Soil properties affecting parameters obtained from two-site reaction modelling of cadmium sorption kinetics

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Abstract

This study investigated the applicability of a two-site reaction model to characterize the dynamic sorption process of Cd in different Chilean cropland soils. Using these results and a set of data previously reported, some soil properties that affect dynamic sorption parameters were established through regression analysis. The two-site reaction model fitted very well data from batch sorption experiments, showing that is possible to simplify the reactions involving the Cd dynamics combining an instantaneous equilibrium process of adsorption and a slow first-order kinetic process of immobilization/dissolution in the soil. It was not found effect of either soils'cation exchange capacity or clay content on the sorption behaviour of Cd. The linear partition coefficient and forward reaction rate constant (immobilization) were positively correlated to the soil pH, and the forward/backward (immobilization/dissolution) rate constants ratio was highly and positive correlated to the Cd in the adsorbed phase and the pH. Sorption parameters can be estimated from the soil pH and the Cd in the adsorbed phase (%) and can be further used in modelling assessment to predict the fate of Cd introduced into cultivated soils through fertilization practices.

Key Words

Reaction rate constants, partition coefficient, immobilization/dissolution, batch experiments, chemical fractioning

Introduction

Cadmium is one of trace elements of major environmental concern due to its toxicity and mobility in the soil-plant-water system. This element is found naturally in the soil, but it can also be incorporated by human agricultural activities like land application of P fertilizers, sewage sludge (SS), and other organic amendments (Chang and Page 2000). The former is the most important input source of Cd to the soil in developing countries. In Chile, for example, the Cd concentration in SS is 10 to 50 times lower than that found in P fertilizers and amounts of up to 288 mg of Cd per kilogram of P can be incorporated annually through the application of P fertilizers (Molina *et al.* 2009). In the receiving soil, Cd is distributed in an aqueous phase and the solid phase represented by the soil's colloids. The solution and solid phases are in dynamic equilibrium through complex chemical reactions that take place at the solid-solution inter-phase. Chen *et al.* (2006) used a two-site model to characterize the dynamic sorption process of Cd in the soil. The model, which combines a linear reaction equilibrium model and a first-order reaction kinetics model, allowed establishing differences between the reaction rates involved in the equilibrium of the solid-solution phase of two California cropland soils.

The objectives of this work were (i) to study the dynamic sorption process of this element in different soils using the two-site model mentioned above, and (ii) to establish relationships between some soil properties and the sorption parameters, using the results obtained in this study and the data previously reported.

Methods

Modelling approach (Chen et al. 2006)

In the model, the different sorption reactions are ascribed to different soil phases: i) Adsorbed phase, the chemically reactive portion of Cd in soil, which includes the Cd in soil solution and electrostatically adsorbed Cd and/or Cd weakly adsorbed on organic and inorganic soil components, and ii) Mineral phase associated to trace elements that are strongly bind to different solid phases with slow reaction rate in the soil. They are occluded by or co-precipitated with metal oxides (Fe, Al and Mn oxides), clay minerals, carbonates or phosphates and other secondary minerals. Assuming the water-to-soil ratio is R (L kg^{-1}) and the initial Cd concentration in the solution phase is C_0 (μg/mL), the mass balance equation in a Cd sorption experiment can be expressed by:

$$Ct \cdot R + K_a \cdot Ct + MP_t = C_0 \cdot R \qquad (1)$$

where K_a is the linear adsorption constant (L/kg) for Cd distribution between the solution and the adsorbed phase, and C_t (μg/L) and MP_t (μg/kg) are the Cd concentration in the solution phase and in mineral phase, respectively, at specific equilibration time (t). The slower reaction kinetics of the immobilized mineral phase can be described by the following first-order reaction equation:

$$\frac{\partial MP}{\partial t} = k_f \cdot (R + K_a) \cdot C_t - k_b \cdot MP \qquad (2)$$

where k_f and k_b are the forward and backward reaction rate constants (h^{-1}) corresponding to the immobilization (in the mineral phase) and dissolution processes, respectively. Combining Eq. (1) and (2), the time-dependent change of Cd in the solution phase and mineral phase is given by:

$$MP_t = \frac{k_f \cdot R \cdot C_0}{k_f + k_b} \cdot (1 - e^{-(k_f + k_b)t}) \qquad (3)$$

$$Ct = \left(\frac{C_0 \cdot R}{R + K_a} - \frac{k_f \cdot C_0 \cdot R}{(k_f + k_b) \cdot (R + K_a)} \right) + \frac{k_f \cdot C_0 \cdot R}{(k_f + k_b) \cdot (R + K_a)} \cdot e^{-(k_f + k_b)t} \qquad (4)$$

