Cu^{2+} is activation of enzyme systems which involves in photosynthesis, and cytochrome. Cu^{2+} in plants is not mobile; therefore, its deficiencies symptoms appear in the youngest plant tissue at first (Mahler, 2004). Cu^{2+} in soil solution is low; it’s solubility is pH dependent, it’s concentrations in soil solution increase with increasing organic complexes (chelated) forms of Cu^{2+}, the availability of Cu^{2+} is high and strongly controlled by organic matter (Jacobs, 2008). In calcareous soils Cu^{2+} retained by a specific adsorption reaction and existence of carbonates in actual fact immobilizes Cu^{2+} by buffering the soil pH (Dudley et al., 1991).

Adsorption is one of the essential chemical processes in soils. It determines the amount of plant nutrients, and other organic chemicals that are maintained on soil surfaces; therefore, it is one of the main processes that effect on movement of nutrients. The electrostatic property affects coagulation and settling (Sparks, 1995). On soil mineral surfaces, sorption reactions potentially dilute toxicity of nutrients in soil solution (Goldberg, 2002). Sorption isotherm analysis supplies useful information about the soil maintenance ability and the force by which the sorbate is detained on to the soil.

There are two types of minerals that effects the adsorption of Cu^{2+} in soils: variable charge minerals such as Al^{3+}, Mn^{2+}, and Fe^{3+} oxides hold charges changeable from negative to positive, depending on pH contains a relatively strong affinity for Cu^{2+} (Bertsch and Seaman, 1999). When the permanent charges of minerals such as montmorillonite carry a negative charge as a product of ion exchange through minerals formation (Atanassova and Okazaki, 1997). The soil adsorption capacity decreases in the order: organic matter > Al^{3+}, Fe^{3+}, and Mn^{2+} oxides >>> clay minerals (Baker, 1990).

The provided spectroscopic evidence (Alcacio et al., 2001) for the hypothesis proposed by McBride (1994) for probable binding relationships of Cu^{2+} on complexes of oxide minerals and organic matter are: (i) Cu^{2+} is bonded to inner-sphere complex on the mineral surfaces only; (ii) Cu^{2+} is bonded to the organic matter which adsorbed by the oxides at high levels and (iii) Cu^{2+} acts as a bridge cation between the organic matter and the oxides that are adsorbed at low levels.

The adsorption of heavy metals occur in the diffuse double layer passive to ionic exchange (non-specific adsorption) by electrostatic attraction, or by surface complexation (specific adsorption) process, where the cations are held powerfully by mainly covalent or coordinate forces (Selim, 1992). Heavy metal such as Cu adsorbs on the edge sites of the montmorillonite (Undabeytia et al., 2002). Cu^{2+} adsorption is based mainly on the study of equilibrium conditions using thermodynamic data that can expect to be only the last state of a system from an initial non equilibrium mode. Though, to rationalize chemical reaction rates knowledge of the kinetics is required (Frost and Pearson, 1961). Levels of ion concentration obtained from soil extracts were used to calculate thermodynamic parameters such as free energy of replacement (Harun et al., 2013). Evaluation of the free energy change corresponding to the element movement from bulk solution into the suitable site in the double layer or clay mineral lattice are helpful to express the sorption process. The high values of ΔG^o indicate to that the reactions are spontaneous. The values of ΔH^o were found to be negative that sorption reaction was exothermic (Adhikari and Singh, 2003). The values of ΔS^o were found to be positive due to the exchange sites of the metal ions with more transportable ions present on the exchangeable sites, causing increase in the entropy, through the adsorption process (Unlu and Ersoz, 2006).

