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Effect of pH on transport of Pb^{2+}, Mn^{2+}, Zn^{2+} and Ni^{2+} through lateritic soil: Column experiments and transport modeling

Srilert Chotpantarat[1,3,*], Say Kee Ong[2], Chakkaphan Sutthirat[3,4], Khemarath Osathaphan[1,5]

1. National Center of Excellence for Environmental and Hazardous Waste Management (NCE-EHWM), Chulalongkorn University, Bangkok 10330, Thailand. E-mail: lertc77@yahoo.com
2. Department of Civil, Construction and Environmental Engineering, Iowa State University, Ames, IA, USA
3. Department of Geology, Faculty of Science, Chulalongkorn University, Phayathai Road, Pathumwan, Bangkok 10220, Thailand
4. Environmental Research Institute, Chulalongkorn University, Phayathai Road, Pathumwan, Bangkok 10330, Thailand
5. Department of Environmental Engineering, Faculty of Engineering, Chulalongkorn University, Phayathai Road, Pathumwan, Bangkok 10330, Thailand

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Abstract

This study investigated the effects of pH on the transport of Pb^{2+}, Mn^{2+}, Zn^{2+} and Ni^{2+} through lateritic soil columns. Model results by fitting the symmetric breakthrough curves (BTCs) of bromide (Br^-) with CXTFIT model suggested that physical non-equilibrium processes were absent in the columns. The heavy metal BTCs were, however, asymmetrical and exhibited a tailing phenomenon, indicating the presence of chemical non-equilibrium processes in the columns. The retardation factors of Pb^{2+} were the largest of the four metal ions at both pH 4.0 (33.3) and pH 5.0 (35.4). The use of Langmuir isotherm parameters from batch studies with HYDRUS-1D did not predict the BTCs well. Rather the two-site model (TSM) described the heavy metal BTCs better than the equilibrium linear/nonlinear Langmuir model. The fraction of instantaneous sorption sites (f) of all four metal ions on the lateritic soil was consistently about 30%–44% of the total sorption sites.

Key words: pH effect; heavy metals; HYDRUS-1D; two-site model; lateritic soil

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Introduction

Pollutions from heavy metals is a very serious threat to both the environment, and also directly to human health, due to their toxicity and non-degradability. Heavy metal contamination of local environments is generated by both anthropogenic and natural sources. Historically, the mining industry is one of the major sources of heavy metal release into the environment (Wei et al., 2009). One of the consequences of mining is acidic mine drainage (Moreno and Neretnieks, 2006) where water infiltrating through the metal sulphide minerals, waste rocks and seepage from tailing dams can promote the leaching, solubilization and release of heavy metals into the surrounding soils and groundwater. According to previous studies, the pH is one of the most significant factors that affects transport and sorption of heavy metals to soils (Mesquita and Vieira, 2002; Scoullos and Pavlidou, 2003; Xiaohong et al., 2008). In addition, many mine soils when removed from the largely anaerobic subsurface, are rapidly oxidized and become acidic, leaching relatively large quantities of cations, such as calcium, manganese and iron. Many studies have focused on the sorption of heavy metals in soils under equilibrium conditions, using batch sorption experiments (Serrano et al., 2005; Arias et al., 2006). However, an alternative approach is used to investigate the transport of heavy metals in mine soils under a continuous flow column transport system, since this usually provides a better approximation of the field conditions and may provide information that is not available using equilibrium batch experiments (Pazka, 2003; Miretzky et al., 2006).

Pang et al. (2002) showed that the breakthrough curves (BTCs) of Cd, Zn and Pb in gravel columns with pore water velocities ranging from 3 to 60 m/day displayed long tailing, suggesting that non-equilibrium sorption conditions occurred in the gravel columns from the increasing pore water velocity. Kookana and Naidu (1998) observed that movement of Cd increased nearly four times in Oxisol soil when the background ionic concentration was increased from 0.03 to 0.15 mol/L $NaNO_3$. Although the pH is one of the major factors affecting sorption and transport of heavy metals, the effect of pH on the sorption and transport of heavy metals has not been evaluated using

* Corresponding author. E-mail: lertc77@yahoo.com

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the continuous flow column approach, especially for mine soils, despite its potential advantages, as mentioned above.

The Akara mining site is one of the active gold mines in Thailand and is actively generating vast masses of mine tailings which might be a major source of heavy metal contaminants in the future. Also, the possibility of acid mine drainage occurring at the site after mine closure is high, which may lead to leaching of heavy metals.

The objective of this research is investigate the effects of aqueous pH conditions on the sorption and transport of four heavy metals ions, Pb^{2+}, Zn^{2+}, Ni^{2+} and Mn^{2+}, through the lateritic soil found near the Akara mine area. Soil column experiments were conducted to understand the sorption and transport of heavy metals in the lateritic soils. The breakthrough curves (BTC) were then modeled using the HYDRUS-1D model (Šimuek et al., 2008) with both the linear and Langmuir sorption models under equilibrium and non-equilibrium conditions.

Table 1 Physical-chemical properties of the Akara mine

Property	Value	Bulk chemical composition	Value
pH	5.3	SiO_2 (wt.%)	48.41
Organic matter (%)	0.16	Al_2O_3 (wt.%)	40.58
Clay fraction (0.0005–0.002 mm) (%)	53.8	Fe_2O_3 (wt.%)	7.93
Silt fraction (0.002–0.075 mm) (%)	24.4	K_2O (wt.%)	0.82
Sand fraction (0.075–2.35 mm) (%)	21.8	CaO (wt.%)	0.85
Soil texture	Clay	MgO (wt.%)	0.58
CEC (cmol/kg)	8.2		
Specific surface area (m^2/g)	48.69		
Bulk density (g/cm^3)	1.23		
Specific gravity (–)	2.71		
Hydraulic conductivity (cm/hr)	3.17		
Permeability (cm^2)	8.01×10^{-9}		