If t is fixed, the right-hand side of Eq. (3) and (4) may be reduced to a linear form in terms of C_0:

$$MP_t = a_1 \cdot C_0 \qquad a_1 = \frac{k_f \cdot R}{k_f + k_b} \cdot \left(1 - e^{-(k_f + k_b)t}\right) \qquad (5)$$

$$C_t = a_2 \cdot C_0 \qquad a_2 = \frac{R}{R + K_a} - \frac{k_f \cdot R}{(k_f + k_b) \cdot (R + K_a)} \cdot \left(1 - e^{-(k_f + k_b)t}\right) \qquad (6)$$

The Cd concentration in the solution phase (C_t) and in the mineral phase (MP_t) at specific t may be obtained for various C_0, and Ct vs. t would be a straight line. When C_0, is fixed, the right-hand sides of Eq. [3] and [4] may be reduced to an exponential form:

$$C_t = \frac{C_0 \cdot R}{R + K_a} - a_1 \ (1 - e^{-bt}) \qquad (7)$$

$$MP_t = a_2 \cdot (1 - e^{-bt}) \qquad (8)$$

$$\text{with} \quad a_1 = \frac{k_f \cdot C_0 \cdot R}{(k_f + k_b) \cdot (R + K_a)} \qquad b = k_f + k_b$$

$$\text{and} \quad a_2 = \frac{k_f \cdot R \cdot C_0}{k_f + k_b}$$

Soils and correlation analysis

Composed soil samples were obtained from the plow layer (0-25 cm) of five different Chilean cultivated soils varying in their physicochemical characteristics. The samples were passed through a 2-mm sieve, air-dried, and characterized for texture by the Bouyoucos hydrometer method, pH and electrical conductivity (soil-to-water ratio of 1:1), organic carbon by the Walkey-Black method, exchangeable bases by using 1 M ammonium acetate extraction at pH = 7.0, and $CaCO_3$ equivalent by a gravimetric method.

A regression and correlation analysis between some soils' characteristics and the Cd sorption and kinetics parameters was performed considering the results of the present study and the results reported by Chen et al. (2006) for the two cultivated soils of California. Parameters included were the K_d, and k_f, k_b (dependent variables). Soil properties as pH, cation exchange capacity (CEC), and clay and organic matter content were considered (independent variables). The $CaCO_3$ content was not included because this characteristic has similar values among soils. In the case of the kinetic parameters, the amounts of Cd present in the adsorbed and mineral phases obtained by the sequential extraction procedure were also considered in the correlations.

Sorption experiments and chemical fractioning procedure
Batch sorption isotherms were carried out at a solution-to-soil ratio of 20:1. Different Cd solutions were applied into centrifuge tubes containing one gram of dry soil and equilibrated for 48 h (fixed time) in a reciprocating shaker. The initial Cd solution concentrations were in the range of 50 to 2000 µg/L in 0.01M $NaNO_3$ background. After the equilibrating period, the supernatant was separated by centrifugation for Cd determination and the solid underwent a chemical fractioning procedure (Chen et al. 2006) to obtain the adsorbed and mineral phase of Cd. A second set of sorption experiments were conducted at initial solution concentration of 100 µg L^{-1} (fixed concentration) and using equilibrating times from two hours to 10 d. In all samples, the Cd concentration was determined by GF-AAS.

Results

The model fit very well the experimental data of instantaneous adsorption and kinetic equilibrium for all soils (R^2>0.900). Figure 1 shows the sorption isotherms of Cd and its distribution between the adsorbed (AD) and the mineral (MP) phases for two soils. The isotherms had a linear behaviour within the concentration range studied (50 to 2000 µg/L), which agrees with the theoretical description (Eqs. (5) and (6)) when the equilibration time (48 h) is fixed.

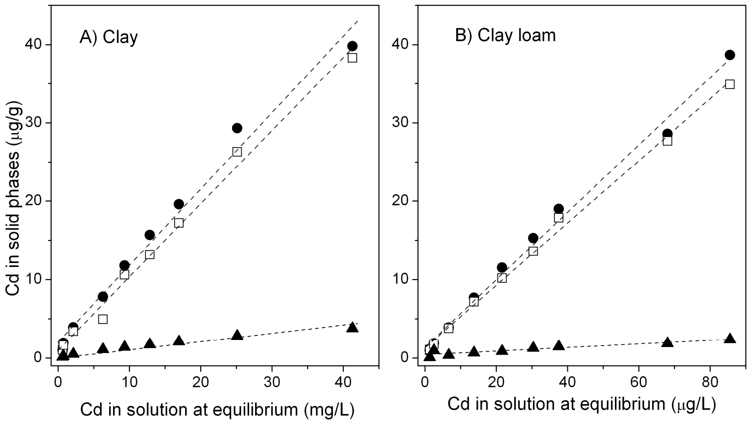

Figure 1. Sorption isotherms for a A) clay (pH=5.6) and B) clay loam (pH= 5.9) soil. Total Cd (●), adsorbed phase (□) and mineral phase (▲).

