# Sorption characteristics of copper in some calcareous soils of western Iran

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**Abstract:**The environmental impact of metal additions to soil depends on its sorption ability. To evaluate the sorption of copper (Cu) on to some soils an experiment was conducted with ten  calcareous soils of Hamadan province in the west of Iran. Half g soil samples were equilibrated at $25\pm1$ and $45\pm1°C$ with 25 ml of 0.01 M $CaCl_2$ containing  0 to 30 $mgL^{-1}$ Cu as $CuSO_4$. Suspensions were centrifuged, filtered and concentration of Cu in the clear extract solution was calculated. The thermodynamic parameters viz. K ,  G ,  H and  S  were determined by using sorption data and concentration of Cu in equilibrium solution at two different temperature. Thermodynamic parameters revealed that Cu sorption increased as the values of K  and   G  increased with rise in temperature from 25 to 45 °C. The   $G^o$ values at 25 and 45°C were negative and ranged from -18.39 to -24.10 and -21.167 to -26.267 kJ $mol^{-1}$ respectively. The values of enthalpy ( $H^o$) and antropy ( S ) were positive and ranged from 8.184 to 42.852 kJ $mol^{-1}$ and 102.457 to 206.184 J $mol^{-1}$ $K^{-1}$. The results showed that Cu sorption is a spontaneous process and endothermic reaction. The results also showed that calcareous soils can  sorb high amounts of Cu and that thermodynamic parameters are useful in describing Cu sorption. [Journal of American Science. 2010;6(11):103-108]. (ISSN: 1545-1003).

## 1.Introduction

Adsorption is one of the most important chemical processes in soils. It determines the quantity of plant nutrients, metals, radionuclides, pesticides and other organic chemicals that are retained on soil surfaces and, therefore, is one of the primary processes that affect transport of nutrients and contaminants in soils. Sorption also affects the electrostatic properties of suspended particles and colloids. The electrostatic properties affect coagulation and settling (Sparks 1995). Sorption reactions on soil mineral surfaces potentially attenuate toxic soil solution (Goldberg 2002). Sorption isotherm analysis is a useful technique to study the retention of metals in soils. Sorption isotherms provide useful information about the soil retention capacity and the strength by which the sorbate is held on to the soil.

Sorption isotherm batch experiments are very important in soil science research. Theoretically, maximum monolayer sorption, empirical adsorption constants, and other important adsorption parameters can be determined by this method.. Selective adsorption of Cu and Zn has been related to their susceptibility to hydration, their charge / radius ratio, their electeronegativity and their Misono softness (McBride 1989). Study of Zn and Cu adsorption onto soils of various kinds and onto certain individual soils fractions and other substrates have shown that the main physical and chemical factors governing these processes are pH and presence of organic and/or inorganic colloids (Lopez et al. 1998; Kardivelu et al. 2001; McBride et al. 1997). Copper is more soluble in acid soils

than in calcareous soils and their marked sorption hysteresis is most marked in the case of sorption by organic soil components (McLaren et al. 1983; Barow et al. 1989; Wu et al. 1999). In the absence of other metals, copper is generally considered to be adsorbed in greater quantities than other metals (Elliott et al. 1986), although they behave more similarly in soils with low organic matter content (Karathanasis 1999).

Adsorption increase with increasing temperature, due to the increase in number of active sites (Yavuz et al. 2003; Bouberka et al. 2005). To gain further insight into sorption process and its mechanism, thermodynamic approach can predict the final state of metal in the soil system from an initial nonequilibrium state (Sposito 1984). A thermodynamic approach was used to study the effect of temperature on the adsorption processes of lindane on a number of adsorbents (Mills and Bigger 1969a, b, c). Evaluation of the free energy change corresponding to the transfer of element from bulk solution into the appropriate site of the double layer or clay mineral lattice are helpful to express the sorption process. Similarly, an understanding of change in enthalpy and entropy helps in determining the free energy change and disorders occurring during sorption process. The high values of   $G^o$ both for Pb and Cd indicated that both the reactions are spontaneous(Adhikari and Singh 2003). The values of  $H^o$ were found to be negative for Cd and positive for Pb concluded that Cd sorption reaction was exothermic while Pb sorption was found to be an endothermic reaction in all the soils. (Adhikari and Singh 2003). The values of  S  were found to be positive due to the