1 Materials and methods

1.1 Soil samples and reagents

Bulk lateritic soils were collected from a depth between 0 and 2 m below the ground surface from the Akara mine area, located between 16°16′25″–16°17′41″N and 100°38′50″–100°40′15″E (Fig. 1). Soil samples were packed, transported back to the laboratory and stored at 4°C prior to use. All samples were crushed, air-dried and sieved through a 2-mm mesh prior to soil characterization and sorption studies. The physical-chemical properties of lateritic soil are summarized in Table 1. The soil texture and permeability were characterized using sieve and sedimentation methods (Allen, 1974), and the falling head permeability method, respectively. The soil pH was measured in distilled water at a 1:1 (V/V) ratio of soil to water (Van Reeuwijk, 1995). Cation exchange capacity was measured using 1 mol/L NH_4OAc (pH 7) solution extraction (Thomas, 1982), and the organic matter content was estimated as reported by Walkley and Black (1934). The specific surface area of the soil was determined using BET (Brunauer et al., 1938) with nitrogen (N_2) as the sorbate. The mineralogical composition of soil samples was determined using an X-ray fluorescence spectrophotometer (Model Axios, PANalytical, Almelo, the Netherlands). The X-ray fluorescence spectrophotometer was equipped with a Rh X-ray tube, a 4-kW generator, and an eight-position crystal changer. The spectrophotometer was interfaced to a computer with SuperQ software. The X-ray tube was operated at 36, 50 and 60 kV and 100, 72 and 60 mA. The four metal ion solutions, Pb^{2+}, Zn^{2+}, Ni^{2+} and Mn^{2+}, were prepared by dissolving $Pb(NO_3)_2$, $Zn(NO_3)_2{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$ and $MnCl_2{\cdot}4H_2O$, respectively, in dis-

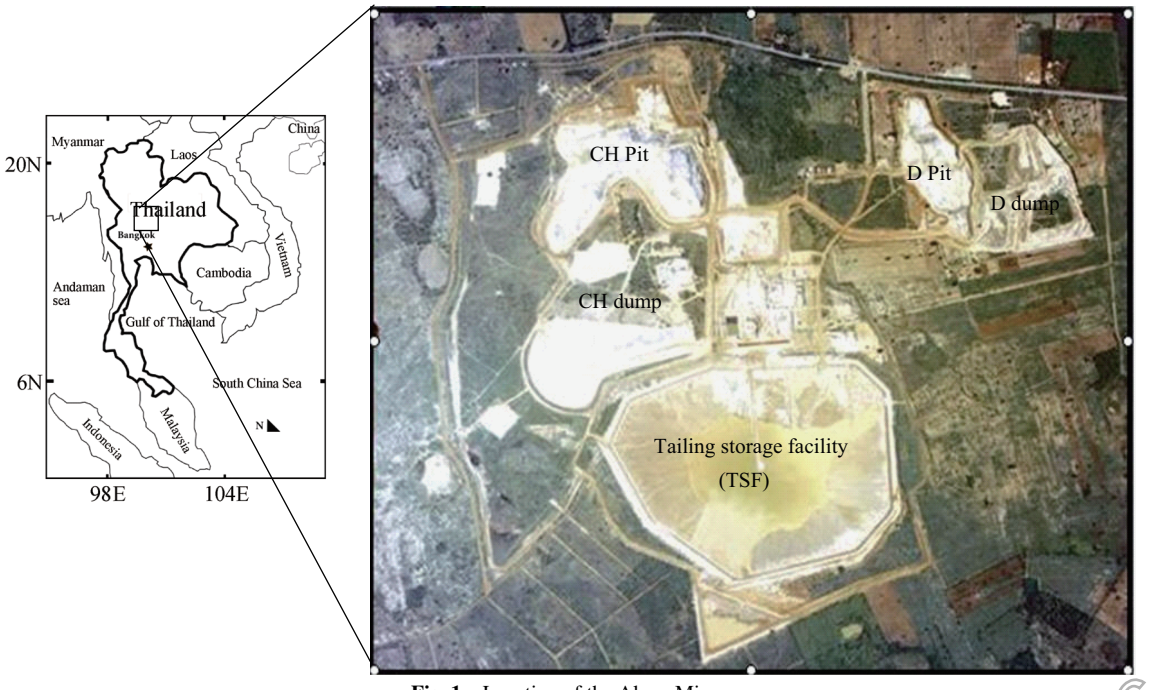

Fig. 1 Location of the Akara Mine.

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tilled water to obtain a 0.10 mol/L solution. A buffer solution containing 0.01 mol/L NaAc (CH_3COONa; pK_α = 4.76, MW = 136.08 g/mol) was used as the aqueous phase. NaOH and HNO_3 were used for the pH adjustments to maintain the pH as stated (pH 4.0 and 5.0). All the glassware used for dilution, storage and experiments were cleaned with non-ionic detergent, thoroughly rinsed with tap water, soaked overnight in a 10% (V/V) HNO_3 solution and finally rinsed with ultrapure quality water before use (Miretzky et al., 2006).