In the study of Cu sorption in some soil of Hamadan province of Iran by (Hosseinpur and Dandanmozd, 2010) they found that calcareous soils have a high capacity for Cu adsorption, and the ΔG^o values at (25 and 45)°C were negative and ranged from (-18.39 to -24.10) and (-21.167 – -26.267) kJ mol^{-1} respectively. The values of enthalpy (ΔH^o) and entropy (ΔS^o) were positive and ranged from (8.184 to 42.852) kJ $mol^{-1}$and (102.457 to 206.184) J mol^{-1} K^{-1} respectively. Overall objectives of this study are to quantify Cu^{2+} adsorption behavior in eight calcareous soils from Duhok governorate at addition different levels of Cu^{2+}, effect of temperature on adsorption process, and determine the thermodynamic parameters of copper in studied soils.

MATERIALS AND METHODS:

Soil samples were collected at (0-30) cm depth from eight calcareous soils (Smail Ava, Khanki, Khirshanya, Esyan, Mahed, Bamerny Suwaratoka, and Tirwanish) from Duhok governorate in the north of Iraq-Kurdistan region. The soils samples were air-dried, grind, and passed through a 2-mm sieve prior to soil analysis and adsorption studies. Some basic physicochemical properties of the soluble soils cations and anions, particle size distribution, pH, EC, CEC, organic matter %, and calcium carbonate % were determined (Table, 1) using standard analytical methods (Liu et al., 1996; Rhoades, 1996; Summer and Miller, 1996 and Nelson and Sommers, 1996). Available concentration of Cu in studied soil was determined using DTPA method (Lindsay and Norvell, 1978). To study Cu adsorption in different soils, 1 g of each soil sample was placed in plastic bottles (100 ml) and equilibrated with 50 ml of solution $CaCl_2$ (0.01M) to keep the ionic strength almost constant, include different levels of Cu, i.e. 0, 2.5, 5, 10, 15, 25, 40 $mg.l^{-1}$ Cu^{2+} as $CuSO_4$ solution. Each adsorption set, for Cu was duplicated twice. The suspension of studied soil shaken for 40 minutes and were equilibrated for 48 hrs at 25±1 and 48±1ºC in an incubator. The suspensions were filtered, and concentrations of Cu in extract were determined using Varian Atomic Absorption Spectro- photometer. The adsorb Cu by soils was calculated by the difference between the initial and final concentration of Cu in the equilibrium solution.

The data were fitted to the Dubinin–Radushkevich (D-R) isotherm (Dubinin and Radushkevich, 1947) and (Dubinin, 1960) which is commonly applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface (Dabrowski, 2001) and (Gunay and Tosun, 2007). The form has often successfully fitted high solute activities and the intermediate range of concentrations data well. The D-R isotherm is more general compared to other equations, because it does not suppose a constant sorption potential or homogeneous surface (Unlu and Ersoz, 2006). The D-R isotherm has the form:

$$\mathbf{\ln q = \ln q_m - k\varepsilon^2}$$

Where q is the quantity of Cu adsorbed by the soil ($mg.g^{-1}$), q_m is the adsorption capacity ($mg.g^{-1}$), k is a constant correlated to the adsorption energy (mol^2 kJ^{-2}) and ε is Polanyi potential (Dubinin–Radushkevich isotherm constant) found according to:

$$\varepsilon = [RT \ln (1 + (1/C_e))]$$

Where R, represent the gas constant, T absolute temperature (K) and C_e adsorbed equilibrium concentration ($mg.L^{-1}$). The mean free energy for adsorption (E) was calculated from the k values by the following equation:

$$E = (-2k)^{-0.5}$$

The importance of E is useful for estimating the kind of adsorption process. If this value is ranged between (8 and 16) kJ mol^{-1}, adsorption process can be clarified by ion exchange (Unlu and Ersoz, 2006).