exchange of the metal ions with more mobile ions present on the exchanger, which would cause increase in the entropy, during the adsorption process (Unlu and Ersoz, 2006). Information about Cu sorption characteristics and sorption thermodynamic parameters (STP) were limited in soils of Iran. The objectives of this research were to study the Cu sorption characteristics and determination of STP in some calcareous soils of Hamadan province in western Iran.

## 2.Materials and Methods

We collected bulk samples of the top soils (0-30cm depth) from ten calcareous soils from Hamadan province in the west of Iran. All samples were air dried, crushed and sieved through a 2-mm prior to soil analysis and sorption studies. Characteristics of the soils such as, particle size distribution, pH, EC, CEC, organic C, and calcium carbonate equivalent were determined using standard analytical methods (Gee and Bauder 1986; Rhodes 1996; Summer and miller 1996; Nelson and Sommers 1996 and Nelson 1982). Concentration of available Cu in soil samples was determined using DTPA method (Lindsay and Norvell 1978).

To study the sorption of Cu by different soils, 0.5 g soil sample was placed in 100 ml plastic bottles and equilibrated with 25 ml of 0.01 M $CaCl_2$ solution containing graded levels of Cu, i.e. 0, 2, 5, 10, 15, 30 mg $l^{-1}$ Cu as $CuSO_4$ solution. Solutions were prepared in 0.01 M $CaCl_2$ to keep the ionic strength almost constant. Each sorption set, for Cu, was replicated thrice. The soil suspension shaken for 30 min and was equilibrated for 24 h at $25\pm1$ and $45\pm1$°C on an incubator. Based on preliminary studies, an equilibrium period of 24 h and soil/solution ratio of 1:50 were found optimum beyond which no significant change in metal content of equilibrium solution was recorded. After equilibration time, the suspension was filtered, and concentration of Cu in the clear extract solution was determined using Varian Atomic Absorption Spectrophotometry. Amount of Cu sorbed by soils was calculated from the difference between the initial and final concentration of Cu in the equilibrium solution. For studying the sorption relationship, the data were fitted to the following equations:

$C_e/q = 1/Kb + 1/bC_e$     Conventional Langmuir
$\log q = \log K_f + n\log C_e$     Freundlich equation

Where $C_e$ is the Cu concentration in the equilibrium solution (mg/l), q is the amount of Cu sorbed by the soil (mg $kg^{-1}$), b is the sorption maxima (mg $kg^{-1}$) and k is the bonding energy coefficient (l $mg^{-1}$). The $K_f$ is the Freundlich distribution coefficient and n is an empirical constant.

Langmuir and Freundlich isotherms don't give any idea about sorption mechanism, but Dubinin-Radushkevich (D-R) isotherm describes sorption on a single type of uniform pores. In this respect the D-R isotherm is an analogue of Langmuir type but it is more general, because it does not assume a homogeneous surface or constant sorption potential (Unlu and Ersoz 2006). In order to understand the adsorption type, D-R isotherms were obtained. The D-R isotherm has the form:

$\ln q = \ln q_m - k \varepsilon^2$
and
$\varepsilon = [RT \ln (1 + (1/C_e))]$

Where $\varepsilon$ is Polanyi potential, q is the amount of Cu sorbed by the soil (mol $g^{-1}$), k is a constant related to the adsorption energy ($mol^2 kJ^{-2}$) and $q_m$ is the adsorption capacity (mol $g^{-1}$). The mean free energy of adsorption (E) was calculated from the k values using the equation:

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

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

Thermodynamic parameters were calculated from the variation of the thermodynamic equilibrium constant, K°, computed by following the procedure outlined by Biggar and Cheung (1973). The value of K° for adsorption reaction can be defined as:

