



# Competitive modeling of sorption and transport of $Pb^{2+}$ , $Ni^{2+}$ , $Mn^{2+}$ AND $Zn^{2+}$ under binary and multi-metal systems in lateritic soil columns

S. Chotpantarat <sup>a,b,\*</sup>, S.K. Ong <sup>c</sup>, C. Sutthirat <sup>b,d</sup>, K. Osathaphan <sup>a,e</sup>

<sup>a</sup> Center of Excellence for Environmental and Hazardous Waste Management (EHWM), Chulalongkorn University, 254 Phayathai Road, Bangkok 10330, Thailand

<sup>b</sup> Department of Geology, Faculty of Science, Chulalongkorn University, 254 Phayathai Road, Pathumwan, Bangkok 10330, Thailand

<sup>c</sup> Department of Civil, Construction and Environmental Engineering, Iowa State University, Ames, IA 50011, USA

<sup>d</sup> Environmental Research Institute, Chulalongkorn University, 254 Phayathai Road, Pathumwan, Bangkok 10330, Thailand

<sup>e</sup> Department of Environmental Engineering, Faculty of Engineering, Chulalongkorn University, 254 Phayathai Road, Pathumwan, Bangkok 10330, Thailand

## ARTICLE INFO

### Article history:

Received 3 January 2012

Received in revised form 4 June 2012

Accepted 22 June 2012

Available online 18 August 2012

### Keywords:

Chemical nonequilibrium two-site model

Heavy metals

HYDRUS-1D

Lateritic soil

Sorption

## ABSTRACT

Transport of heavy metals from acid mine drainage through soils can impact valuable water resources and have a deleterious effect on their associated ecosystems. The movement of single, binary and multi-metal systems through lateritic soil columns were experimentally determined and then modeled with the HYDRUS-1D using a local equilibrium convection–dispersion ( $CD_{eq}$ ) model, or chemical nonequilibrium two-site model (TSM) with first order kinetics. The TSM model described the breakthrough curves better than the  $CD_{eq}$  model in both binary and multi-metal systems. The  $(Q_{max})/(Q_{max}^*)$  ratios were generally greater than unity suggesting that the presence of other metals reduced sorption through competition for sorption sites. Ratios of  $(Q_{max})_{Pb^{2+}}/(Q_{max})_{secondary\ metals\ (Mn^{2+}, Zn^{2+}, Ni^{2+})}$  (ranging from 0.92 to 1.09) were lower than ratios of  $(Q_{max}^*)_{Pb^{2+}}/(Q_{max}^*)_{secondary\ metals\ (Mn^{2+}, Zn^{2+}, Ni^{2+})}$  (ranging from 0.94 to 2.80), which indicated the highest sorption affinity of  $Pb^{2+}$  was under both binary and multi-metal systems. Furthermore, the fraction of the instantaneous equilibrium site ( $f$ ) of all metals, particularly for secondary metals, tended to increase with increasing metal concentrations in the system, suggesting that diffusion probably dominates the sorption and transport of heavy metals in the system.

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## 1. Introduction

Surface and groundwater pollution are largely caused by human activities, such as mining and smelting, agrochemical application, industrial discharges, energy production and improper waste disposal. The mobility of heavy metals through soils and groundwater is affected by many factors, such as the properties of the heavy metals, physical–chemical properties of the soil, and climatic conditions. Prediction of movement and distribution of heavy metals through the subsurface aquifer require knowledge of the sorption and transport properties of the porous media. Batch sorption experiments have generally been performed to investigate the sorption of two or more metals onto soils (Arias et al., 2006; Covelo et al., 2007; Elliott et al., 1986; Gomes et al., 2001; Jain and Ram, 1996; Serrano et al., 2005). For example, using batch studies for the competitive sorption of Cd and Pb onto four soils, Serrano et al. (2005) showed a higher retention of Pb over Cd in all four soils tested and the interaction between Pb and Cd sorption was found to a function of the soil properties. However, to obtain

transport information under non-equilibrium conditions, a packed soil column with continuous flow is typically used (Miretzky et al., 2006; Pang et al., 2004). To explain the transport of heavy metals in porous media, column experiments have been conducted but most of these studies are focused on a single metal under various flow conditions (Chotpantarat et al., 2011a; Liu et al., 2006; Miretzky et al., 2006; Pang et al., 2004; Strawn and Sparks, 2000; Yolcubal and Akyol, 2007). At typical contaminated sites, such as acid mine drainage sites, the presence of several heavy metals in groundwater is common and they may compete with each other for soil sorption sites, resulting in enhanced transport of heavy metals in the porous media. Several papers (Fonseca et al., 2011; Lafuente et al., 2008; Rodríguez-maroto et al., 2003) have addressed the sorption of heavy metals in multi-metal systems. For example, using columns with calcareous soils to evaluate Cr, Cu, Pb, Ni, Zn and Cd sorption, Lafuente et al. (2008) reported that sorption of Cr, Cu and Pb were higher than those of Ni, Zn and Cd under competitive conditions. Fonseca et al. (2011) reported that for a soil column with loamy sand soil, Cr and Cu were found to be more strongly sorbed due to an increase in the soil pH as compared to Cd, Pb and Zn. Furthermore, in order to predict the transport and distribution of heavy metals more accurately, reliable transport-related parameters of heavy metals in groundwater or subsurface environments need to be evaluated, but many studies to date have focused on the sorption of heavy metals under equilibrium conditions.