Thermodynamic parameters for soil studied were calculated from the difference of the thermodynamic equilibrium constant, K°, calculated by the subsequent procedure summarized by Biggar and Cheung (1973). The value of K° for adsorption reaction can be described as:

$$K^o = a_s/a_e = \gamma_s C_s/ \gamma_e C_e$$

Where

$\mathbf{a_s}$ indicates activity of adsorbed metals, $\mathbf{a_e}$ to metals activity in equilibrium solution, $\mathbf{C_s}$ to metals adsorbed ($mg.l^{-1}$) of solution in contact with the surface of adsorbent, C_e solute ($mg.l^{-1}$) of solution in equilibrium solution, $\boldsymbol{\gamma_s}$ is the activity coefficient of the sorbed metals and $\boldsymbol{\gamma_e}$ indicates the activity coefficient of metals in equilibrium solution. Since at lower concentration, activity coefficient approaches unity, above Eq. was decreased to:

$$K^o = Cs/Ce$$

The values of K° were finding by plotting ln ($\mathbf{C_s/C_e}$) against **Cs** and extrapolating to zero $\mathbf{C_s}$. The standard free energy of Cu (ΔG°) was found as follows:

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

The standard enthalpy of Cu (ΔH°) was found by Vant Hoff equation:

$$\ln K^o_2/K^o_1 = - \Delta H^o/R[1/T_2 - 1/T_1]$$

The standard entropy (ΔS°) was calculated as

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

RESULTS AND DISCUSSIONS:

Physico-chemical properties of the studied soils (Table.1) showed the texture of soil samples were clay to silty loam. Amount of soil organic matter ranged between (6.5 to 39.6) g kg^{-1}, calcium carbonate varied from (6.3 to 237.7) g kg^{-1}, the CEC ranged from (18.05 to 31.03) cmol. kg^{-1}, pH of the soils ranged between (7.48 to 8.00) which indicated that all the soils were alkaline, EC of the soil varied from (0.29 to 0.73) dSm^{-1} this indicate the soils are non-saline soils. The extractable Cu by DTPA ranged from (48.80 to 69.65) mg kg^{-1}.

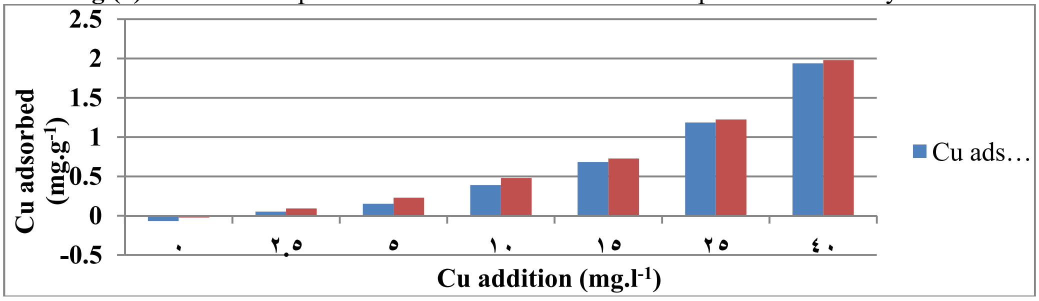
Table (1): Some physico-chemical properties of studied soil.

Soil Samples	Clay	Silt	Sand	Texture	pH	EC dSm^{-1}	CEC Cmol. kg^{-1}	O.M g kg^{-1}	$CaCO_3$ g kg^{-1}	Cu^{2+} DTPA mg kg^{-1}
	g kg^{-1}									
Smail Ava	593.40	334.00	72.60	Clay	7.92	0.73	30.97	6.50	237.70	69.65
Khanki	593.40	334.00	72.60	Clay	7.82	0.70	31.03	6.80	178.20	68.80
Khirshanya	467.20	430.00	102.80	Silty clay	7.78	0.62	25.08	8.60	196.10	67.25
Esyan	406.30	438.00	155.70	Silty clay	7.48	0.51	21.82	7.50	171.90	66.15
Mahed	434.40	284.00	281.60	Clay	7.61	0.59	23.98	11.30	161.30	60.40
Suwaratoka	319.80	352.40	327.80	Clay loam	8.00	0.45	23.91	39.60	6.30	63.80
Bamerny	252.20	545.00	202.80	Silty loam	7.67	0.37	18.05	27.20	111.60	48.80
Tirwanish	384.40	318.00	297.60	Clay loam	7.53	0.29	21.00	8.90	127.30	62.30

