A KINETIC SORPTION MODEL FOR CITRATE IN SOIL

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Abstract

Citrate is a low-molecular weight organic acid anion that is frequently released by plant roots into the rhizosphere. The negatively charged carboxylate has been found to beneficially influence plant growth by solubilizing nutrients (mainly phosphorus, iron, zinc) or by detoxifying rhizotoxic metals (aluminum).The beneficial effect of citrate in soil is determined by the proportion that is available in the soil solution. Therefore sorption is a fundamental soil process which needs to be accurately described. In this work we develop a new kinetic sorption model for citrate based on non-linear ordinary differential equations. The model incorporates two Freundlich sorption curves as stable steady states which represent ad- and desorption isotherms respectively. We describe the model development and parameter estimation based on experimental data for a specific soil type. Results of the of the kinetic sorption model showed good agreement with the observed kinetic data.

Keywords: Mathematical modelling, kinetic sorption, Freundlich isotherm

Presenting Author's Biography

Daniel Leitner graduated in mathematics at the Vienna University of Technology. He did his doctoral thesis about the simulation of blood flow at the Austrian Research Centers. He currently works as a postdoctoral research fellow at the University of Natural Resources and Applied Life Sciences in Vienna where he develops mathematical models describing rhizosphere processes. His main interests are continuous modelling and simulation, especially multiscale models, as well as the application of homogenisation and averaging techniques.

1 Introduction

The release of organic acid anions (e.g. citrate) by plant roots is considered an important plant response mechanism in order to increase nutrient availability or to detoxify heavy metals. [1]. The functional efficiency of citrate in soil is determined by the proportion that is available in soil solution which is commonly described using Freundlich sorption curves [2, 3].

Considering the dynamics of chemical reactions in the rhizosphere, the knowledge of long time sorption behaviour as described by the Freundlich equations is often not sufficient to describe changes in solution concentrations. Dynamic models are needed to accurately describe sorption kinetics. There are several different modelling approaches: The simplest is using a time dependent explicit empirical equation (e.g. an extension to the Freundlich equation) that is fitted to kinetic data [4]. Another approach is using multi-reaction models, which describe the reaction by ordinary differential equations using different pools with different reaction rates for the sorbed concentration (e.g. a slow and a fast pool) [5, 6] Finally, sorption can be described by diffusion into the matrix of the adsorbing material [3, 7].

In general parametrisation of kinetic sorption models is a difficult task, since the number of model parameters is high and initial conditions can often not be obtained by experimental measurements (e.g. differentiation of the sorbed concentration in a slow and in a fast pool). Furthermore, adsorption and desorption processes often show a different kinetic pattern, resulting in a so-called hysteresis effect. In this work we develop a new kinetic sorption model based on two Freundlich sorption curves, which represent ad- and desorption isotherms respectively. We first fit these two curves and determine the corresponding Freundlich parameters. In a second step, the remaining two parameters of the sorption model can be estimated from the kinetic data.

In the following we demonstrate our modelling approach with observations performed in the Bs horizon (30-45 cm) of a Podzol soil under sheep-grazed grassland at Abergwyngregyn, Wales, UK. A more detailed description of the experimental soil is given in [1]. The model is motivated by the observed hysteresis in sorption of citrate in soil. It is designed to describe all the observed effects in one model using only measured concentrations as variables.

2 The model

We describe the kinetic sorption of citrate by a model, which is based on the Freundlich equation. In the following we will first describe the fitting of Freundlich parameters to ad- and desorption isotherm data following the approach presented in [3]. Secondly, we will develop a new kinetic model utilizing these two sorption curves. The sorption curves enter the model as stable steady state solutions of an ordinary differential equation.

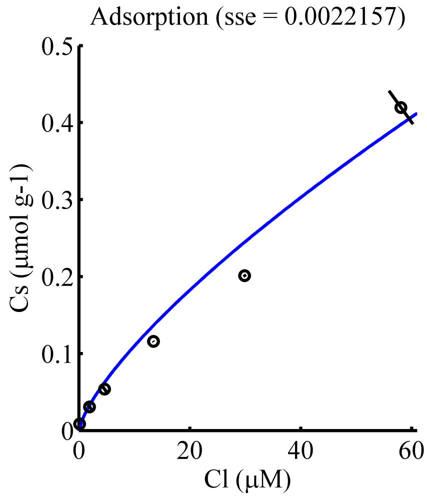

Fig. 1 A Freundlich sorption curve for adsorption ($k_{ad} = 0.02$, $n_{ad} = 0.731$), error bars are plotted along the line $c_s = c_{t,i} - ssr \cdot c_l$.