\* Corresponding author at: Department of Geology, Faculty of Science, Chulalongkorn University, 254 Phayathai Road, Pathumwan, Bangkok 10330, Thailand. Tel.: +66 831785470; fax: +66 22185464.

E-mail address: [csrlert@gmail.com](mailto:csrlert@gmail.com) (S. Chotpantarat).

However, some of the issues with multi-metal systems, such as possible competition between heavy metals for sorption sites, mass transfer and non-equilibrium sorption and transport on soils, and particularly soil that consists mainly of clay, are not completely known.

Many computer programs such as to CXTFIT (Toride et al., 1999), HYDRUS-1D (Šimunek et al., 2008), MACRO (Larsbo and Jarvis, 2003; Larsbo and Jarvis, 2005), SIMULAT (Diekkrüger, 1996), and VADOFT (Carsel et al., 1997) have been applied to model the transport of water and solutes. But for steady state conditions, CXTFIT is frequently used to describe tracer breakthrough curves using the analytical solutions for tracer or conservative miscible displacement tests as shown in the following studies: Vanderborght et al. (1997, 2002), Wallach and Parlange (2000), Kamra et al. (2001), Seo and Lee (2005), Yolcubal and Akyol (2007).

In addition, solute transport modeling under transient flow conditions requires a large number of model parameters, which are typically estimated from experimental results. These numerical models (i.e., MACRO, SIMULAT, VADOFT) including HYDRUS-1D, have many options to numerically estimate such parameters. However, HYDRUS-1D has been selected in this study because it has been used in hundreds of studies and is continually improved (Šimunek et al., 1998, 2005, 2008) to implement new modules such as Langmuir two-site model which are not included in MACRO, SIMULAT and VADOFT. HYDRUS-1D is a published program, which can be downloaded as freeware and has similar window interface with CXTFIT, making the programs easy to use in estimating water, conservative and non-conservative solutes.

The objective of this paper was to model the effects of heavy metal concentrations in single, binary and multi-metal systems on the competitive sorption and kinetic mechanisms in lateritic soil column experiments and to explain the competitive mechanisms in terms of the estimated sorption capacities, retardation factors and the fraction of instantaneous equilibrium sorption sites ( $f$ ). Lateritic soils (consisting of 53.8% clay) were collected from a gold mine site in Thailand and the breakthrough curves (BTCs) from column experiments, as reported by Chotpantarat (2008), were used in the modeling efforts. To this end, HYDRUS-1D (Šimunek et al., 2008), a local convection–dispersion equilibrium ( $CD_{eq}$ ) model with linear and nonlinear (Langmuir) isotherms and the chemical nonequilibrium two-site (TSM) model, plus CXTFIT (Toride et al., 1999), an analytical solution of the one-dimensional advection–dispersion equilibrium equation which include exchange between a mobile and an immobile region and the use of linear sorption, were used. Information obtained from this study may be used to explain the behavior of multi-metal transport in contaminated sites.

## 2. Materials and methods

### 2.1. Column experiments

Column experiments were conducted using lateritic soils obtained from Akara gold mine, Phichit Province, Thailand at a depth of 0–2 m below ground surface. The soil has a bulk and particle density of 1.23 and 2.71 g cm<sup>-3</sup>, respectively and the percent of sand, silt and clay were 21.8, 24.4 and 53.8, respectively. The pH of the soil was 5.3 while the cation exchange capacity (CEC) was 28.8 cmol kg<sup>-1</sup>. The organic matter and specific surface area of the soil were 0.16% and 48.69 m<sup>2</sup> g, respectively. Details of the experimental methodology column experiments used here have been reported previously (Chotpantarat, 2008; Chotpantarat et al., 2011b). Briefly, lateritic soils were uniformly packed in acrylic columns with an inner diameter of 2.50 cm and a depth of 10 cm. The soil column was initially saturated with deionized water from the bottom to eliminate entrapped air (Miretzky et al., 2006). After the saturation procedure, a solution of 30 mg L<sup>-1</sup> of bromide (Br<sup>-</sup>) was injected from the bottom at a rate of 8 ± 0.5 mL hr<sup>-1</sup> and the column effluent was collected using a fraction collector at various times. The system was maintained at a