$K° = a_s/a_e = \gamma_s C_s/\gamma_e C_e$

where $a_s$ denotes activity of adsorbed metals, $a_e$ to activity of metals in equilibrium solution, $C_s$ to milligrams of metals adsorbed per litre of solution in contact with the adsorbent surface, $C_e$ to milligrams of solute per litre of solution in equilibrium solution, $\gamma_s$ is the activity coefficient of the sorbed metals and $\gamma_e$ represents the activity coefficient of metals in equilibrium solution. Since at lower concentration, activity coefficient approaches unity, above Eq. was reduced to:

$K° = C_s/C_e$

The values of K° were obtained by plotting ln $(C_s/C_e)$ vs. $C_s$ and extrapolating to zero $C_s$. The standard free energy ($\Delta G°$) was calculated as follows:

$\Delta G° = -RT \ln K°$

The standard enthalpy ($\Delta H°$) was obtained from integrated form of the Vant Hoff equation:

$\ln K°_2/K°_1 = -\Delta H°/R[1/T_2 - 1/T_1]$

The standard entropy ($\Delta S°$) was calculated as

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

## 3.Results and Discussion

Selected chemical and physical characteristics of the soils are presented in Table 1. The texture of the soil samples are clay loam to sandy clay loam. The calcium carbonate equivalent ranged from 5 to 53.8%. Organic matter content ranged from 0.68% to 2.40%. The pH of the soils ranged from 7.44 to 8.20 which indicated that all of the soils are alkaline. The CEC ranged from 10 to 25.1 $Cmol_{(+)}$ $Kg^{-1}$. The DTPA extractable Cu ranged from 0.49 to 4.15 mg $kg^{-1}$.

For proper evaluation of the environmental threat posed by Cu or of its availability, it is necessary to supplement the individual sorption characteristics. Sorption isotherm for these soils exhibited difference in the amounts retained. Cu sorption didn't described by Langmuir equation ($R^2$=0.11-0.60). Freundlich and D-R equation were described Cu sorption (Table 2). Constants of these equations were shown in Table 2. Freundlich distribution coefficient ($K_f$) ranged from 798.18 to 73063.42 mg kg$^{-1}$. Distribution coefficient represents the sorption affinity of the metal cations in solution for the soil solid phase and can be used to characterize the mobility and retention of Cu in a soil system. A distribution coefficient can be related to both plant uptake and environmental pollution. Low distribution coefficients indicate that most of the metals present in the system remain in the solution and are available for transport, chemical processes and plant uptake (Jalali and Moharrami 2007).Whereas higher values indicate lower mobility and higher retention of metal in the soil. Soil no 8 had the highest $K_f$, its high CEC and clay content. Soil no 10 had the lowest $K_f$, its low CEC and equivalent calcium carbonate. So that Cu in soil no 8 had the lowest mobility and Cu in soil no 10 had the highest mobility. Freundlich distribution coefficient order was:

soil no 8>soil no 5>soil no 7> soil no 9>soil no 2>soil no 6>soil no 4>soil no 3>soil no 1> soil no 10

Freundlich constant n which indicates adsorption intensity (Jalali and Moharrami, 2007) ranged from 0.86 to 1.75. Soil no 3 and 10 had highest and lowest n respectively. Elzinga et al. (1999) also evaluated the batch sorption data and established general purpose, Freundlich isotherms for different heavy metals in soils. Mafton et al. (2000) reported that Zn adsorption in eight calcareous soils of Iran followed a Freundlich adsorption isotherm.