2.1 Fitting the adsorption curve

Experimental setting: To determine the sorption behaviour of citrate in the different experimental soils, adsorption isotherms in a 1:10 soil-to solution ratio were carried out. Soil (1 g dry weight) was heat sterilized (30 min, 80°C) and shaken with 10 ml of 1, 5, 10, 25, 50 and 100 μM ^{14}C-citrate (0.3 kBq g^{-1}) for 1 hour on a reciprocal shaker at 200 rev min^{-1}. Samples were centrifuged (5 min 18 000 $\times$ g) and the remaining ^{14}C-citrate concentration in the supernatant was determined by liquid scintillation counting using Wallac Optiphase HiSafe 3 scintillation fluid (Wallac EG&G, Milton Keynes, UK) and a MicroBeta TriLux counter (Perkin Elmer Life and Analytical Sciences Inc., Waltham, MA). All data points were carried out in duplicate. The amount of adsorbed citrate was calculated as difference between added concentration and concentration measured in the soil solution after the equilibration time.

Data fitting: We fit the Freundlich equation to the adsorption isotherm. The Freundlich equation is given by

$$c_s = k \cdot c_l^n, \tag{1}$$

where c_s is concentration of adsorbed citrate (μmol g^{-1}), c_l is the concentration of citrate in soil solution (μM), and k_f and n are the Freundlich parameters.

When fitting the Freundlich parameters to observed data it must considered that c_s and c_l are dependent,

$$c_s = c_t - ssr \cdot c_l, \tag{2}$$

where c_t is the total concentration in soil (μmol g^{-1}) and ssr is the solution soil ratio (L g^{-1}). Therefore a measurement error of c_l will result in an error of c_s. According to our model both Eqns (1) and (2) must be fulfilled. Therefore, the squared distance between an

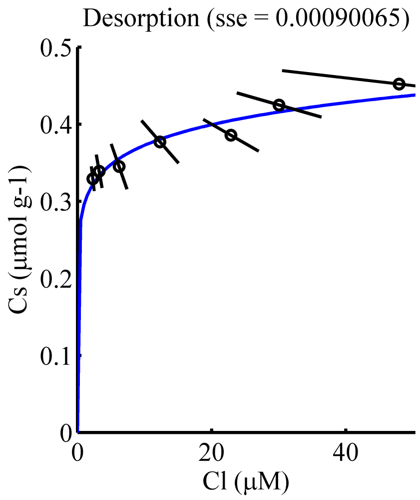

Fig. 2 A Freundlich sorption curve for desorption ($k_{de} = 0.296$, $n_{de} = 0.1$), error bars are plotted along the line $c_s = c_t - ssr_i \cdot c_l$.

observed data point ($c_{s,i}$, $c_{l,i}$) and the Freundlich sorption curve is obtained by first intersecting Eqn (1) and Eqn (2):

$$c_{t,i} - ssr \cdot c^*_{l,i} = k \cdot {c^*_{l,i}}^n, \tag{3}$$

where $c_{t,i}$ is the initial total concentration for observation i and ($c^*_{l,i}$,$c^*_{s,i}$) is the intersection point, where $c^*_{s,i} = c_{t,i} - ssr \cdot c^*_{l,i}$. The summed squared error sse is then given by

$$sse = \sum_{i=1}^{N} ssr^2 \cdot (c^*_{l,i} - c_{l,i})^2 + (c^*_{s,i} - c_{s,i})^2 \tag{4}$$

where N is the number of observations. Minimization of Eqn (4) yields the Freundlich parameters k_{ad} and n_{ad}. In Figure 1 we show the adsorption isotherm data with the corresponding Freundlich sorption curve. The error bars have the slope $-ssr$, see Eqn (2).