1.2 Tracer and heavy metals transport experiments

The columns used were acrylic tubes with a length of 10 cm and an internal diameter of 2.5 cm. The lateritic soil were packed into the columns by using a wet packing technique where a slurry of lateritic soil (soil:water (V/V) ratio of 1.3:1) was added in increments of 0.5 cm depth followed by gentle tapping of the column to consolidate the soil and remove air bubbles. The bottom cap consisted of an acrylic plate with small holes, covered with a fine 0.15 mm mesh to distribute the inflow. The soil column inflow was maintained at 8 mL/hr using a piston pump. The column experiments were conducted at room temperature (25 ± 1)°C. The soil column was initially saturated from the bottom with deionized water and at least six pore volumes (PVs) of deionized water was pumped through the column at a rate of 8 mL/hr, using a piston pump to eliminate trapped air and to minimize the possibility of preferential flow (Pang et al., 2004). After the saturation procedure, distilled water containing 30 mg/L of bromide (Br^-) at a rate of 8 mL/hr was injected from the bottom. After the tests were carried out, the bromide breakthrough curves were fitted by CXTFIT (Toride et al., 1999) to estimate the hydrodynamic dispersion coefficient (D), regardless of pH conditions. The value of D was then used to estimate the sorption parameters for the metal ions at pH 4.0 and 5.0. The column effluent was collected using a fraction collector of (8.5±0.5) mL fractions which were filtered and then analyzed for bromide using an ion chromatographer (IC) (Model Dionex ICS-2500, Sunnyvale, USA) equipped with an ED 50 Electrochemical Detector, GP50 Gradient Pump, AS50 Autosampler with temperature control, and a LC30 Chromatography Oven. After the test, about 6 PVs of the buffer solution was injected to establish the pH of the column. When the pH of soil column was constant (at pH 4.0 or pH 5.0 as required), as measured in the effluent from the column, one of the four metal solutions (Pb^{2+}, Mn^{2+}, Zn^{2+} or Ni^{2+}) at a concentration of 5.05 mmol/L was injected from bottom. The effluent was collected every one hour with a fraction collector. During the experiment, samples were taken from the test solution periodically to monitor the influent concentrations of metals and pH. The metal concentrations in the effluent were determined by flame atomic absorption spectrophotometry (FAAS) (Analytik Jena model ZEEnit 700, Jena, Germany). The BTC, expressed as the relative concentrations (C/C_0) and pore volume (V/V_0), where C_0 is the initial concentration added and V_0 is the pore volume of soil column, were plotted. Two column tests, Ni^{2+} at pH 4.0 and Pb^{2+} at pH 5.0, were duplicated to assure the consistency of column packing and reproducibility of the experiments.

1.3 Area method

The breakthrough data of the heavy metal ion studies were analyzed to determine their respective retardation factor (R) in the soil. This was estimated by the area above the frontal limb of the normalized BTCs and the line with a relative concentration (C/C_0) of 1.0 (Nkedi-Kizza et al., 1987). The retardation factors were calculated as Eq. (1):

$$R_{\text{area}} = \text{PV}_1 - \sum_{i=0}^{\text{PV}_1} \left(\frac{C}{C_0}\right) \Delta\text{PV} \tag{1}$$

where, C (mg/L) is the effluent concentration, C_0 (mg/L) is the influent concentration, and PV_1 is the number of the pore volume at which the relative concentration is 1.0.

1.4 Transport models

The CXTFIT model (Toride et al., 1999) was used to simulate the transport of conservative tracer to examine any stagnant (immobile) water in the columns and the HYDRUS-1D model (Šimuek et al., 2008) was used to evaluate the linear/nonlinear equilibrium and chemical non-equilibrium processes of heavy metal ion sorption and transport in the columns.

1.4.1 CXTFIT model

The CXTFIT 2.0 (Toride et al., 1999) program presents a number of analytical solutions for a one-dimensional transport model based on the convection-dispersion equation (CDE). The equilibrium CDE may be written as:

$$\frac{\partial C}{\partial t} = D_{\text{L}} \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} - \frac{\rho}{\theta} \frac{\partial C^*}{\partial t} \pm \left[\frac{\partial C}{\partial t}\right]_{\text{rxn}} \tag{2}$$

where, C (mg/L) is the concentration of solute in liquid phase; t (hr) is the time; D_{L} (cm^2/hr) is the longitudinal dispersion coefficient; v_x (cm/hr) is the average linear groundwater velocity; ρ (g/cm^3) is the bulk density of aquifer; θ is the volumetric moisture content or porosity for saturated media; C^* (mg/g) is the amount of solute sorbed per unit weight of solid; rxn is the subscript indicating a biological or chemical reaction of the solute (other than sorption).

It should be noted that the sorption parameters obtained from the CXTFIT program correspond to the K_{d} values of the linear isotherm. However, sorption is generally not linear for heavy metal ions. Therefore, the HYDRUS-1D model was applied to evaluate heavy metal ion sorption and transport in the columns.

1.4.2 HYDRUS-1D model

The HYDRUS-1D model (Šimuek et al., 2008) can be used to simulate the transport of heavy metal ions in soils and the model can be applied for different equilibrium and non-equilibrium flow and transport in both a direct and an inverse mode. The equilibrium convection-dispersion (CD_{eq}) transport model are shown (Eq. (2)), and the chemical non-equilibrium model or the two-site model (TSM)

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using Langmuir isotherm model as presented (Eq. (3)) (Selim et al., 1976):

$$\left(1+\frac{f\rho}{\theta}\left[\frac{Q_{\max}b}{(1+bC)^2}\right]\right)\frac{\partial C}{\partial t}= D\frac{\partial^2 C}{\partial x^2}-v\frac{\partial C}{\partial x}-\frac{\alpha\rho}{\theta}\left[(1-f)\frac{Q_{\max}bC}{1+bC}-s_2\right] \quad (3)$$

where, f is the fraction of equilibrium sites, α (day^{-1}) is a first-order kinetic rate coefficient, s_2 (mg/g soil) is the solid phase concentration at site 2, Q_{max} (mg/g) is the maximum sorption capacity of heavy metal ions per unit weight of soil and b (L/mg) is the Langmuir constant related to energy of sorption. The numerical solution in the HYDRUS-1D code (Šimuek et al., 2008) was used to optimize Q_{max}, b, α, and f.

1.5 Parameter estimation

The hydrodynamic dispersion coefficient (D) of the soil was estimated from the bromide BTCs using the nonlinear least-squares parameters optimization method in CXTFIT (Toride et al., 1999). The equilibrium convection-dispersion (CD_{eq}) model, with retardation factor (R) set to 1 and the two-region non-equilibrium convection-dispersion, was applied to examine any physical non-equilibrium processes in the system. The hydrodynamic dispersion coefficient estimated from the bromide BTC was then used to estimate the soil dispersivity, $\lambda = D/v$. The average dispersivity (λ_{avg}) of three bromide BTCs was introduced into the convection-dispersion model of HYDRUS-1D (Šimuek et al., 2008) to estimate sorption parameters of the heavy metal ions under different pH conditions using linear and nonlinear sorption isotherm models. Also, the chemical non-equilibrium TSM was used to estimate the sorption parameters (Q_{max} and b) and non-equilibrium parameters (f and α) for transport of the heavy metal ions. Sum of square errors (SSEs) were used to determine the appropriateness of the curve fitting. In addition, the column-determined sorption coefficients were compared with the previously reported batch-determined sorption coefficients (Putthividhya and Chotpantarat, 2007).