The results of sorption experiments at fixed initial concentration and at different equilibrium times for two soils are given in Figure 2. As predicted by Eqs. (7) and (8), while the amount of Cd in the solution phase dropped, the concentration in the mineral phase raised, exponentially with equilibrium time. In the evaluated soils, k_f values were higher than those for k_b.

In Table 1, the results of the correlation analysis are shown. The pH of the soil accounted for more that 90% of the variability seen in the values of K_d. It was found neither correlation with other soil properties nor an improvement in the fit of the regression when a second independent variable was added. Our results are in agreement with those reported in other sorption studies in which soil pH was the factor that had the largest effect on the values of K_d in natural and contaminated soils.

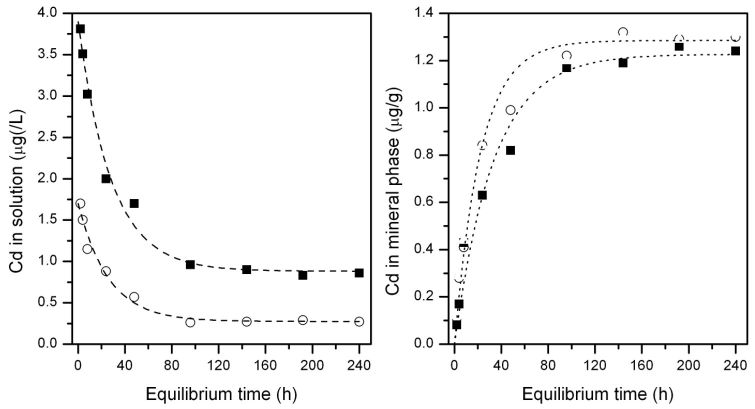

Figure 2. Cadmium in soil solution (left) and in mineral phase (right) for a clay (○)and clay loam (■) soil after different equilibrium times.

For example, Christensen (1989) working with Cd in low concentrations in 63 soils found that pH was the factor that most affect the K_d, and found no relationship of this parameter with the CEC. The correlation analysis showed that also k_f depended mainly on the pH of the soil (R=0.987). There was no effect of pH on k_b, but there was a certain tendency for it to increase with the Cd present in the MP. In turn, the k_f/k_b ratio was significant and positively affected by the amount of Cd present in the AD (R=0.984), and negatively affected by both the organic matter content (R=-0.999) and the Cd present in MP (R=0.967). The k_f/k_b ratio was highly correlated to Cd in the AD (%) and the soil pH.

Table 1. Correlation analysis between the average values of K_d, k_f, k_b, and k_f/k_b ratio and selected soil properties.

Independent variable	K_d		k_f		k_b		k_f/k_b ratio	
	R	p	R	p	R	p	R	p
pH	0.9299	0.010	0.9287	0.022	-	ns	0.8757	0.052
Clay (%)	-	ns[¶]	-	ns	-	ns	-	ns
Clay+Silt (%)	-	ns	-	ns	-	ns	-	ns
OM (%)[§]	0.9590	0.010	-	ns	0.8997	0.038	-0.9995	<0.001
CEC (cmol kg^{-1})	-	ns	-	ns	-	ns	-	ns
AD (%)[†]	-	-	-	ns	-	ns	0.9848	0.002
MIN (%)[‡]	-	-	-	ns	0.8679	0.056	-0.9674	0.007
AD and pH	-	-	0.9667	0.033	-	ns	0.9999	<0.001

[§] OM = organic matter, [†] AD: Cd in adsorbed phase, [‡] MIN: Cd in mineral phase.

[¶] ns: non-significant at p<0.05.

Conclusion

For all the soils evaluated, it was possible to fit adequately the experimental data from batch sorption experiments to the two-site reaction model. Sorption parameters can be estimated from the soil pH and the Cd present in the adsorbed phase, and can be further used in modelling assessment to predict the fate of Cd introduced into cultivated soils through the application of P fertilizers and other soil amendments.

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