Adsorption of Cu^{2+} increased with increasing both of Cu^{2+} concentration in the equilibrium solution from (0 – 40) mg L^{-1} and temperature from (25 to 45) ºC in all studied soils (Fig. 1). The amount of adsorbed Cu ions increased as the initial concentration increased (Igwe and Abia, 2007), and Cu^{2+} adsorption in soils involves multiple adsorbing sites (Alcacio et al., 2001). An increase in Cu adsorption with increasing temperature is referring to the increases in number of active sites (Yavuz et al., 2003 and Bouberka et al., 2005). High adsorption found in Smail Ava soils this attributed to the high quantity of CEC, Cu-DTPA and clay content in soil.

The variation in adsorption of Cu^{2+} between soils (high and low adsorption) may be due to the higher variation in clay, organic matter, exchangeable bases, higher CEC and soil pH of the soils **(**Yu et al., 2002**)**. In the absence of other metals, a high concentration of copper in general adsorbed than other metals **(**Elliot et al., 1986**)**, although in soils with low organic matter content the adsorption of Cu^{2+} behave more similarly **(**Karatanasis, 1999**)**. After fitting the data to the Dubinin–Radushkevich (D-R) isotherm (Fig. 2) to know the adsorption mechanism, the constant values of k in equation which correlated to the adsorption energy ranged between (-2×10^{-4} to -4×10^{-3}) mol^2kJ^{-2}.

Fig (1): Effect of temperature and Cu addition on Cu adsorption in Khirshanya soils.



The high adsorption energy (k) found in soil of Suwaratoka location, this correlate with high organic matter content (39.6 g kg^{-1}) and soil pH but the lowest value of k initiated in soil of Bamerny location, may be due to low clay, CEC and Cu-DTPA in comparing with other locations (Table.1). The values of q_m constant in (D-R) isotherm which represented the adsorption capacity vary from (1.139 to 214.344) mg g^{-1} (Table 2). Similar findings observed by Hosseinpur and Dandanmozd (2010) in the study of Cu^{2+} adsorption in some calcareous soil of Hamadan province in Iran. The high adsorption capacity (q_m) noted in soil of Smail Ava location, this agreement with high Cu-DTPA, Clay, EC and CEC, but the low value of (q_m) found in Bamerny location, due to its low clay content and Cu-DTPA (Table.1).

