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Transport of cadmium, nickel, and zinc in Taoyuan red soil using one-dimensional convective–dispersive model

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Abstract

Pollution of agricultural lands by heavy metals has become more serious with increasing pollutants emitted from electroplate plants of northern Taiwan. This study aimed to assess the retardation factor (R) and the dispersion coefficient (D) using one-dimensional convective–dispersive model by comparing the breakthrough curve (BTC) and least squares methods. An acrylic column, with an inner diameter of 9 cm and a length of 15 cm, was uniformly packed with soil for metal leaching experiments. An unpolluted surface (0–20 cm) of the Taoyuan red soil was collected for this study. In miscible displacement experiments, a mixture of 4 mg L^{-1} $CdCl_2$, 20 mg L^{-1} $NiCl_2$, and 60 mg L^{-1} $ZnCl_2$ was leached from top of the column and the effluent was collected in increments with the aid of a fraction collector. The retardation factor (R) calculated from the least squares method was close to the R value observed from breakthrough curves. The R value showed the trend: Cd>Zn>Ni, indicating the rate of metals transport in red soils: Ni>Zn>Cd. Their reactivity was assessed within the framework of the hard–soft acid–base principle (HSAB). From sequential extractions, most of the Cd remained in exchangeable fractions, and Ni and Zn were found to exist in residual Fe- or Mn-oxides, and organic matter fractions.

Keywords: Breakthrough curve; Dispersion coefficient; Hard soft acid base principle; Red soil; Retardation factor

1. Introduction

Transport of hazardous pollutants to ground water is affected markedly by the extent of sorption by soils and aquifer materials (Alloway, 1995; Camobreco et al., 1996; McBride et al., 1997, 1999; Richards et al., 1998). In addition, chemical processes in soil can influence sorption reactions, and control the concentrations of pollutants in solution and their transport through the pedon (Akhtar et al., 2003). Therefore, the predictive accuracy of using solute transport to assess the fate of pollutants in soil profile is usually dependent on the proper determination of the adsorption constant and/or retardation factors

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(Chang et al., 2001). There are many methods for describing the transport of pollutants in soil profiles, such as chromatography (Valocchi et al., 1981), statistical approaches (Dagan and Bresler, 1979), and macroscopic methods (Wann and Uehara, 1978a,b; Smith and Schwartz, 1980). There are also previous studies on ammonium and nitrate (Misra and Mishra, 1977), pesticide transport (van Genuchten and Wagenet, 1989; Gamerdinger et al., 1990), chelation of Fe and Zn (Lahav and Hochberg, 1975), and dissolution and transport of gypsum (Keisling et al., 1978; Glas et al., 1979), salts (Melamed et al., 1977), and contaminants (Brusseau, 1994; Scotter and Ross, 1994) simulated in soil profile using the one-dimensional convection–dispersion model. This study aimed to assess the retardation factor (R) and dispersion coefficient (D) using such a model by comparing the breakthrough curve (BTC) and least squares methods.

2. Theory

Soil is a complex porous material. It is difficult to understand the fate of pollutants in soils. Because it is difficult to observe and measure the pollutants in agricultural lands, application of a mathematics model is thus recommended. Biggar and Nielsen (1962, 1963) and Barry and Sposito (1988) used a one-dimensional convection–dispersion equation to describe solute transport in soils. The equation expresses physical and chemical processes by the mathematics model:

$$R\frac{\partial C}{\partial t}=D\frac{\partial^2 C}{\partial x^2}-\bar{v}\frac{\partial C}{\partial x} \tag{1}$$

where the initial and boundary conditions are $C(0,t)=C_0,\ t\geq 0;\ C(x,0)=C_\mathrm{i},\ x\geq 0;\ C(\infty,t)=0,\ t\geq 0$.

Thus, the analytical solution according to the above assumption is:

$$C_\mathrm{e}(t)=\frac{1}{2}erfc\left[\frac{Rx-\bar{v}t}{2\sqrt{DRt}}\right]+\frac{1}{2}\exp\left(\frac{\bar{v}x}{D}\right)erfc\left[\frac{Rx+\bar{v}t}{2\sqrt{DRt}}\right] \tag{2}$$

Many studies have proposed analytical, numerical, and empirical solutions of Eq. (1). However, a simplified analytical solution was proposed by Danckwerts (1953) and Rifai et al. (1956), cited by van Genuchten and Wierenga (1986), which assumes that concentration changes due to dispersion alone and the sorption process can be described by a linear or linearized equilibrium isotherm:

$$C_\mathrm{e}(V/V_0)=\frac{1}{2}erfc\frac{R-\frac{V}{V_0}}{2\sqrt{\frac{D}{\bar{v}L}R\frac{V}{V_0}}} \tag{3}$$

where C_e is the solution phase concentration; V is the effluent volume (m^3); V_0 is the soil pore volume (m^3); $\bar{v}$is the pore water velocity (m s^{-1}); D is the dispersion coefficient (m^2 s^{-1}); L (cm) and R are the length of column and retardation factor, respectively; and erfc is the complementary error function. The right-hand side of Eq. (3) would be true if $\bar{v}L/D$ approaches infinity. Therefore, application of mathematical models fitted to the data of BTC of solutes flowing through the soil column can be described by Eq. (3); thus R and D were determined.

This study uses the convection–dispersion equation to describe solute transport in soils; R and D values were determined analytically by the (i) BTC method (van Genuchten and Wierenga, 1986; Skaggs and Leij, 2002) and (ii) least squares method (Amoozegar-Fard et al., 1983). The least squares calculation was reported in detail by Amoozegar-Fard et al. (1983).

According to Nielsen and Biggar (1963), the shape and position of the BTC are important for understanding the behavior of solute flowing through the soil column. Maraqa et al. (1998) reported that asymmetrical BTC is caused by either solute nonequilibrium or high dispersion. Nonequilibrium may be due to slow solute diffusion and/or chemical reaction. Therefore, if pore volume is set to unity, from BTCs of Cd, Ni, and Zn, the pore volumes required to wash $C/C_0=1$ are 41.3, 33.9, and 38.5, respectively. Because V_0, $\bar{v}$, and L are known parameters in Eq. (3), R and D can be determined by fitting BTC data to the equation. In this study, the retardation factors were estimated by BTC and least squares methods. van Genuchten and Wierenga (1986) used the number of pore volumes eluted as retardation factor when solute concentration of effluent equals half of the initial concentration (i.e., $C=0.5C_0$). The D and R were estimated according to Eq. (4):

$$\bar{v}L/D=4\pi R^2 S_\mathrm{R}^2 \tag{4}$$