constant pH of 5 with NaAc buffer solution. The mixed heavy metal solutions were then injected from the bottom of the column and the effluent collected periodically to monitor the concentrations of the respective heavy metals and pH in the effluent. The metal concentrations were determined by flame atomic absorption spectrophotometry (FAAS). The BTCs, expressed as the relative concentrations ( $C/C_0$ ) versus pore volume ( $V/V_0$ ), were plotted, where  $C_0$  is the initial concentration added and  $V_0$  is the pore volume of the soil column. The column experiments conducted were (i) single metal systems comprising of 5 mM of Pb<sup>2+</sup>, Mn<sup>2+</sup>, Ni<sup>2+</sup> or Zn<sup>2+</sup> at pH 5, (ii) binary metal experiments comprising of combinations of Pb<sup>2+</sup> and Mn<sup>2+</sup>, Pb<sup>2+</sup> and Ni<sup>2+</sup>, and Pb<sup>2+</sup> and Zn<sup>2+</sup> at pH 5 with Pb<sup>2+</sup> concentration fixed at 5 mM and Mn<sup>2+</sup>, Ni<sup>2+</sup> and Zn<sup>2+</sup> concentrations at 3 mM, 5 mM and 10 mM for each column run and (iii) a multi-metal system using all four metals, Pb<sup>2+</sup>, Mn<sup>2+</sup>, Ni<sup>2+</sup> and Zn<sup>2+</sup>, together at 5 mM each at pH 5.0.

### 2.2. Numerical transport modeling of column experiments

The BTCs obtained from the tracer experiments were analyzed with CXTFIT, a nonlinear least squares optimization computer program (Toride et al., 1999) with a number of analytical solutions for one-dimensional solute transport based on the convection–dispersion equation (CDE) and the two-region non-equilibrium model (TRM) for the estimation of hydrodynamic dispersion coefficient ( $D$ ), including the non-equilibrium parameters.

The  $CD_{eq}$  may be written as shown in Eq. (1) below:

$$\frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} - \frac{\rho}{\theta} \frac{\partial C^*}{\partial t} \pm \left[ \frac{\partial C}{\partial t} \right]_{rxn} \quad (1)$$

where  $C$  is the concentration of solute in liquid phase (mg L<sup>-1</sup>);  $t$  is the time (hr);  $D_L$  is the longitudinal dispersion coefficient (cm<sup>2</sup> hr<sup>-1</sup>);  $v_x$  is the average linear groundwater velocity (cm hr<sup>-1</sup>);  $\rho$  is the bulk density of aquifer (g cm<sup>-3</sup>);  $\theta$  is the volumetric moisture content or porosity for saturated media;  $C^*$  is the amount of solute sorbed per unit weight of solid (mg g<sup>-1</sup>) and rxn is the subscript indicating a biological or chemical reaction of the solute (mg L<sup>-1</sup> hr<sup>-1</sup>).

Unfortunately, CXTFIT is limited in that it does not have the analytical solutions for the transport of nonlinear sorbing solutes. Therefore, to assess the BTCs for nonlinear sorption of metals in the lateritic soil column experiments, HYDRUS 1D was used (Šimunek et al., 2008).

HYDRUS-1D was applied in both the direct and the inverse mode to assess the experimental BTCs using linear, nonlinear ( $CD_{eq}$  model) and rate-limited two-site sorption model (TSM model) as presented by Eq. (2) (Brusseau et al., 1991; Fetter, 1993):

$$\left( 1 + \frac{f\rho}{\theta} \left[ \frac{Q_{max}b}{(1+bC)^2} \right] \right) \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} - \frac{\alpha\rho}{\theta} \left( (1-f) \frac{Q_{max}bC}{1+bC} - s_2 \right) \quad (2)$$

where  $f(-)$  is the fraction of equilibrium sites and  $\alpha$  (day<sup>-1</sup>) is a first-order kinetic rate coefficient and  $S_2$  (mg g<sup>-1</sup> soil) is the solid phase concentration at site 2.

### 2.3. Parameter estimation

The columns were assumed to be homogeneously packed with the soil and saturated with water while the water flow and solute transport in the soil-filled columns were assumed to be one-dimensional. The hydrodynamic dispersion coefficient ( $D$ ) of the soil was estimated by curve fitting the bromide BTCs with the nonlinear least-squares parameters optimization method of CXTFIT (Toride et al., 1999). The two-region approach was then applied to examine any physical non-equilibrium processes in the system. The value of  $D$ , as obtained from the bromide BTC, was then used to estimate the average soil dispersivity,  $\lambda_{avg} = D_{avg}/v$ , which was then used to estimate the sorption parameters of metals, as provided by the HYDRUS-1D code version 4.Beta 1 (Šimunek et al.,

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