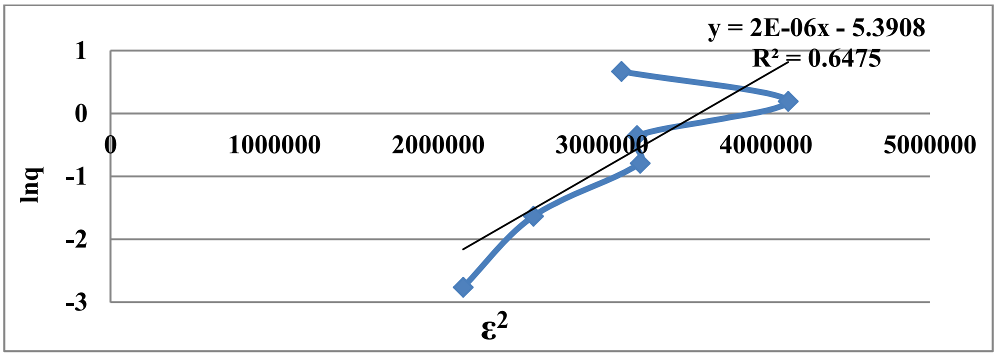


Fig. (2): Dubinin-Radushkevich Adsorption Isotherm in Smail Ava Soil

Table (2): D-R equation constants of studied soils

Characterizes Soil Samples	k mol^2kj^{-2}	q_m $mg.g^{-1}$	E $kJ.mol^{-1}$
Smail Ava	-2×10^{-3}	214.344	50.000
Khanki	-5×10^{-4}	6.896	31.623
Khirshanya	-1×10^{-3}	21.417	15.811
Esyan	-6×10^{-4}	9.820	22.361
Mahed	-1×10^{-3}	121.142	22.361
Suwaratoka	-4×10^{-3}	3.560	11.180
Bamerny	-2×10^{-4}	1.139	28.868
Tirwanish	-5×10^{-4}	1.918	31.623

The mean free energy for adsorption (E) in D-R isotherm is useful for estimating the type of adsorption process. The (E) values for Cu ranged from 11.180 to 50 kJ mol^{-1} (Table. 2). According to Unlu and Ersoz (2006) the adsorption mechanism of Cu^{2+} ions on soils of Khirshanya and Suwaratoka locations can be explained by ion exchange process because it is less than 16 kJ mol^{-1}.

The thermodynamic parameters (K^o, ΔG^o, ΔH^o, ΔS^o) supply mechanism of Cu^{2+} adsorption in the soils. The values of the thermodynamic equilibrium constant (K^o) increased with increasing the temperature from 25°C (782-1098) and at 48°C (1087-3175) (Fig. 3 and Table. 3), the high value of (K^o) recorded in soil of Smail Ava location at 25°C and 48 °C but the lowest value found in Bamerny soil at 25°C and Suwaratoka soil at 48°C.

The values of free energy at equilibrium (ΔG^o) in all studied soils for both temperatures (25 and 48)°C were negative and ranged from (-16.505 to -17.346) kJ mol^{-1} at 25 ºC and ranged (-18.658 to -21.519) kJ mol^{-1} at 48 ºC, these negative values designate that the adsorption process is spontaneous (Table. 3). At high temperature the free energy (ΔG^o) of the Cu adsorption was more negative value, which pointed that the spontaneity of the process increased with increasing in temperature. The high value of (ΔG^o) demonstrate in soil of Smail Ava location at (25 and 48) °C this concord with high clay, calcium carbonate, Cu-DTPA, and CEC but the low values of (ΔG^o) observed in Bamerny location at 25 ºC and Suwaratoka location at 48 ºC , due to its low clay and calcium carbonate content.

The values of enthalpy at equilibrium (ΔH^o) of studied soils were positive and varied from (2.678 to 36.716) kJ mol^{-1} (Table.3). The positive results of (ΔH^o) showed that Cu^{2+} adsorption is an endothermic reaction. Similar results were found also by Adhikari and Singh (2003); Unlu and Ersoz (2006); Dali-youcef et al., (2006) and Hosseinpur and Dandanmozd (2010). The high value of (ΔH^o) at both temperatures observed in soil of Smail Ava and Khirshanya locations this demonstrate that have high relation with clay, Cu-DTPA, and CEC but the low values of (ΔH^o) noted in Suwaratoka location.

The heat of adsorption values ΔH^o (5.0 to100) kcal mol^{-1} (20.9 – 418.4) kJ mol^{-1}, represent the heat of chemical reactions, that are frequently supposed as the comparable values for the chemical adsorption processes (Unlu and Ersoz, 2006). The endothermic nature of the adsorption processes illustrate that these processes don’t energetically stable **(**Biggar. and Cheung, 1973**)**. For heavy metals if the values of ΔH^o of adsorption for ion exchange range between (8.4 -12.6) kJ mol^{-1} it proposed that the adsorption process of those ions is of ion exchange in nature **(**Helfferich, 1962**)**.

