

Application of linear and non-linear P-sorption models for describing phosphate transport

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Abstract

Phosphate transport in small columns was described using a two-site linear sorption model and using a non-linear adsorption-precipitation model. Using both approaches reasonable to good agreement with experimental breakthrough could be obtained. This result suggests the applicability of the simple linear model for engineering purposes, besides the more general applicability of the more involved non-linear model.

Keywords: phosphate, adsorption, precipitation, kinetics, transport, leaching

Introduction

The transport of phosphate (P) in soil is of interest from the scope of environmental concern due to the hazard of P-leaching in areas receiving large quantities of animal manure or sewage effluent. To describe phosphate transport in small columns, van der Zee et al. (1989) developed a non-linear P-sorption/precipitation model in which adsorption was described with the Langmuir equation and with P-precipitation given by a semi-empirical function of $I = \int (c - c_e) dt$. Here c is the concentration, c_e the equilibrium concentration, and t is time. Parameter assessment for this model was quite involved as adsorption and precipitation may occur simultaneously. Due to the non-linearity of the sorption model, no analytical solutions could be found to describe P-breakthrough, of use to directly fit experimental breakthrough curves. For the simpler two-site or dual porosity model (van Genuchten & Wierenga, 1976), with linear equilibrium adsorption in conjunction with a linear, first order kinetics sorption such a solution can be found. This allows parameter assessment directly from experimental breakthrough curves (Parker & van Genuchten, 1984). Therefore we tested the applicability of both models for describing P-breakthrough.

Theory

The applicability of the linear two-site model, with for site 1 and 2, respectively:

$$Q_1 = k_1 c \quad (1)$$

$$dQ_2/dt = k_r(k_2 c - Q_2) \quad (2)$$

(Q is adsorbed amount, k_1 and k_2 are the adsorption constants, and k_r is the adsorption rate constant) may be tested with the mathematical formulation of the dual porosity model as these models are mathematically indistinguishable. In the latter model sorption and transport occur in a mobile soil region. First order mass transfer describes the diffusional transfer to solute from mobile to immobile parts of the soil where also sorption occurs. Sorption in both regions is an equilibrium process following a linear isotherm. Assuming near-equilibrium between the mobile and immobile zones, which appeared justified from preliminary fitting analyses, the breakthrough curves should be fitted with

$$c_r = \frac{c(L,t) - c_i}{c_0 - c_i} = 0.5 \operatorname{erfc} \left[\frac{RL - vt}{2(DRt)^{0.5}} \right] + 0.5 \exp \left(\frac{vL}{D} \right) \operatorname{erfc} \left[\frac{RL + vt}{2(DRt)^{0.5}} \right] \quad (3)$$

where c_r is the relative concentration, $c(L,t)$ is the effluent concentration, L the column length, c_i the initial concentration, c_0 the feed concentration, v the flow velocity, D the dispersion coefficient and R the retardation factor, and where erfc is the complementary error function.

Materials and methods

The used NKR-1 soil (20-40 cm depth) was derived from a field in grassland in coversand parent material and was described by van der Zee & van Riemsdijk (1986). Analytical procedures to estimate sorption parameters were also given by van der Zee et al. (1989). Breakthrough curves were obtained for P ($c_0 = 3 \text{ mol m}^{-3}$) and chloride ($c_0 = 0.1 \text{ mol l}^{-1} \text{ NaCl}$, $c_i = 0.01 \text{ mol l}^{-1} \text{ NaCl}$) in columns with length 10 cm and with diameter 3.9 cm. Curve-fitting of Equation 3 was done with the CXTFIT-code of Parker & van Genuchten (1984), and yields estimates for R and D .

Results and discussion

For the non-linear P-sorption model (van der Zee et al., 1989) the sorption parameters were obtained from independent sorption and desorption experiments.

