



Competitive sorption and transport of Pb^{2+} , Ni^{2+} , Mn^{2+} , and Zn^{2+} in lateritic soil columns

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ABSTRACT

Knowledge of sorption and transport of heavy metals in soils in the presence of other metals is crucial for assessing the environmental risk of these metals. Competitive sorption and transport of four metals, Pb^{2+} , Ni^{2+} , Zn^{2+} , and Mn^{2+} , were investigated using multi-metal column experiments with lateritic soils obtained from a gold mine impacted by acid mine drainage. Based on Pb^{2+} breakthrough time for single-metal system at a pH of approximately 5, the sorption capacity of Pb^{2+} was estimated to be higher in lateritic soil than the other metals. For multi-metal systems, the estimated retardation factors for the metals from highest to lowest were: $Pb^{2+} > Zn^{2+} \sim Ni^{2+} > Mn^{2+}$, suggesting the mobility of metals through lateritic soil for a multi-metal system would be in the order of $Mn^{2+} > Ni^{2+} \sim Zn^{2+} > Pb^{2+}$. For binary and multi-metal systems, the estimated sorption capacities of individual metals were found to be lower than the sorption capacities in single metal system – indicating possible competition for sorption sites. Mass recoveries estimates showed that the sorption of metals was more reversible under competitive multi-metal systems than in single metal systems.

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1. Introduction

The transport of heavy metals through soils has been investigated with great interest by both environmental and soil scientists. Heavy metals in wastes generated by anthropogenic activities and in disturbed geological formations can leach into the environment and contaminate soils and groundwater systems [1–3]. Pollution from heavy metals is a very serious threat not only to the environment but also to human health due to their toxicity, persistency and non-degradability. These metals include but are not limited to Cr, Mn, Ni, Zn, Cu, Pb, As, Cd, and Hg. For example, within a zone of 1 km from a copper mining and smelting site in southwestern Poland, Roszyk and Szerszen [4] found that the soils contained 250–10,000 $mg\ kg^{-1}$ of Cu, 90–18,000 $mg\ kg^{-1}$ of Pb, 0.3–10.9 $mg\ kg^{-1}$ of Cd, and 55–4000 $mg\ kg^{-1}$ of Zn. Mining activities generally release substantial amounts of wastes, caused by poorly designed and maintained storage facilities, poor environmental management of mining wastes and the consequences of acid mine drainage [2].

An understanding of the sorption and transport behavior of heavy metals is essential to assess the extent of contamination through subsurface aquifer for a contaminated site. Mining soils, when removed from the subsurface, are rapidly oxidized and become acidic, leaching large quantities of cations such as calcium, manganese, and iron. Batch sorption experiments are typically performed to investigate the sorption of two or more metals onto soils [5–8]. Batch competitive sorption studies, conducted by Vega et al. [9] for Cd, Cr, Cu, Ni, Pb and Zn onto five mine soils from Galicia, Spain, showed that Pb was the preferred retained metal, followed by Cr, Ni, Cd, and Zn, and the soils organic matter and oxide contents played an important role in controlling Pb sorption. Rodríguez-Maroto et al. [10] conducted batch sorption studies and indicated that the smaller hydrated radius of Pb^{2+} relative to Cd^{2+} was a likely reason for the higher retention of lead over cadmium under binary metal systems.

Column experiments can be used as an alternative to investigate the sorption and transport of metals and are considered to reflect field conditions more closer than batch studies and may provide information that are not available using equilibrium batch experiments [11–13]. Although there are more than one metal in the contaminated plume for most contaminated sites, many column studies on heavy metals sorption are focused on a single metal system [11,12]. The few papers on sorption of heavy metals in multi-metal systems include the work done by Lafuente et al. [14]

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Table 1
Physical–chemical properties of Akara lateritic soil.

Property	Value
pH	5.3
Organic matter (%)	0.16
Clay fraction (%)	53.8
Silt fraction (%)	24.4
Sand fraction (%)	21.8
CEC (cmol kg ⁻¹)	28.8
Specific surface area (m ² g ⁻¹)	48.69
Bulk density (g cm ⁻³)	1.23
Specific gravity (–)	2.71
Hydraulic conductivity (cm h ⁻¹)	3.17
Bulk chemical composition	
SiO ₂	48.41
Al ₂ O ₃	40.58
Fe ₂ O ₃	7.93
K ₂ O	0.82
CaO	0.85
MgO	0.58

where they studied competitive sorption and mobility of six metals, Cr, Cu, Pb, Ni, Zn, and Cd, in calcareous soil columns. They showed that competition between metals resulted in higher retention of Cr, Cu and Pb than Ni, Zn and Cd. The retention of Cr and Pb was hypothesized to be mainly regulated by the formation of strong covalent bonds as well as the possibility of formation of salts of the metal [15]. In the batch and column studies by Rodríguez-Maroto et al. [10], Pb was found to be more preferably sorbed than Cd onto agricultural soil. As a consequence, cadmium was more mobile and would move further in the soil. They also found that Langmuir isotherm including competitive sorption isotherms obtained from batch experiments were able to predict the results of the column experiments. However, some of the issues with multi-metal system such as interactions and competition between heavy metals for sorption sites and non-equilibrium sorption and mass transfer of metals are not completely known.