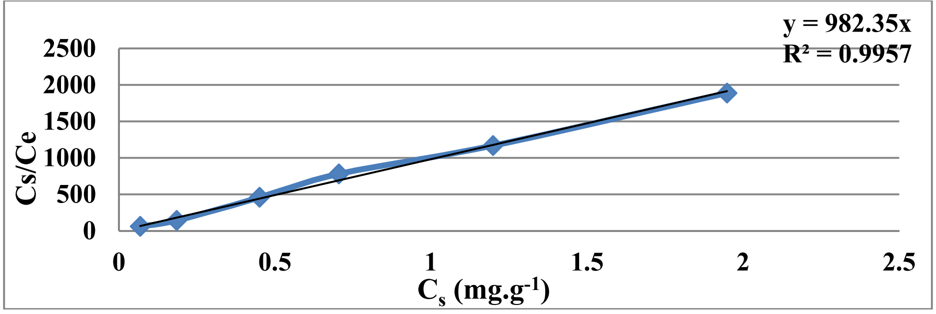


Fig. (3): The relation between Cs/Ce with Cs in Mahed soil at 25˚C.

Table (3): Thermodynamic parameters of copper in studied soil.

Soil Samples	K^o		ΔG^o KJ mol^{-1}		ΔH^o KJ mol^{-1}	ΔS^o (J $mol^{-1}K^{-1}$)	
	(25°C)	(48°C)	(25°C)	(48°C)		(25°C)	(48°C)
Smail Ava	1098.000	3175.000	-17.346	-21.519	36.716	181.416	181.417
Khanki	895.300	1685.000	-16.840	-19.828	21.866	129.886	129.888
Khirshanya	798.500	2297.000	-16.557	-20.656	36.536	178.166	178.169
Esyan	1043.000	1473.000	-17.219	-19.469	11.936	97.837	97.836
Mahed	982.300	1254.000	-17.070	-19.039	8.444	85.617	85.617
Suwaratoka	1006.000	1087.000	-17.129	-18.658	2.678	66.466	66.467
Bamerny	782.000	1298.000	-16.505	-19.131	17.522	114.183	114.183
Tirwanish	1002.000	1628.000	-17.119	-19.736	16.783	113.764	113.766

By comparing ΔH^o values of this study for Cu^{2+} with the noted range found by Helfferich **(**1962**),** the ΔH^o values of soil in Esyan and Mahed locations (11.936 and 8.444 KJ mol^{-1} respectively) located in this range therefore, the adsorption process is ion exchange, but in other soils is less or more than this range, it suggested other mechanism for adsorption Cu^{2+} ions occur on soil beside ion exchange mechanism.

The values of entropy at equilibrium (ΔS^o) for Cu^{2+} adsorption in all studied soil were positive and varied from (66.466 to 181.417) J mol^{-1}K^{-1}. The positive values of ΔS^o designates of raising randomness at solid-solution interface through the adsorption of this cation on sorbent, whereas the negative value of ΔS^o designates the decline of the degree of randomness at the surface of the sorbent during the adsorption process ions. The declining in the randomness lead to an increase in the adsorption capacity of the ion on sorbent **(**Abou-Mesalam, 2003**)**.

The thermodynamic equilibrium constant (K^o) at 25°C have negative correlation with silt (-0.62) non significantly, whereas at 45°C is positive significantly ($p< 0.05$) correlated with Clay (0.70*) and $CaCO_3$ (0.75*) (Table. 4). Free energy at equilibrium (ΔG^o) at 25°C is significantly correlated with silt (0.64*), but at 45°C correlated with Clay (0.73*), organic matter (0.64*) and highly negative correlated with $CaCO_3$ (-0.80**). Enthalpy (ΔH^o) and entropy at equilibrium (ΔS^o) at 25°C and 45°C have positive correlated with $CaCO_3$ (0.77*), (0.78*) respectively.

Table (4): Correlation coefficient between soil properties with adsorption isotherm and thermodynamic parameters.

