Thermodynamics of Copper Desorption from Soils as Affected by Citrate and Succinate

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Abstract: Desorption of Cu and low molecular weight dissolved organics are the primary factors that impact fate and transport of Cu in soils. To improve predictions of the toxicity and threat from Cu contaminated soil, it is critical that time-dependent desorption behaviour be understood. In this paper, the effect of organic ligands citrate and succinate on the kinetics of Cu desorption from contaminated soils varying widely in soil characteristics was investigated at three different temperatures. The results showed that the first order equation adequately described the kinetics of Cu desorption from clay and sandy soils under isothermal conditions. The reaction rate constant (k_d) values of the first order kinetic equation for Cu desorption increased consistently with temperature, indicating faster release of Cu at higher temperatures. The Cu desorption rate from the studied soils at all three temperatures was as follows: citric > succinic. The E_a values indicates that Cu desorption from the studied soils in the presence of two organic ligands is a diffusion controlled reaction. The negative values of ΔH^* suggest that the desorption reactions are not energy consuming process. The higher negative values of (ΔH^*) for Cu desorption from the studied soils in the presence of succinic ligand indicate that the heat energy required to overcome the Cu desorption barrier was greater than that for Cu desorption in the presence of citric ligand. Computation of the free energy of activation (ΔG^*) yielded values ranging for 87 to 87.9 kJ/mol. The largest value represents ΔG^* for Cu desorption for clay soil in the presence of succinic acid while the lowest value represents ΔG^* for Cu desorption for sandy soil in the presence of citric acid. The information in this study is quite necessary to construct full functioning models that will help scientists to better understand mobility and bioavailability of metals in soils.

Keywords: kinetics; thermodynamic parameters; low molecular weight organic acids

Copper is a biotoxic heavy metal regarded as an important environmental pollutant in agricultural soils because of the potential adverse effects it may pose to food quality, soil health and the environment. Soil pH and organic matter were reported to account for approximately 70% of the variability in Cu partitioning and 80% of the variability of bioavailable Cu in 40 soils collected from around the world (IMPELLITERI *et al.* 2003). Up to 56% of Cu in soil solution was in the form of organic complexes (SAEKI *et al.* 2002). The bioavailability of copper in the contaminated soils is largely controlled by sorption-desorption and dissolution-precipitation reactions at the soil particle-water interface (CHAIGNON *et al.* 2003). However, researchers often rely on maximum adsorption levels and neglect desorption behaviour to predict the fate and transport of contaminants such as Cu in the environment. This is unfortunate because a through understanding of kinetics of Cu desorp-

tion is required for successful immobilization and soil remediation. Kinetic factors usually govern the phase that forms over a short period of time which is primarily dictated by the activation energy barrier of a reaction (Ainsworth *et al.* 1994).

Low-molecular-weight organic acids originated from decomposition of soil organic matter in the upper soil horizons play an important role in the fate of metals (Chen *et al.* 2003; Collins *et al.* 2003). Low molecular weight organic acids are commonly found in the soil system, whose rate of production depends on the time and nature of environment (Naidu & Harter 1998) Minimal information is available on the release behaviour of Cu in the presence of organic ligands in soil-water system. In this study, therefore, we have investigated the influence of temperature upon the kinetics of Cu desorption from two typical Egyptian soils varying widely in chemical characteristics as effected by two organic ligands to determine E_d, ΔG^*, ΔH^* and ΔS^* through applying the Arrhenius model. Information obtained from this study will give insights to scientists that may lead to improve remediation strategies, disposal practices, and risk assessments.

MATERIALS AND METHODS

Soils

Samples of two surface soils (0–30 cm) which differed in location, origins, texture and calcium carbonate content were used. One was a clay alluvial soil (Torrifluvents) and the second was a sandy loam desert soil (Quartzipasmment). Hereafter, the soils will be referred to as clay and sandy soils respectively.