2 Results and discussion

2.1 Bromide BTCs

The best model fits for the equilibrium and the two-region non-equilibrium models of CXTFIT are presented in Fig. 2. The estimated column parameters are presented in Table 2. All bromide BTCs are symmetrical, indicating that equilibrium transport occurred in the columns. Moreover, the results of the two-region non-equilibrium model for the bromide BTCs gave β value of 1 and ω value of 100, suggesting that all the water in the system was mobile and the equilibrium model should be used for analyzing the bromide data (Pang et al., 2002). Comparison of the experimental results of the bromide BTCs (Fig. 2 and Table 2) showed that there were no significant differences in the dispersivity values. Thus, the average values of the dispersivity from the three columns were used in

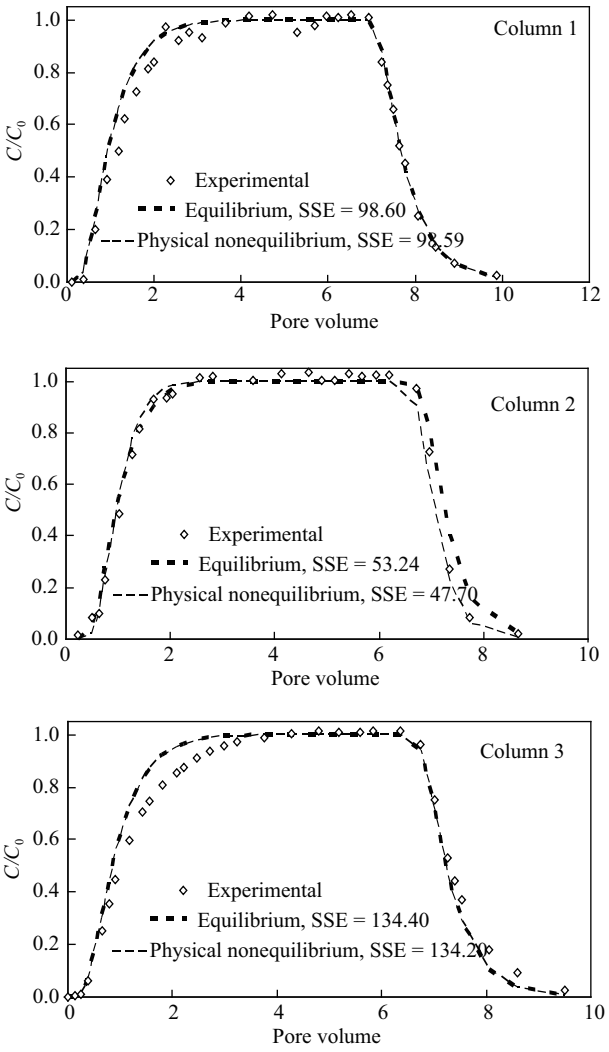

Fig. 2 Experimental and CXTFIT-simulated concentrations of the bromide BTCs. SSE: sum of square errors.

Table 2 Equilibrium convection-dispersion (CD_{eq}) and two-region model (physical non-equilibrium model) parameter values estimated from the bromide data

Experimental conditions		CD_{eq}			Two-region model				
Column	Measured velocity (cm/hr)	D (cm^2/hr)	λ (cm)	SSE	D (cm^2/hr)	λ (cm)	β	ω	SSE
1	2.54	4.71 ± 1.16	1.73 ± 0.49	98.60	4.48 ± 1.19	1.76 ± 0.47	1 ± 0.93	100	98.59
2	2.60	2.49 ± 0.64	0.96 ± 0.25	53.24	1.79 ± 0.48	0.69 ± 0.18	1 ± 0.66	100	47.70
3	2.64	4.15 ± 1.53	1.57 ± 0.58	134.40	4.15 ± 1.65	1.57 ± 0.58	1 ± 1.20	100	134.20

Data are presented as mean ± 95% confidence interval.

D: the longitudinal dispersion coefficient; λ: despersivity; SSE: sum of square errors; β: the partitioning coefficient between the equilibrium and nonequilibrium phases; ω: the mass transfer coefficient.

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Table 3 Physical-chemical and sorption isotherm parameters of the lateritic column at pH 4.0 and 5.0

	Metal	C_0 (mmol/L)	L (cm)	ρ (g/cm^3)	η (cm^3/cm^3)	q (mL/hr)	v (cm/hr)	R_{area}*	Sorbed metal (mmol/g soil)	Mass recovery (%)	PV
pH 4.0	Pb^{2+}	5.28	10	1.03	0.62	7.65	2.52	33.3	0.091	73.47	28.42
	Zn^{2+}	4.67	10	0.96	0.65	8.15	2.57	19.6	0.069	82.91	30.48
	Ni^{2+}	5.06	10	1.1	0.59	7.54	2.61	11.2	0.036	92.56	27.19
	Ni^{2+}**	5.28	10	1.03	0.62	7.53	2.48	11.2	0.043	91.18	33.49
	Mn^{2+}	4.87	10	0.93	0.66	7.97	2.47	17.9	0.067	79.87	31.49
pH 5.0											
	Pb^{2+}	5.05	10	1.03	0.62	7.76	2.55	35.4	0.117	73.45	31.50
	Pb^{2+}**	5.01	10	1.00	0.63	7.92	2.55	38.7	0.134	73.17	31.17
	Zn^{2+}	4.61	10	0.92	0.66	8.43	2.61	30.2	0.095	68.49	29.54
	Ni^{2+}	4.89	10	0.92	0.66	7.57	2.40	28.7	0.108	74.06	30.90
	Mn^{2+}	4.81	10	0.93	0.66	8.19	2.54	19.2	0.069	81.86	29.97

* Estimated from area method (Maraqa, 2001); **Duplicated column.
C_0: initial concentration, L: column length, ρ: bulk density, η: porosity, q: flow rate, v: average pore-water velocity, R: retardation factor, PV: pore volume of the soil column.

subsequent modeling of the heavy metal ion BTCs. The average dispersivity, λ_{avg}, obtained from CXTFIT program was equal to 1.42 cm.