Soil properties	**Clay**	**Silt**	**Sand**	**pH**	**EC**	**CEC**	**O.M**	**$CaCO_3$**	**Cu-DTPA**
K^o at (25°C)	0.30	-0.62	0.15	0.02	0.18	0.30	-0.16	0.07	0.49
K^o at (48°C)	0.70*	-0.13	-0.71*	0.32	-0.06	0.63	-0.55	0.75*	0.55
ΔG^o at (25°C)	0.30	0.64*	0.18	-0.02	-0.20	-0.31	0.17	-0.06	-0.49
ΔG^o at (48°C)	0.73*	0.11	0.75*	-0.24	-0.001	-0.61	0.64*	-0.80**	-0.57
ΔH^o	0.61	0.12	0.80**	0.23	-0.07	0.49	-0.57	0.77*	0.39
ΔS^o at (25°C)	0.62	0.10	0.80**	0.23	-0.06	0.50	-0.58	0.78*	0.40
ΔS^o at (48°C)	0.62	0.10	-0.80**	0.23	-0.06	0.50	-0.58	0.78*	0.40
k	0.07	0.31	-0.33	-0.74*	0.24	-0.24	-0.63	0.53	-0.27
qm	0.54	-0.43	-0.28	0.27	-0.23	0.54	-0.34	0.56	0.30
E	0.54	-0.17	-0.48	0.04	0.17	0.44	-0.50	0.62	0.16

Conclusion

The results of this research illustrate that alkaline calcareous soils in Duhok adsorbed high quantities of Cu^{2+}, the Cu^{2+} adsorption increased with increasing temperature and thermodynamic parameters are helpful in describing Cu^{2+} adsorption. In studied soils thermodynamic parameters of Cu^{2+} adsorption reaction were spontaneous and endothermic. The soil properties such as clay, O.M, and CEC play an important role in Cu sorption.

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رەفتارا نویسیانا سفری ل هندەك ئاخێن كلسی ل پارێزگەها دهوكێ

كورتی:

ئاخ ژ تەخا سەرڤەی ئەردی هاتنە وەرگرتن ل هەشت جهان ل پارێزگەها- دهوكێ هەرێما كوردستانا عیراقێ ئەو ژی ئەڤە نە (سمائیل ئاڤا، خانك، خرشەنیا، ئێسیان، مەهەد، سوارەتوكا، بامەرنێ وتروانش) بو خاندنا نویسیانێ وپیڤەرێ گەرموكە لڤین (سێرمودینامیكی) یێن Cu^{2+} وەكی نەگورێ هاوسەنگێ سێرمودینامیكی K^o، وتێهنا ئازاد یانویسیانێ ΔG^o، گوهورینا گەرمێ ΔH^o وهەرەمەكی یا نویسیانێ ΔS^o هاتە پیڤان ب كارئینانا ئەنجامێن نویسیانێ یێن Cu^{2+} وتیراتیاوی ل گیراوێ هاوسەنگدا ل بن دوو پلێن گەرمێ یێن جیاواز.