The soils were air-dried, passed through a 2 mm sieve and stored in plastic bags before use. The pH values of the soils were measured in 1:2 soil-water, conductivity (EC) was measured and soluble cations and anions were determined in the soil paste extracts. The organic matter content was determined by the method of Walkly and

Black (Nelson & Sommers 1982) and the cation exchange capacity by the method of Thomas (1982). Particle size analysis was determined by the hydrometer method (Black 1965). Selected chemical and physical properties of the two soils studied are shown in Table 1.

Organic acids

Organic acids that occur naturally in soils and differ in number of functional groups were selected for the study. The selected organic acids are citric and succinic. Table 2 lists some of the characteristics of the organic acids (Serjeant & Dempsey 1979).

Kinetic experiments (desorption)

Sub-samples of the soils were treated with 150 μg/g Cu as $CuSO_4$. After adding Cu, the soils were incubated at field capacity for 6 weeks, during which the soils were subjected to four wet-dry cycles. After 6 weeks the soils were air dried, crushed to pass through a 2 mm sieve and stored in polyethylene bag for chemical analysis.

Kinetic batch experiments were carried out by adding 10 g of contaminated soil samples to 40 ml of organic acid (3mM) in a reactor unit. The mixtures were stirred at selected time intervals (5, 10, 20, 40, 60, 120, 240, 480 min) an aliquot of about 10 ml was removed and filtered. The filtrate was analyzed for Cu using atomic absorption spectrometry (AAS) and a first order kinetic model was applied to describe the desorption. The kinetic experiments were carried out at, 15, 25 and 35°C, temperatures.

Kinetic modeling

First order kinetic model was applied to the desorption data to better understand the effects of organic ligands and time on the desorption process. The first order equation used in the study can by represented by an expression of the form (Laidler 1965):

Table1. Selected chemical and physical characteristics of the two soils

Type of soil	pH	EC (dS/m)	Clay (%)	Silt (%)	Sand (%)	Total carbonate (%)	C_{ox} (%)	CEC (mmol (p$^+$)/kg)
Clay	8.4	0.75	44.6	14	41.9	3	1.4	330
Sandy	8.0	1.12	19.4	1.3	79.3	19	0.79	110

EC – conductivity, CEC – cation exchange capacity

$$dq/dt = k_d (q_0 - q) \tag{1}$$

where:

q – amount of Cu desorbed at time t,

q_0 – amount of Cu desorbed at equilibrium,

k_d – apparent desorption rate coefficient

Integrated with appropriate boundary conditions $t_0 = 0$, $q = 0$, Eq. (1) becomes:

$$\ln (q_0 - q) = a - k_d t \tag{2}$$

The ln q vs. t relationship is linear if the rate of Cu desorption follows first order kinetics.

Calculation of thermodynamic parameters for copper desorption

A graph of log k_d against $1/T$ was plotted for each soil concentration studied (Figure 1), where T is the temperature in Kelvin and k_d is the apparent desorption rate coefficient. From the integrated form of the Arrhenius equation (LAIDLER 1965), the energy of activation for Cu desorption (E_d) can be determined:

$$1n\, k_d = (-E_d/RT) + 1n\, A$$

where:

R – gas constant (8.314 kJ/mol),

A – universal frequency factor.

It can be seen that the slope is given by $-E/R$ and the intercept by ln A. Therefore, the thermodynamic parameters can be obtained using the following equation:

$$\Delta H^* = E - RT$$

$$(\Delta S^*/R) = 1n\, A - 1n\, (Bte/h)$$

$$\Delta G^* = \Delta H^* - T\Delta S^*$$

where:

ΔH^* – standard enthalpy of activation,

ΔS^* – standard entropy of activation

ΔG^* – standard Gibbs free energy of activation,

B – Boltzman's constant (1.380658×10^{-23} J/K)

Figure 1. Arhenius plots of Cu desorption from clay and sandy soils in the presence of succinic and citric acids at three different temperatures

h – Planck's constant ($6.6260755 \times 10^{-34}$ J s),

e – electronic charge

Values for the thermodynamic parameters with their standard deviations were determined by the application of the least squares procedure to all the individual values of the rate constant for each soil using a computer.

Statistical Analysis

All data were processed by Microsoft Excel (Microsoft 2000) and the regression of linear and nonlinear and other statistical analyses were conducted using the programs of SAS Release 6.12 (SAS Institute 1996).