Table 1. Physicochemical properties of the experimental soils

| Soil. No. | pH (1:2.5) | CEC cmol(+)kg$^{-1}$ | EC ds.m$^{-1}$ | O.M | Clay | Silt | CaCO3 | Zn- DTPA (mg kg$^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| | | | | | | % | | |
| 1 | 7.80 | 10.9 | 0.23 | 0.90 | 27.0 | 7.5 | 11.0 | 1.09 |
| 2 | 8.10 | 11.5 | 0.30 | 1.03 | 33.2 | 15.0 | 14.1 | 4.15 |
| 3 | 7.96 | 14.2 | 0.19 | 0.83 | 34.2 | 19.1 | 33.5 | 1.49 |
| 4 | 7.45 | 23.5 | 0.13 | 0.68 | 38.3 | 10.3 | 5.0 | 0.66 |
| 5 | 8.20 | 16.0 | 0.34 | 2.40 | 22.0 | 15.0 | 53.8 | 0.49 |
| 6 | 8.00 | 15.5 | 0.20 | 0.80 | 20.8 | 25.3 | 17.1 | 0.56 |
| 7 | 7.44 | 20.9 | 0.19 | 1.06 | 27.0 | 27.8 | 22.1 | 0.63 |
| 8 | 7.90 | 25.1 | 0.20 | 1.10 | 36.4 | 25.9 | 27.4 | 0.65 |
| 9 | 7.90 | 14.5 | 0.26 | 0.80 | 38.1 | 17.6 | 39.4 | 1.15 |
| 10 | 7.85 | 10.0 | 0.30 | 1.40 | 27.6 | 9.5 | 6.1 | 2.56 |

Table 2. Freundlich and D-R equation constants of soils

| Soil no | Freundlich constants | | | D-R constants | | | |
|---|---|---|---|---|---|---|---|
| | $k_f$ l kg$^{-1}$ | n | $R^2$ | K Mol2kJ-2 | $q_m$ mmolg$^{-1}$ | E kJmol$^{-1}$ | $R^2$ |
| 1 | 1498.99 | 1.02 | 0.92** | -0.0043 | 2.086 | 10.783 | 0.99** |
| 2 | 4652.65 | 1.31 | 0.74* | -0.0082 | 15.182 | 7.8087 | 0.79* |
| 3 | 2310.47 | 0.86 | 0.99** | -0.0044 | 1.313 | 10.660 | 0.99** |
| 4 | 4152.41 | 0.99 | 0.93** | -0.0055 | 2.434 | 9.535 | 0.96** |
| 5 | 30881.61 | 1.09 | 0.98** | -0.0054 | 4.192 | 9.623 | 0.97** |
| 6 | 4296.35 | 1.12 | 0.98** | -0.0062 | 3.560 | 8.980 | 0.99** |
| 7 | 27567.67 | 1.57 | 0.95** | -0.0088 | 56.591 | 7.538 | 0.97** |
| 8 | 73063.42 | 1.75 | 0.95** | -0.0094 | 223.347 | 7.293 | 0.97** |
| 9 | 25852.35 | 1.51 | 0.94** | -0.0084 | 42.712 | 7.715 | 0.95** |
| 10 | 798.18 | 0.89 | 0.87** | -0.0036 | 2.513 | 11.785 | 0.96** |

* Significant at the 0.05 probability level
** Significant at the 0.01 probability level

Distribution coefficient significantly correlated with CEC(Table 3). Reyhanitabar et al. (2007) studying Zn retention of 20 calcareous soils of central Iran, reported a significant relationship between Freundlich $K_f$ with percentage of clay, CEC and CCE. Karimian and Moafpourian (1999)

reported that in calcareous soils of the southern part of Iran, Freundlich $K_f$ showed a highly significant relationship with soil pH and Clay, but it don't significantly correlated with CEC, CCE and OM.

Freundlich n didn't significantly correlate with soil properties. Reyhanitabar et al. (2007) reported a significant relationship between Freundlich n with percentage of clay. Elrashidi and O'Connor (1982) reported a significant relationship between Freundlich coefficients and percentage of clay, CEC and pH, but not O.M.

The values of $q_m$ constant (D-R isotherm) which is the adsorption capacity ranged from 1.313 to 223.347 (mol $g^{-1}$) (Table 2). Soil no 8 had the highest qm, its high CEC and clay content and soil no 9 had the lowest qm, its low OM and CEC. This parameter significantly correlated with percentage of clay and CEC(Table 3).