2.2 Metal transport

The BTCs for the four heavy metal ions were evaluated under two different pH conditions. Table 3 shows the properties of the columns used in the heavy metal column studies. The Ni^{2+} column at pH 4.0, and the Pb^{2+} column at pH 5.0, were chosen for duplicate column tests as they had the lowest and highest retardation factors, respectively.

The retardation factors (Table 3) were estimated using the area methods (Maraqa, 2001) and the retardation factors for Pb^{2+} ions were the largest of the four heavy metals at both pH 4.0 and 5.0 with the following trend: $Pb^{2+} > Zn^{2+} > Mn^{2+} > Ni^{2+}$ for pH 4.0 and $Pb^{2+} > Zn^{2+} > Ni^{2+} > Mn^{2+}$ for pH 5.0. The difference in retardation factor sequences for Mn^{2+} and Ni^{2+} is due to a change in retardation factors for Ni^{2+} by more than 2 times from pH 4.0 to pH 5.0 while the retardation factors for Mn^{2+} remained similar in magnitude for both pHs. This probably suggests a change in the surface charges of the soil at different pH values due to less protonated Si-OH and Al-OH groups at pH 5.0, which affected the sorption of Ni^{2+} more than Mn^{2+}. The retardation factors were similar to those of Taoyuan soil; where Cd^{2+} (37.10) > Zn^{2+} (30.28) > Ni^{2+} (27.52) (Liu et al., 2006), and of the lateritic soil; where Cr^{3+} (98) > Pb^{2+} (50) > Zn^{2+} (17) ≈ Ni^{2+} (16) > Cd^{2+} (10) (Chalermyanont et al., 2008).

Schwertmann and Taylor (1989) found that sequence of the retention of heavy metal ions for goethite was in the order of Cu > Pb > Zn > Cd > Co > Ni > Mn, while hematite gave the same sequence except for an exchange in position of Cu and Pb. Gomes et al. (2001) investigated the distribution coefficients of heavy metals for seven agriculture soils and found that the most common sequences of the magnitude of the distribution coefficients were: Cr > Pb > Cu > Cd > Zn > Ni and Pb > Cr > Cu > Cd > Ni > Zn. The sequences of retention of other studies were similar to those for the column studies with $Pb^{2+} > Zn^{2+} > Mn^{2+} > Ni^{2+}$. The trend is also in line with the sorption capacity for this soil (Table 3), showing the highest sorption capacity in the order of $Pb^{2+} > Zn^{2+} > Mn^{2+} > Ni^{2+}$ for pH 4.0 and $Pb^{2+} > Zn^{2+} > Ni^{2+} > Mn^{2+}$ for pH 5.0.

As mentioned above, because of the stronger affinity for Pb^{2+}, the retardation factors were larger than the other tested metals at both pH 4.0 and 5.0, and consequently the BTCs of Pb^{2+} were longer than those of the other three metal ions (Fig. 3). Likewise, the sorbed metal ions per gram soil was higher for Pb^{2+} than the other three tested metal ions at both pH 4.0 and pH 5.0 (Table 3). Indeed, Pb^{2+} has been reported to have the strongest affinity to clays, peat and Fe-oxide when compared to other metals (Jain and Ram, 1996; Sauvé et al., 2000). As shown in Table 3, the retardation factors of these metals at pH 5.0 were higher than at pH 4.0 because there are less hydrogen ions (H^+) in the system at pH 5.0 than at pH 4.0 and, moreover, the Si-OH and Al-OH groups, the principal constituents of soils, are less protonated at pH 5.0 and, hence, they are more available sites to retain the heavy metals in solutions (Martínez-Villegas et al., 2004). As shown in Fig. 4, the sorption capacities (ca. 130.4% increase) and retardation factors (ca. 155.6% increase) of Ni^{2+} were significantly greater than those of the other three heavy metal ions with increasing pH, suggesting that the

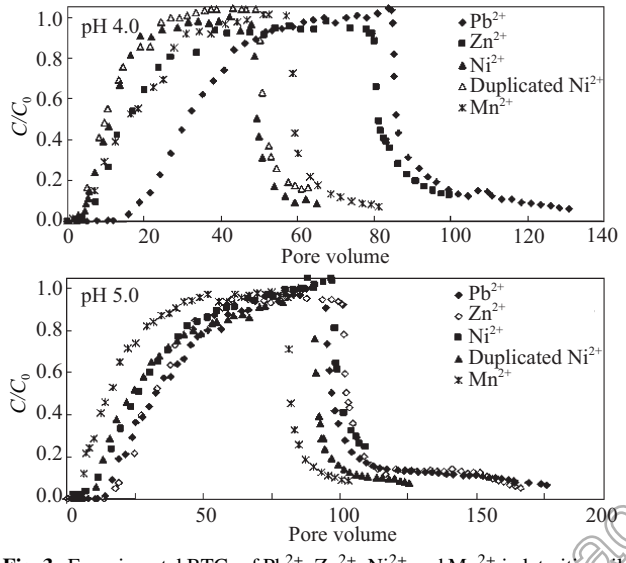

Fig. 3 Experimental BTCs of Pb^{2+}, Zn^{2+}, Ni^{2+} and Mn^{2+} in lateritic soil at pH 4.0 and pH 5.0.