Using the dispersivity found for chloride breakthrough (i.e. $D/v = 0.71 \text{ cm}$), P-breakthrough was calculated numerically for two columns. In Column 1 (Fig. 1) the flow velocity was held constant at 3.28 cm h^{-1} and in Column 2 (Fig. 2) it was in-

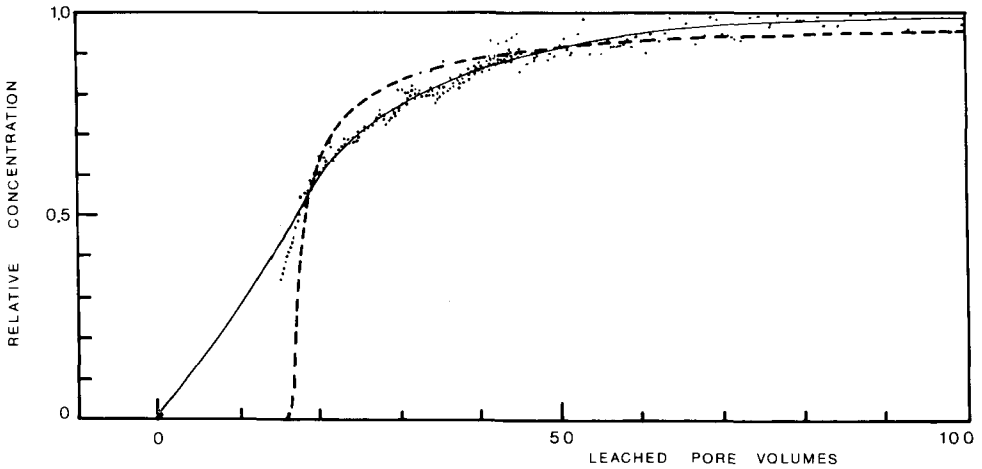


Fig. 1. Phosphate breakthrough for column 1. Experimental data (●), independent prediction with adsorption-precipitation model (dashed line), and fitted breakthrough curve with the two-site sorption model (solid line). Shown is the relative concentration, c_r (Equation 3) as a function of the percolated number of pore volumes ($= vt/L$), both being dimensionless.

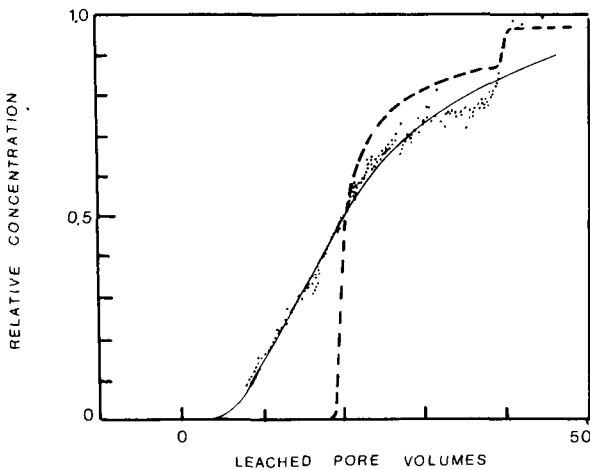


Fig. 2. Phosphate breakthrough for column 2. Experimental data (●), independent prediction with adsorption-precipitation model (dashed line), and fitted breakthrough curve with the two-site sorption model (solid line). Shown is the relative concentration, c_r , (Equation 3) as a function of the percolated number of pore volumes ($= vt/L$), both being dimensionless. The flow velocity (v) was increased after 331 hours or about 40 percolated pore volumes, which was accounted for in the non-linear model calculations only.

creased after 331 hours from 1.20 to 5.65 cm h⁻¹. Results are shown to agree reasonable with experimental data for Column 1 and for Column 2 only after initial breakthrough.

Better agreement was obtained by fitting Equation 3 (two side model) to the data. This equation was fitted for Column 2 on the basis of results for time smaller than 331 hours. Retardation factors found for both columns were in good agreement (R is 23 and 25), but apparent dispersion coefficients (D) for P varied significantly (11 for Column 1 and 3 for Column 2).

These results suggest that if a system is considered that resembles the experimental one closely, the two-site sorption approach may be use for optimizing system variables. Such a situation may be relevant in e.g. wastewater purification systems. If, however, conditions (such as the feed concentration) may differ significantly from those of the experimental situation, prediction with the adsorption-precipitation model is preferred in view of the non-linearity of P-sorption over a wide range of P-concentrations, and its better mechanistic background.

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