2.2 Fitting the desorption curve

Experimental setting: Desorption behaviour of citrate in the experimental soils was determined by using a parallel batch approach. As extraction solution 1 mM KCl was chosen because it does not interact with citrate. Heat sterilized soil Soil (1 g dry weight) was incubated with ^{14}C labelled citrate (0.5 mol g^{-1}) for 30 minutes. In the next step, different volumes of KCl (1 mM) were added to the experimental soils resulting in final soil-to-solution ratios of 1:1, 1:2.5, 1:5, 1:10, 1:25, 1:50, and 1:75. All treatments were carried out in triplicate. Samples were shaken for 1 hour at 200 rpm and then centrifuged. Desorbed ^{14}C citrate in the supernatant was determined by liquid scintillation counting as described above.

Data fitting: The fitting is done in the same way as for adsorption. The only difference is that c_t is constant for all observation but ssr is not. Therefore Eqn (3) is replaced by

$$c_t - ssr_i \cdot c^*_{l,i} = k \cdot {c^*_{l,i}}^n, \tag{5}$$

and $c^*_{s,i}$ is given by $c^*_{s,i} = c_t - ssr_i \cdot c^*_{l,i}$. Minimization of Eqn (4) yields the Freundlich parameters k_{de} and n_{de}. The desorption isotherm data with the corresponding Freundlich sorption curve is presented in Figure 2. The slopes of the error bars are different for each observation i and are given by $-ssr_i$.

2.3 A new kinetic model

The two sorption curves have a different shape, see Figures 1 and 2. This means that in our timescale there are two different equilibria for desorption and adsorption processes. Our aim is to develop a model that can describe this hysteresis effect.

We seek the simplest possible ordinary differential equations which has two stable steady states given by the two sorption curves:

$$\begin{aligned} c_t - ssr \cdot c_l &= k_{ad} \cdot c_l^{n_{ad}} \qquad (6)\\ c_t - ssr \cdot c_l &= k_{de} \cdot c_l^{n_{de}}, \qquad (7) \end{aligned}$$

where k_{ad} and n_{ad} are the Freundlich parameter for adsorption, k_{de} and n_{de} for desorption. On the left hand side of the equations the sorbed concentration c_s is expressed in terms of c_l. The dynamic model is given by

$$\frac{dc_l}{dt} = \frac{r}{ssr} f_{ad}(c_l, ssr) \cdot f_{us}(c_l, ssr) \cdot f_{de}(c_l, ssr), \tag{8}$$

where r represents a rate and the functions f_{ad} and f_{de} represent the two stable steady states given by

$$\begin{aligned} f_{ad} &:= (c_t - ssr \cdot c_l) - k_{ad} \cdot c_l^{n_{ad}} \text{ and} \qquad (9)\\ f_{de} &:= (c_t - ssr \cdot c_l) - k_{de} \cdot c_l^{n_{de}} \qquad (10) \end{aligned}$$

The function $f_{us}(c_l, ssr)$ represents an unstable steady state which must lie between the two stable steady states. A simple functional form of f_{us} is linearly interpolating between the f_{ad} and f_{de}:

$$f_{us} := \theta \cdot f_{ad} + (1 - \theta) \cdot f_{de}, \tag{11}$$

where θ is a value between 0 and 1.

The kinetic sorption model is given in Eqn (8). It has six parameters: two Freundlich parameters for adsorption (k_{ad}, n_{ad}), two Freundlich parameters for desorption (k_{de}, n_{de}), the rate k and the value θ. In the next section we present how the model parameters can be estimated from kinetic data.

2.4 Fitting the kinetic sorption model

Experimental setting: Adsorption kinetics were determined by measuring the change in concentration of ^{14}C-citrate in the soil solution over time after the addition of 0.5 mol citrate g^{-1} soil. Briefly, 10 ml of ^{14}C labelled citrate (0.3 kBq g^{-1}, 50 μM) were added to 1 g heat sterilized soil and the remaining concentration of ^{14}C-citrate in the soil solution was determined after 1,

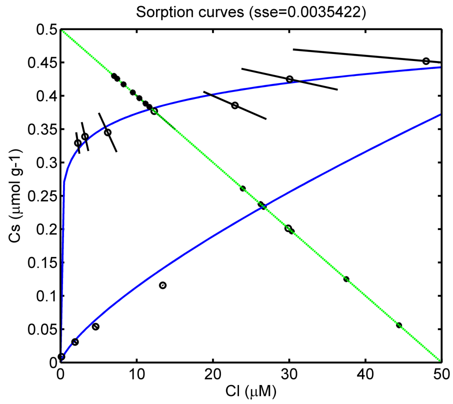

Fig. 3 Ad- and desorption equilibria after full parameter estimation. The plot shows: desorption curve (upper blue line), adsorption curve (lower blue line), the kinetic data lie on the line $c_t = c_s - ssr \cdot c_l$ (dotted green line).