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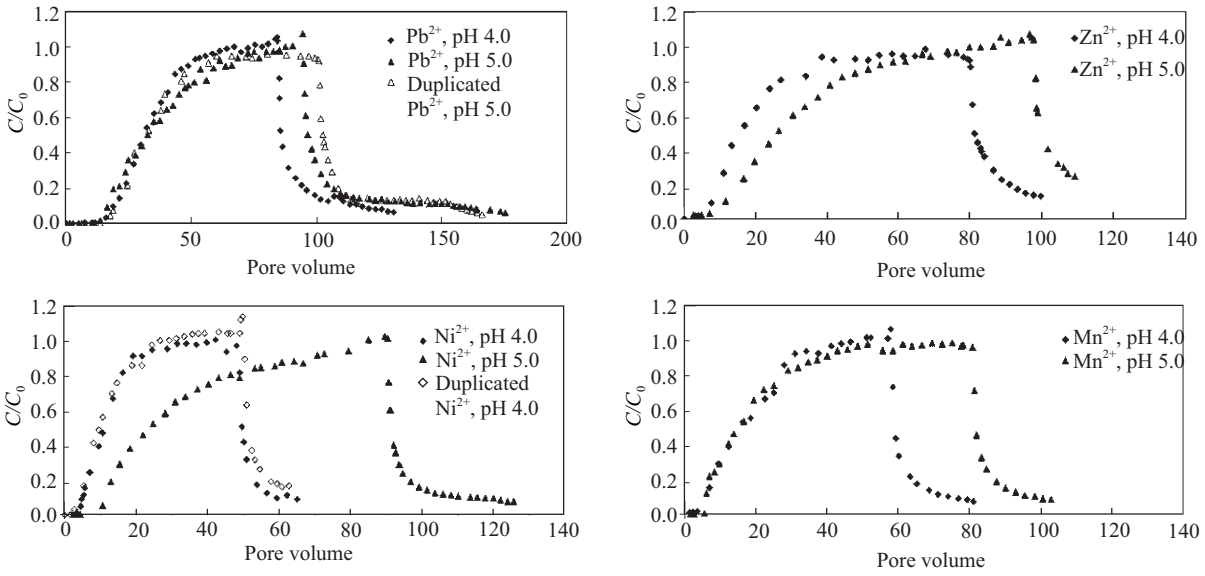

Fig. 4 Effect of pH on BTCs for Pb^{2+}, Zn^{2+}, Ni^{2+} and Mn^{2+} in lateritic soil.

hydrolyzed form, which was affected by pH, may be more important in Ni^{2+} sorption. This result is in agreement with the reported sorption of heavy metal ions in Brazilian soil, where the sorption of Ni^{2+} was found to be positively correlated to the pH (Gomes et al., 2001). Additionally, as shown in Table 3 and Fig. 4, the results of the duplicated columns were similar, showing consistency in column packing and experimental procedures.

2.3 Heavy metal transport–HYDRUS-1D Modeling results

Figure 5 shows the experimental data and simulated BTCs for Pb^{2+} pH 4.0 and 5.0 using HYDRUS-1D with the linear and nonlinear sorption equilibrium models and the non-equilibrium TSM to describe the main mechanisms controlling the heavy metal ion transport in lateritic soil. Similar BTCs and simulated curves for other metals are not presented here; however, Table 4 summarizes the estimated parameters for the metals using HYDRUS-1D.

2.3.1 Prediction of BTC using batch sorption data

Using the sorption parameters (Q_{max} and b) derived from the batch tests (Putthividhya and Chotpantarat, 2007) and the dispersivity (λ) values from the tracer test, HYDRUS-1D, with the local equilibrium assumption (LEA), was applied to generate the predicted BTCs of heavy metals at pH 4.0. Results from batch tests were adequately described by Langmuir sorption model with the estimated parameters as follows: Q_{max} at 0.16, 0.14, 0.10 and 0.08 mmol/g for Pb^{2+}, Zn^{2+}, Ni^{2+} and Mn^{2+}, respectively; and b at 0.22, 0.19, 0.24 and 0.26 L/mmol for Pb^{2+}, Zn^{2+}, Ni^{2+} and Mn^{2+}, respectively. As shown in Fig. 5a, the predicted Pb^{2+} BTC showed large deviations from the experimental data, except for the duplicated column of Ni^{2+} (SSE = 0.254). The predicted heavy metal ion BTCs using batch sorption parameters were unable to describe the experimental data at pH 4.0, suggesting that the resident time in the soil was not long enough for some sorption sites to reach equilibrium. The predicted Ni^{2+} BTCs were better than the predicted-BTCs for the other three metal ions, which may be due to the shorter time needed to reach equilibrium conditions for Ni^{2+} than the other tested metal ions (Chotpantarat, 2008). Another explanation for the deviations between the observed and predicted heavy metal ion BTCs may be due to the differences in soil: solution (V/V) ratios between the batch and column experiments (Bugisser et al., 1993). Unlike the bromide BTCs, heavy metal ion BTCs were asymmetrical and exhibited tailing, especially in the case of Pb^{2+} (Figs. 3 and 4), which might be due to the presence of non-equilibrium processes in the system. According to the bromide BTCs, the system was not influenced by physical non-equilibrium, suggesting that non-equilibrium conditions occurring in the lateritic soil column at this pore water velocity were primarily chemical non-equilibrium process. The observed non-equilibrium transport behavior was probably caused by rate-limited sorption.

2.3.2 Application of Linear and Langmuir isotherm using HYDRUS-1D with local equilibrium assumption

Using the local equilibrium assumption (LEA), linear and nonlinear Langmuir isotherm parameter estimations were performed to curve fit the heavy metal ion BTCs using the HYDRUS-1D code, as shown in Fig. 5. The Langmuir isotherm explained the experimental data better than the linear isotherm, a result which is similar to the batch tests (Putthividhya and Chotpantarat, 2007). The Q_{max} values derived from batch tests were similar to those derived from the fitting column experimental data with a Langmuir isotherm, but, in contrast, the binding energy values (b) of these metal ions derived from fitting the column experimental data (Table 4) were much greater than those obtained from the batch tests. Differences in the estimated b values between the batch and the column studies might be due to a difference in the soil: solution (V/V) ratios in the system, and to different flow schemes (i.e., a closed versus an open flow system for the batch and

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Table 4 Estimated transport parameters for heavy metal ion BTCs from equilibrium convection-dispersion and non-equilbrium approaches (2-site model) generated by HYDRUS-1D