Table 3- Correlation between soil properties and adsorption isotherm parameters

| Soil | Freundlich constants | | | D-R constants | |
|------|------|------|------|------|------|
| Properties | n | $k_f$ | K | $q_m$ | E |
| CCE | -0.25 | 0.23 | -0.11 | 0.29 | 0.09 |
| Clay | -0.19 | 0.33 | -0.63* | 0.69* | -0.62* |
| Silt | -0.61* | 0.53 | -0.32 | 0.32 | -0.27 |
| O.M | 0.045 | 0.04 | 0.11 | -0.17 | 0.07 |
| EC | 0.002 | -0.16 | -0.01 | -0.05 | -0.05 |
| CEC | -0.47 | 0.66* | -0.44 | 0.61* | -0.42 |
| pH | 0.07 | -0.01 | 0.1 | -0.08 | 0.09 |

* Significant at the 0.05 probability level

The magnitude of E which is calculated from D-R isotherm is useful for estimating the type of adsorption process. In this study, E values for Cu ranged from 7.29 to 10.78 kJ $mol^{-1}$ (Table 2) that are between the values of ion exchange. Therefore it is possible to say that adsorption mechanism of Cu ions on soils can be explained with an ion-exchange process.

The values of k (D-R isotherm) which is constant related to the adsorption energy ranged from -0.0036 to -0.0094 $mol^2$ $kJ^{-2}$. Soil no 8 had the highest k, its high CEC and Clay. Soil no 10 had the lowest k, its low CEC and CCE.

Evaluation of thermodynamic parameters viz. K°, G°, H°, S° provide an insight into mechanism of Cu sorption in the soils. The data in Tables 4 indicates that value of K° increased with rise in temperature from 25 to 45 ºC in all the soils. The G° values for Cu were negative in all the soils (Tables 4). These negative values indicate that the sorption process is spontaneous. The G° at 25 ºC ranged from -18.391 to -24.101 kJ $mol^{-1}$. The G° at 45ºC ranged from -21.167 to -26.267 kJ $mol^{-1}$. In all the soils, the free energy ( G°) of the Cu sorption was more negative at higher temperature, which suggested that the spontaneity of the process increased with rise in temperature.

Table 4. Thermodynamic parameters of Cu sorption

| Soil no | K | | G° (KJ $mol^{-1}$) | | H° | S° (J $mol^{-1}K^{-1}$) | |
|---------|------|------|------|------|------|------|------|
| | 25ºC | 45ºC | 25ºC | 25ºC | (KJ $mol^{-1}$ | 25ºC | 45ºC |
| 1 | 1814.56 | 5385.15 | -18.591 | -22.714 | 42.853 | 206.184 | 206.184 |
| 2 | 1862.36 | 3409.43 | -18.655 | -21.506 | 23.821 | 142.538 | 142.538 |
| 3 | 4517.89 | 7700.96 | -20.851 | -23.660 | 21.001 | 140.467 | 140.467 |
| 4 | 2861.21 | 5447.98 | -19.719 | -22.745 | 25.369 | 151.303 | 151.303 |
| 5 | 7396.78 | 11883.43 | -22.072 | -24.807 | 18.676 | 136.740 | 136.740 |
| 6 | 5604.92 | 7069.89 | -21.385 | -23.434 | 9.147 | 102.457 | 102.457 |
| 7 | 4539.63 | 6555.11 | -20.863 | -23.234 | 14.473 | 118.576 | 118.576 |
| 8 | 16772.57 | 20645.53 | -24.101 | -26.267 | 8.184 | 108.338 | 108.338 |
| 9 | 4065.39 | 6481.45 | -20.589 | -23.204 | 18.374 | 130.751 | 130.751 |
| 10 | 1674.21 | 2998.90 | -18.391 | -21.167 | 22.962 | 138.771 | 138.771 |

Soil no 8 had the highest G° at 25 and 45 ºC, its high CEC and calcium carbonate equivalent. Soil no 10 had the lowest G° at 25 and 45ºC, its low CEC and calcium carbonate equivalent.