Table 2. Relevant properties of low-molecular-weight used in the study

Organic acids	Chemical formula	Molecular weight (g)	Ligand form	pk_a^+
Succinic	$HOOCCH_2CH_2COOH$	118.09	H_2L	4.16, 5.61
Citric	$C(OH)(COOH)(CH_2COOH)_2$	192.13	H_3L	3.13, 4.78, 6.43

pk_a^+ values were adopted from SERJEANT and DEMPSEY (1979)

RESULTS AND DISCUSSION

Temperature effects on Cu desorption kinetics

The first order equation adequately described the kinetics of Cu desorption from clay and sandy soil under isothermal conditions as evidenced by high *r* values (Table 3). The first order equation assumes that the rate of Cu desorption is proportional to either the number of occupied sites on the surface or the concentration of Cu in the occupied sites. Successful representations of heavy metal desorption from soils have also been reported (Elkhatib *et al.* 1992). The first order equation constants (k_d and *a*) were obtained from the slope and intercept of the linear plots. Values of k_d and *a* for the soils are listed in Table 3. In all cases k_d values were higher in the sandy soil than in the clay soil. The clay soil under study showed higher values for organic matter, clay content and cation exchange capacity (CEC) than sandy soil (Table 1). The low Cu desorption associated with the clay soil suggests that most Cu ions are specifically chemically sorbed by both organic matter and layer silicate clays. The higher soil CEC generally coexisted with higher content of clay and organic matter and showed strong ability on sequestration of metals and vise versa (Stewart *et al.* 2003).

The reaction rate constant (k_d) values of the first order kinetic equation for Cu desorption increased consistently with temperature (Table 3), indicating faster release of Cu at higher temperatures. This is in agreement with Bronsted' reaction rate theory and Arrhenius equation (Daniels & Alberty 1975). The Cu sorption rates on the sorbents at all three temperatures were higher in the presence of citric than in presence of succinic. When comparing the apparent rate constants of Cu desorption from the studied soils in the presence of citric and/or succinic (Table 3), the highest rate of Cu desorption was from sandy soils in the presence of citric acid (3.01×10^3 min^{-1}) at 35°C and the lowest rate was from clay soil in the presence of succinic acid (2.38×10^3 min^{-1}) at 15°C. The greater stability of the citrate Me^{z+} complexes led to the greater efficacy of citric acid in desorbing Cu from soils than succenic acid. Besides, succenic acid with a smaller acid dissociation constant (pK_a value 4.16) provided fewer anions for complexing with Cu than the citric acid (Serjeant & Dempsey 1979). Therefore, the observed effects could be explained by the ligand-enhanced dissolution of the sorbent phases, the formation of aqueous organo-metal complexes, and the interaction of these complexes with the surfaces. Scheckel and Sparks (2001) indicate that organic ligands especially (citrate) reduced Ni sorption on gibbsite and pyroplyllite by suppressing the formation of surface reduced Ni precipitates.

Thermodynamic activation parameters of Cu desorption

The energy of activation measures the magnitude of the forces to be overcome during the process of desorption reactions. Energies of activation below 42 kJ/mol indicate diffusion controlled processes and higher values represent chemical reaction processes (Sparks 1995). The values of E_d ranged

Table 3. Reaction constants (k_d) of the first order kinetic equation and correlation coefficients (*r*) for Cu desorption as influenced by temperature and organic ligands

Organic ligand	$k_d \times 10^3$ (min^{-1})			*r**		
	288k	298k	308k	288k	298k	308k
Sandy soil						
Succinic	2.883	2.893	2.911	0.921	0.955	0.956
Citric	2.921	2.972	3.011	0.958	0.974	0.963
Clay soil						
Succinic	2.380	2.481	2.682	0.955	0.922	0.944
Citric	2.433	2.660	2.691	0.965	0.936	0.965

*significant at *P* = 0.01 level

from 0.35 to 1.12 kJ/mol in the sandy soil, and from 0.43 to 4.5 kJ/mol in the clay soil (Table 4). It is, therefore, concluded that Cu desorption from the studied soils in the presence of two organic ligands is a diffusion controlled reaction.