No		Metal	λ** (cm)	Measured velocity (cm/hr)	Equilibrium model fitting				
					Linear		Langmuir		
					K_d ± 95%CI (L/g)	SSE	Q_{max} ± 95%CI (mmol/g)	b ± 95%CI (L/mmol)	SSE
1	pH 4.0	Pb^{2+}	1.42	2.52	20.40 ± 0.04	0.428	0.16 ± 0.03	6.71 ± 1.03	0.133
2		Zn^{2+}	1.42	2.57	9.45 ± 0.02	0.328	0.07 ± 0.03	1.69 ± 0.76	0.114
3		Ni^{2+}	1.42	2.61	6.46 ± 0.06	0.298	0.05 ± 0.01	1.82 ± 0.24	0.115
4		Ni^{2+} (Dup.)	1.42	2.48	7.54 ± 0.08	0.125	0.06 ± 0.03	0.38 ± 0.10	0.080
5		Mn^{2+}	1.42	2.47	11.25 ± 0.02	0.397	0.08 ± 0.02	0.83 ± 0.13	0.253
6	pH 5.0	Pb^{2+}	1.42	2.58	20.39 ± 0.01	0.428	0.17 ± 0.01	10.75 ± 0.21	0.148
7		Pb^{2+} (Dup.)	0.96*	2.55	24.53 ± 0.01	0.765	0.16 ± 0.07	6.09 ± 2.42	0.104
8		Zn^{2+}	1.42	2.61	20.31 ± 0.05	0.344	0.13 ± 0.06	1.34 ± 0.33	0.226
9		Ni^{2+}	1.42	2.40	12.81 ± 0.01	0.733	0.09 ± 0.09	4.24 ± 3.49	0.259
10		Mn^{2+}	1.73*	2.54	11.53 ± 0.01	0.281	0.08 ± 0.04	1.26 ± 0.80	0.166

No	pH	Metal	λ** (cm)	Non-equilibrium model fitting 2-site (TSM)				
				Q_{max} ± 95%CI (mmol/g)	b ± 95%CI (L/mmol)	f ± 95%CI	α ± 95%CI (hr^{-1})	SSE
1	pH 4.0	Pb^{2+}	1.42	0.15 ± 0.03	2.95 ± 0.57	0.44 ± 0.16	0.018 ± 0.007	0.036
2		Zn^{2+}	1.42	0.11 ± 0.04	1.09 ± 0.76	0.40 ± 0.06	0.016 ± 0.006	0.025
3		Ni^{2+}	1.42	0.06 ± 0.03	0.90 ± 0.39	0.35 ± 0.11	0.039 ± 0.023	0.049
4		Ni^{2+} (Dup.)	1.42	0.08 ± 0.03	0.44 ± 0.19	0.44 ± 0.05	0.039 ± 0.018	0.024
5		Mn^{2+}	1.42	0.10 ± 0.02	1.78 ± 0.39	0.33 ± 0.14	0.019 ± 0.010	0.069
6	pH 5.0	Pb^{2+}	1.42	0.20 ± 0.04	3.34 ± 0.78	0.31 ± 0.05	0.011 ± 0.001	0.020
7		Pb^{2+} (Dup.)	0.96*	0.20 ± 0.04	2.39 ± 0.54	0.42 ± 0.12	0.012 ± 0.005	0.044
8		Zn^{2+}	1.42	0.19 ± 0.03	0.65 ± 0.10	0.41 ± 0.05	0.016 ± 0.003	0.043
9		Ni^{2+}	1.42	0.18 ± 0.02	2.94 ± 0.38	0.34 ± 0.03	0.008 ± 0.001	0.050
10		Mn^{2+}	1.73*	0.12 ± 0.03	0.80 ± 0.26	0.33 ± 0.06	0.018 ± 0.007	0.047

* dispersivity derived from tracer test; ** average dispersivity derived from average of dispersivity values of three tracer columns.
CI: confidence interval.

the column studies, respectively). Although the optimized BTCs using the Langmuir isotherm fitted the data better than the linear isotherm, the curve-fitted BTCs using the Langmuir isotherm showed sharp concentration fronts which lagged the experimental data at both pH 4.0 and pH 5.0. The asymmetrical shape of the heavy metal ion BTCs, especially the long tailings (as for Pb^{2+}), have previously been shown to be described better by a non-equilibrium transport model (Pang et al., 2002; Tsang and Lo, 2006).

2.3.3 Application of chemical non-equilibrium two-site model (TSM)

The non-equilibrium TSM approach has been explored before to explain the failure of the local equilibrium model to describe heavy metal ion BTCs in soils (Pang et al., 2002). As mentioned above, the non-equilibrium is probably due to the kinetics of sorption occurring in the columns. As shown in Fig. 5, the TSM could describe the BTC of all four heavy metal ions in the system better than the linear and Langmuir models based on LEA, as seen by the SSEs at pH 4.0; $SSE_{TSM} < SSE_{Langmuir} < SSE_{Batch\ tests\ Langmuir} < SSE_{Linear}$. Applying the t-test on the average SSEs obtained from the chemical non-equilibrium TSM and the CD_{eq} model with Langmuir isotherm, it was found that the curve-fitted results of the chemical non-equilibrium TSM were significantly different from the CD_{eq} model for pH 4.0 and pH 5.0 (t-test, $P < 0.05$). This likely indicates that the fitted values by the chemical non-equilibrium TSM presented a better agreement with the experimental results (statistically significant, $P< 0.05$) than the CD_{eq} model. Because of the heterogeneous nature of the lateritic soil, sorption to some surfaces may not be in equilibrium. Certainly, the two metal cations, Cd^{2+} and Cu^{2+}, were spontaneously sorbed on exchangeable and carbonate fractions and equilibrium was attained within 30 min, but sorption on the other three fractions (oxide, organic matter and residual fractions) required a much longer time (ca. 7 days) to achieve equilibrium (Tsang and Lo, 2006). The latter three fractions reflect the rate-limited sorption behavior in that system. In Table 4, in the soil from the Akara mine, the maximum sorption capacities estimated by TSM were $Q_{max,Pb^{2+}} > Q_{max,Zn^{2+}} \approx Q_{max,Mn^{2+}} > Q_{max,avg.Ni^{2+}}$ for pH 4.0; and $Q_{max,avg.Pb^{2+}} \approx Q_{max,Zn^{2+}} \approx Q_{max,Ni^{2+}} > Q_{max,Mn^{2+}}$ for pH 5.0. Of the four metal ions, Pb^{2+} had the highest sorption capacity at both pH 4.0 and pH 5.0, which is in agreement with results of the batch studies (Putthividhya and Chotpantarat, 2007) and retardation factors obtained by the area method. The fraction of instantaneous site (f) of all four metal ions for the lateritic soil was consistently about 30%–44% of the total sorption sites, which may reflect the sand and silt fraction of the lateritic soil. Moreover, Pb^{2+} had the highest binding energy (b) in both the Langmuir model and the TSM model, which is in line with Pb^{2+} BTCs having a long tailing and showing the lowest recovery (Table 3).