The values of isoteric heat (enthalpy) of Cu sorption ( H°) were positive and ranged from 8.184 to 42.853 kJ $mol^{-1}$ (Table 4). This provides an indication that sorption reaction was endothermic for Cu. Similar findings were also observed by

Bigger and Chung (1973), Adhikari and Singh (2003), Dali-youcef et al. (2006) and Unlu and Ersoz (2006).

Although there are no certain criteria related to the H° values that define the adsorption type, the heat of adsorption values between 5.0 and 100 kcal $mol^{-1}$ (20.9-418.4 kJ $mol^{-1}$), which are heats of chemical reactions, are frequently assumed as the comparable values for the chemical adsorption

processes (Unlu and Ersoz, 2006). Soil no 1 had the highesr $H^o$, and soil no 8 had the lowest $H^o$.

The values of $H^o$ were calculated from plots of ln $K^o$ versus 1/T. The linear nature of the plot indicates that the mechanism of adsorption is not changed as temperature changed. But the amount of adsorption is changed because the supply of thermal energy is different. The endothermic nature of the adsorption processes shows that these processes don't energetically stable (Bigger and Cheung 1973).

If the values of $H^o$ for heavy metals had been within the range of the enthalpy change of adsorption for ion exchange (8.4-12.6 kJ mol$^{-1}$) suggesting that the adsorption process of those ions is of ion exchange in nature (Helfferich 1962). The values of $H^o$ for Cu in this study were greater than 12.6 kJ mol$^{-1}$ which indicated that the presence of other mechanism for the adsorption of these ions occure on soil beside ion exchange mechanism.

Table 5. Correlation coefficients between soil properties and thermodynamic parameters

| Soil propertiess | $K^o$ (25) | $K^o$ (45) | $G^o$ (25) | $G^o$ (25) | $H^o$ (25) | $S^o$ (25) | $S^o$ (45) |
|---|---|---|---|---|---|---|---|
| CCE | 0.74* | 0.71* | -0.72* | -0.68* | -0.23 | -0.17 | -0.17 |
| Clay | 0.41 | 0.33 | -0.53 | -0.42 | -0.25 | -0.22 | -0.22 |
| Silt | 0.08 | 0.37 | -0.20 | -0.30 | 0.05 | 0.08 | 0.08 |
| O.M | 0.54 | -0.10 | -0.33 | 0.12 | -0.59 | -0.59 | -0.59 |
| EC | 0.12 | 0.02 | 0.07 | 0.13 | -0.05 | -0.06 | -0.06 |
| CEC | 0.63* | 0.14 | -0.71* | -0.29 | -0.65* | -0.62* | -0.62* |
| pH | 0.21 | 0.34 | -0.10 | -0.30 | 0.19 | 0.21 | 0.21 |

* Significant at the 0.05 probability level

The values of $S^o$ for Cu sorption were positive and ranged from 102.457 to 206.184 J mol$^{-1}$ K$^{-1}$. The positive values of $S^o$ indicates that the increased randomness at solid-solution interface during the adsorption of this cation on sorbent, while the negative value of $S^o$ indicates the decrease of the degree of randomness at the surface of the sorbent during the adsorption process ions. This decreasing 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 significantly correlated with calcium carbonate equivalent and CEC, while at 45°C it only correlated with CCE. Standard free energy ($G^o$) at 25°C significantly (p<0.05) correlated with CCE and CEC, but at 45°C it highly correlated (p<0.05) with CCE. Standard enthalpy ($H^o$) and standard entropy ($S^o$) were significantly correlated with CEC (Table 5).

## Conclusion

The results of this research showed that calcareous soils have a high capacity for cu sorption. The experimental data were better fitted by D-R than Freundlich equation. The soil properties such as clay and CEC play an important role in Cu sorption.

Thermodynamic parameters revealed that Cu sorption reaction in soils studied were spontaneous and endothermic. These suggested that the sorption capacity of these soils enhanced with increased in temperature. Thus, for developing suitable strategies for proper management of heavy metal pollution, moreover soil properties and nature of pollutant, soil condition, particularly temperature needs to be considered. Thermodynamic parameters significantly correlated with CCE and CEC.

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