The enthalpy (ΔH^*), entropy (ΔS^*) and Gibbs free energy (ΔG^*) of activation values are presented in Table 4. The ΔH^* values are a measure of the energy barrier that must be overcome by reacting molecules (Jencks 1969). The values for ΔH^* (−1.19 to −2.12 kJ/mol) suggest that the desorption reactions are exothermic, meaning that they are not energy consuming process. The higher negative values of ΔH^* for Cu desorption from the two studied soils in the presence of succinic ligand indicate that the heat energy required to overcome the Cu desorption barrier was greater than that for Cu desorption in the presence of citric ligand (Elkhatib *et al.* 1993).

The values of ΔS^* are an indication of whether or not a reaction is an associative or dissociative mechanism (Atwood 1997). The entropy of activation ΔS^* parameter is often regarded as a measure of the width of the saddle point of the potential energy surface over which reactant molecules must pass as activated complexes (Sparks 1995). Entropy values > −10 kJ/mol generally imply a dissociative mechanism. However, in Table 4 one sees large negative values for ΔS^* suggesting that Cu desorption from the studied soils in presence of two organic ligands is an associative mechanism. Free energies of activation are considered to be the difference between the activated complex and the reactants from which it was formed (Laidler 1965). Computation of the free energy of activation (ΔG^*) yielded values ranging from 87 to 87.9. The largest value represents ΔG^* for Cu desorption for clay soil in the presence of succinic acid while the

lowest value represents ΔG^* for Cu desorption for sandy soil in the presence of citric acid.

Typically the ΔG^* values determine the rate of the reaction (rate increase as ΔG^* decreased) and once the energy requirement is fulfilled, the reaction proceeds. This is seen when comparing the data from Tables 3 and 4. In Table 3, the highest rate of Cu desorption was from sandy soils in the presence of citric acid (3.01×10^3 min^{-1}) at 35°C and the lowest rate was from clay soil in the presence of succinic acid (2.38×10^3 min^{-1}) at 15°C. Table 4 illustrates this trend for ΔG^* showing that the highest k_d value corresponds to the lowest ΔG^* value.

The information in this study is helpful to scientists seeking models capable of describing all possible sorption/desorption conditions and reactions within the soil environments. Moreover, temperature studies are quite necessary to construct full functioning models that will enable scientists to better understand and product mobility and bioavailability of metals in soils.

CONCLUSION

We examined the influence of two organic acids (succinate and citrate) on kinetics of Cu desorption from clay and sandy soils. The release rate from the studied soils followed first order kinetics. The Cu release rate in the presence of citrate was higher than that of succinate. The observed effects could be explained by the ligand-enhanced dissolution of the sorbent phase. As the temperature of the reaction increased from 15 to 35°C, the rate of Cu released from all soils increased. Such results indicate that rate of metal release depends in part on soil temperature. Various thermodynamic parameters such as activation energy

Table 4. Energies of activation (E_d) and thermodynamics activtion patameters for Cu desorption as affected by two organic ligands

Organic ligand	E_d	ΔH^*	ΔS^*	ΔG^*
	(kJ/mol)		(J/mol/k at 298k)	(kJ/mol at 298k)
Sandy soil				
Succinic	0.35 ± 07	−2.12 ± 08	−300 ± 0.26	87.50 ± 0.16
Citric	1.12 ± 07	−1.36 ± 07	−297 ± 27	87.0 ± 0.14
Clay Soil				
Succinic	4.5 ± 1.77	−2.02 ± 1.76	−287.9 ± 3.5	87.9 ± 3.53
Citric	0.43 ± + 0.1	−2.05 ± 0.1	−301 ± 0.3	87.7 ± 0.19

(E_d), the enthalpy (ΔH^*), entropy (ΔS^*) and Gibbs free energy (ΔG^*) have been calculated. The data showed that Cu desorption process is a diffusion controlled and exothermic reaction. Therefore, temperature studies are necessary to understand and predict bioavailability and mobility of metals in soils.

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