The TSM provided a better prediction of the early tailing effect of the asymmetrical portion of the heavy metal ion BTCs than the local equilibrium model, but did not describe well the extended tailing of these heavy metals. This probably reflects that the rate of desorption can not

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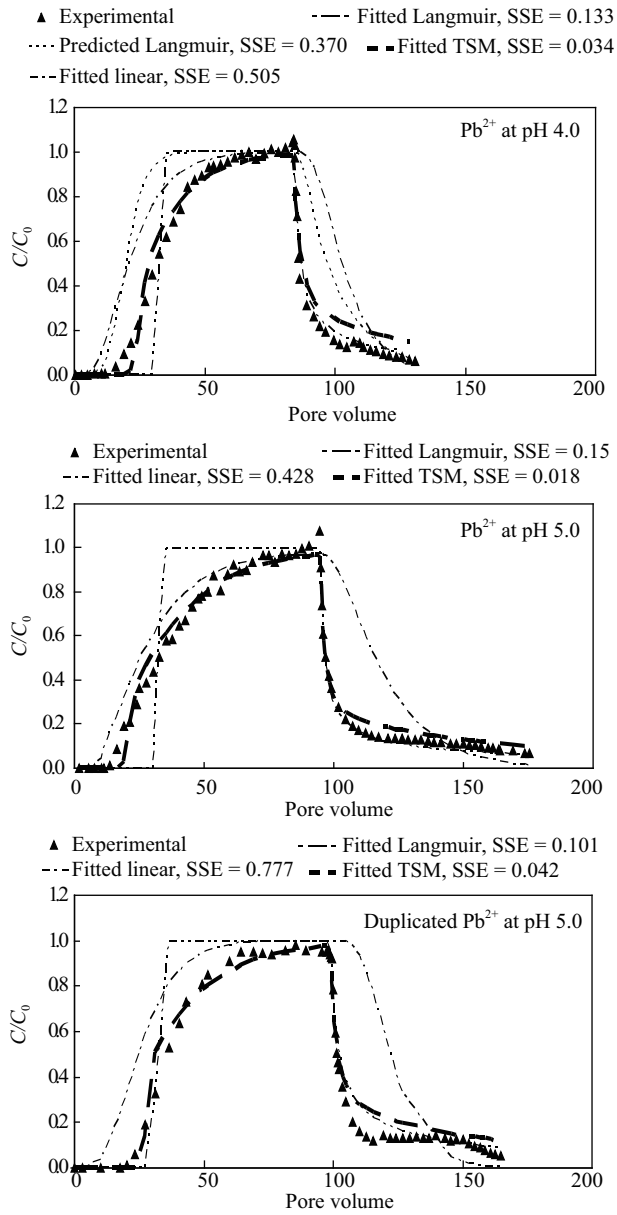

Fig. 5 Heavy metal breakthrough data for lateritic soil. Curves represent predictions of heavy metal concentrations using the convection-dispersion model (CDE) with independent parameters from batch experiments and tracer tests, optimized curve-fitting with linear and Langmuir isotherm, and the optimized curve-fitting with two-site model (TSM) model.

be described by a first-order rate constant (Selim, 1999) or that at least one other type of kinetic rate is needed to explain the system in addition to the instantaneous sorption and first-order rate constant. Along these lines, Selim (1999) observed that the sorption/desorption behavior of Cu^{2+} for a McLaren soil showed hyteresis behavior or nonsingularity at high concentrations, which could not be explained using a first-order rate constant. In addition, the extended tailings seen here may be controlled by mass transfer diffusion which was not accounted for in the TSM model (Beigel and Pietro, 1999). The kinetics of sorption/desorption, along with hyteresis and/or mass transfer, need to be further studied and, more precisely, represented for an accurate modeling and prediction of heavy metal ion transport through this soil. Based on the above analysis, the use of the batch-determined sorption parameters would not be proper for elucidating the transport of heavy metal ions when the residence time in soil is not long enough to reach equilibrium.

3 Conclusions

In this study, column experiments were carried out to investigate heavy metal transport through a lateritic soil at pH 4.0 and 5.0. Experimental BTCs of four heavy metal ions (Pb^{2+}, Zn^{2+}, Mn^{2+} and Ni^{2+}) showed that Pb^{2+} had the highest sorption capacity and retardation factor at both pH 4.0 and pH 5.0. The sorption capacity of heavy metals, particularly for Ni^{2+}, increased with increasing pH due to competition between hydrogen ions and metals as the aluminol and silanol groups become less protonated at higher pH values.

The symmetrical shape of Br^- BTC indicates absence of physical non-equilibrium conditions in the lateritic column. On the other hand, the asymmetrical shape of the heavy metal BTCs with long tailing (especially Pb^{2+}) may be caused by chemical non-equilibrium conditions during heavy metal ion transport through the lateritic soil.

The curve-fitted results of the HYDRUS-1D model indicated that the chemical non-equilibrium TSM described the observed data better than the CD_{eq} model (both linear and Langmuir isotherm) or by using the batch sorption parameters. The results suggest that care should be taken when using batch sorption isotherm and/or equilibrium approach to predict heavy metal transport. However, TSM was unable to describe the extended tailing of the BTCs of the heavy metals which may require addition of further processes in the model. Furthermore, the estimated fraction of instantaneous sorption was between 0.30 and 0.44 for all four metal ions at pH 4.0 and at pH 5.0, indicating non-equilibrium sorption exist for the bulk of the surfaces.

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