2, 5, 10, 30, 60, 120, 240 and 480 minutes by analyzing a small aliquot (100 μl) of the soil suspension by liquid scintillation counting. For the desorption kinetics, heat sterile soil previously incubated with 0.5 μmol g^{-1} ^{14}C-citrate were shaken with 10 ml of 1 mM KCl 200 revolutions per minute. Soil suspension aliquots were sampled at the same time intervals as described for the adsorption kinetics and the amount of desorbed ^{14}C citrate was determined by liquid scintillation counting. All data points were carried out in duplicate.

Data fitting: Parameter estimation is performed by minimizing the summed squared error

$$sse = \sum_{i=1}^{N} ssr^2 \cdot (c^*_{l,t_i} - c_{l,t_i})^2 + (c^*_{s,t_i} - c_{s,t_i})^2 \quad (12)$$

where c_{l,t_i} are the observed kinetic data at times t_i, and c^*_{l,t_i} are the model results which are obtained by numerically integrating of Eqns (8)-(11) using the Matlab function `ode15s`. The sorbed concentrations are calculated from the total concentration c_t: $c_{s,t_i} = c_t - ssr \cdot c_{l,t_i}$ and $c^*_{s,t_i} = c_t - ssr \cdot c^*_{l,t_i}$.

The total summed squared error is obtained by adding up the errors of the ad- and desorption data (Eqn (4)) and the kinetic ad- and desorption data Eqn (12). In a first step the Freundlich parameters k_{ad}, k_{de}, n_{ad} and n_{de} are obtained. These parameters are used in the second step as initial parameters for the fitting of the full model.

3 Results

In Figure 3 we show the experimental observations and the sorption curves after the final model estimation. The kinetic data lie on the curve $c_s = c_t - ssr \cdot cl$, which is represented by the green dotted line. The Freundlich parameters changed less than 1.5 %. The parameters after the final model estimation were: $k_{ad} = 0.020674$, $k_{de} = 0.29263$, $n_{ad} = 0.73924$, $n_{de} = 0.10595$, $r = 3.2015$ and $\theta = 0.0139$. The summed squared error is $sse = 0.0057308$.

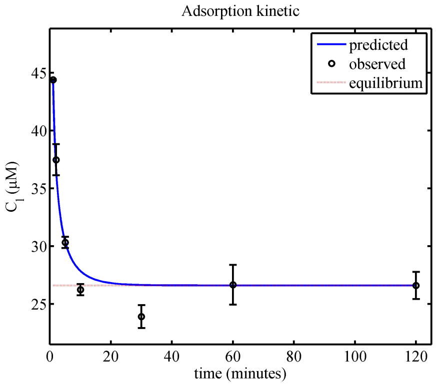

Fig. 4 Model results for kinetic adsorption.

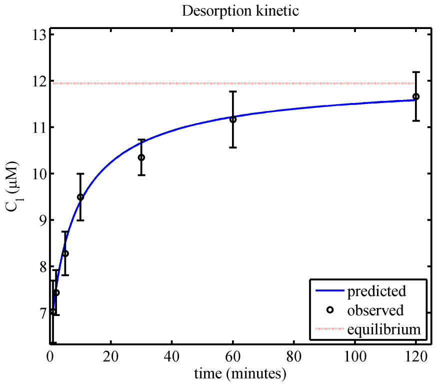

Fig. 5 Model results for kinetic desorption

For ad- and desorption we plotted the data points versus time in Figures 4 and 5 and showed the dynamic model results. The dotted horizontal line represents the equilibrium which is approached with increasing time. Model results matched the experimentally observed kinetic data within the expected error ranges.

4 Conclusion

We presented a new dynamic model describing the kinetic sorption of citrate. The model is able to capture the effect of hysteresis and is able to accurately represent the experimental observations. In contrast to multi reaction models our new model is parametrised using only measurable variables. This makes it a simple and adjustable tool to describe kinetic ad- and desorption processes.

Acknowledgements

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