ئەنجاما دیار كر زێدەبوونا چەندیا نویسیانا Cu^{2+} ی دگەل زێدەبوونا Cu^{2+} یێ زێدەكری وپلا گەرمێ د هەمی ئاخێن ڤەكولینێ دا. بهایێن K^o و ΔG^o زێدەدبن دگەل زێدەبوونا پلا گەرمێ ژ 25°C بو 48°C . ژمارێێن ΔG^o نێگەتیڤ بوون دهەردوو پلێن گەرمێ دا ودگەڤنە د ناف بەرا (−16.505 هەتا −17.346 و − 18.658 هەتا −21.519) كج مول$^{-1}$ لدیف ئێك وئەف ژمارێن نێگەتیڤ نیشانا هندێ نە كو پروسێسا نویسیانێ بخو چێدبیت. بهایێن ΔH^o و ΔS^o یێت پوسیتیڤ بوون ودكەڤنە دناف بەرا (2.678 هەتا36.716) كج مول$^{-1}$ و (66.466 هەتا 181.417) جول مول$^{-1}$ كلفن$^{-1}$. ژمارێێن پوسیتیڤ یێت ΔH^o دیاردكەن كو نویسیانا Cu^{2+} كارلێكا گەرم مێژە. ئەنجام دیاردكەن كو ئاخێن كلسی یێت تفت ل پارێزگەها دهوكێ گەلەك Cu^{2+} پێڤە دنوێسیت وپیڤەرێ سێرمودینامیكی یێ ب مفانە بو دیاركرنا نویسیانا Cu^{2+}، بهایێن بلند یێن K^o، ΔG^o، ΔH^o و ΔS^o یێن Cu^{2+} ل پلێن (25°C) و (48°C) بومە دیاربون ل ئاخا سمایل ئاڤا دا بەلێ بهایێن نزم یێن ΔH^o و ΔS^o یێن Cu^{2+} دیاربون ل ئاخا سوارەتوكا. جورێ پروسێسا نویسیانێ ل ئاخا خرشەنیا و سوارەتوكا دێتە شلوڤەكرن بگوهرینا ئایونی ژبەر تێكراییا تێهنا ئازاد یانویسیانێ (E) ل هەر دوو جهێن ناڤبری كێم تر بو ژ 16 كج مول$^{-1}$.

سلوك امتزاز النحاس في بعض الترب الكلسية في محافظة دهوك

الخلاصة:

تم أخذ عينات ترب سطحية من ثمانية مواقع في محافظة دهوك–اقليم كردستان العراق وهي (اسماعيل افا، خانك، خرشنيا، اسيان، مهد، سوارتوكا، بامرني وطروانش) لدراسة الامتزاز والمعايير الثرموديناميكية للنحاس مثل (ثابت الاتزان K^o الثرموديناميكي والطاقة الحرة للامتزاز ΔG^o والتبادل الحراري ΔH^o والعشوائية ΔS^o) حيث قدرت الامتزاز باستعمال بيانات الامتزاز للنحاس وتركيزه في محلول الاتزان تحت درجتين حراريتين مختلفتين. بينت النتائج زيادة في كمية النحاس الممتز مع زيادة كل من كمية النحاس المضاف ودرجة الحرارة في جميع ترب الدراسة. قيم ثابت الاتزان الثرموديناميكي (K^o) والطاقة الحرة للامتزاز (ΔG^o) يزدادان مع زيادة درجة الحرارة من (25 الى 48) م°. قيم الطاقة الحرة كانت سالبة لكلتا درجتي الحرارة (25 و 48) م° ويتراوح بين (−16.505الى− 17.346 و− 18.658 الى −21.519) كج مول$^{-1}$ على التوالي. هذه القيم السالبة تدل على أن عملية الامتزاز هي تلقائية. قيم الانثالبي (ΔH^o) والانتروبي (ΔS^o) في جميع ترب الدراسة كانت موجبة وتراوحت بين (2.678 الى 36.716) كج مول$^{-1}$ و (66.466 الى 181.417) جول مول$^{-1}$ كلفن$^{-1}$، وأظهرت النتائج الموجبة لـ(ΔH^o) أن امتزاز النحاس هو تفاعل ماص للحرارة. كما أظهرت النتائج أيضا أن التربة الكلسية القلوية في محافظة دهوك يمتز كميات كبيرة من النحاس، وأن المعايير الثرموديناميكية مفيدة في وصف امتزاز النحاس. تم العثور على قيم عالية منK^o ، ΔG^o، ΔH^o و ΔS^o للنحاس في (25 و 48) م° في تربة موقع إسماعيل افا، بينما القيم المنخفضة لـ ΔH^o وΔS^o للنحاس وجدت في موقع تربة سوارتوكا. وان نوع عملية الامتزاز في تربة موقعي خرشنيا وسوارتوكا يمكن تفسيرها بالتبادل الأيوني لأن معدل الطاقة الحرة للامتزاز (E) في الموقعين كانت أقل من 16 كج مول$^{-1}$.