The objectives of this study were to investigate the influence of one or more heavy metals in mine tailings leachate and their concentrations on the retention and mobility of heavy metals through lateritic soil found at a gold mine. In this study, the heavy metals were Pb²⁺, Ni²⁺, Mn²⁺, and Zn²⁺ as these four metals were found in relatively high concentrations in the mine tailing leachate at a gold mine [16,17]. To accomplish these objectives, column studies were conducted to investigate the simultaneous transport of heavy metals in single, binary metal and multi-metal systems in lateritic soil.

2. Materials and methods

2.1. Soil samples and reagents

Bulk lateritic soils were collected at a depth of 0–2 m below ground surface from the Akara gold mine area, Phichit Province, Thailand. Soil samples were packed, transported back to the laboratory, and stored at 4 °C prior to use. All samples were air-dried, and sieved through 2-mm mesh prior to soil characterization and sorption studies. Table 1 presents the physical–chemical properties of the lateritic soil. Soil texture were determined using sieve and sedimentation methods [18] for a soil sample size of 200 g; the hydraulic conductivity was measured using the falling head method [19] which is suitable for cohesive sediment with low conductivities; bulk density was determined by core method [20] where undisturbed soil cores were used; specific gravity was determined according to ASTM Standard D854 [21]; soil pH was measured with a pH glass electrode for a 1:1 ratio of soil to water [22]; cation exchange capacity was measured using the 1 M NH₄OAc (pH 7) solution extraction method [23]; organic matter

content was estimated by the Walkley and Black method [24]; and soil specific surface area was determined using the BET method [25] using nitrogen (N₂) as the sorbate.

The mineralogical composition of the lateritic soils was determined using an X-ray fluorescence spectrophotometer. The four metals (Pb²⁺, Zn²⁺, Ni²⁺ and Mn²⁺) were prepared by dissolving amounts of Pb(NO₃)₂(s), Zn(NO₃)₂·6H₂O(s), Ni(NO₃)₂·6H₂O(s), and MnCl₂·4H₂O(s) in distilled water to obtain 0.1 mol L⁻¹ solutions. A buffer solution containing 0.01 M NaAc (CH₃COONa; pK_a = 4.76, MW = 136.08 g mol⁻¹) was used as the aqueous phase. NaOH and HNO₃ were used for pH adjustments to maintain a pH of 5. 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) HNO₃ solution and finally rinsed with ultra-pure quality water before use [26].

2.2. Tracer and heavy metals transport experiments

Acrylic columns with an inner diameter of 2.50 cm and a depth of 10 cm were uniformly packed layer by layer with lateritic soils. The packed soil columns may be assumed to be homogeneous. The soil column was initially saturated with deionized water from the bottom with at least 6 pore volumes (PVs) to eliminate entrapped air and to minimize the possibility of preferential flow [11]. Due to the very fine texture of the lateritic soil, the wet soil could not be compacted to a typical field soil bulk density. A bulk density about 1 g cm⁻³ was obtained. After the saturation procedure, a solution of 30 mg L⁻¹ of bromide (Br⁻) was injected from the bottom at a rate of 8 ± 0.5 mL h⁻¹ and the column effluent was collected using a fraction collector. The effluent was filtered and analyzed using ion chromatography. After injecting the Br⁻, about 6 PVs of NaAc buffer solution were injected to maintain a constant pH of 5. A solution pH of 5 was used since the pH of the lateritic soil was approximately 5.0 (see Table 1). The mixed metal solution was then injected from the bottom of the column and the effluent collected periodically to monitor the effluent concentrations of the metals and effluent pH. The metal concentrations in the effluent were determined by flame atomic absorption spectrophotometry. The breakthrough curves (BTC), expressed as the relative concentrations (C/C₀) versus pore volume were plotted, where C is the effluent metal concentration and C₀ is the influent concentration. The binary and multi-metal experiments conducted at different concentrations are presented in Table 2. Pb²⁺ was used as the main metal while Mn²⁺, Ni²⁺ and Zn²⁺ were used as the secondary metals. Peclet numbers for the column experiments were estimated to range from 5.85 to 9.37 which suggest that diffusion processes may be important. However, Bromly et al. [27] found that soils with the clay contents greater than 29.8% have larger dispersion coefficients than soils with less than 29.8% clay. The high clay content in the lateritic soil (53.8%) would indicate that dispersion is important.

2.3. Area method

The area method [28,29] presented below was used to determine the retardation factor (R) of each metal from the breakthrough curves of the column studies:

$$R = PV_1 - \sum_{i=0}^{PV_1} \left(\frac{C}{C_0} \right) \Delta PV \quad (1)$$

where PV₁ is the number of the pore volume at which the relative concentration is 1.0.

Table 2
Column experiments for binary metal and multi-metal systems.

System	Metals	Concentration (mmol)		pH
		Pb ²⁺	Mn ²⁺ or Ni ²⁺ or Zn ²⁺	
Single metals	Pb ²⁺ , Mn ²⁺ , Ni ²⁺ , Zn ²⁺	5	5, 5, 5	5
Binary metals	Pb ²⁺ –Mn ²⁺	5	3, 5, 10	5
	Pb ²⁺ –Ni ²⁺	5	3, 5, 10	5
	Pb ²⁺ –Zn ²⁺	5	3, 5, 10	5
Multi-metals	Pb ²⁺ –(Mn ²⁺ –Ni ²⁺ –Zn ²⁺)	5	5/5/5	5

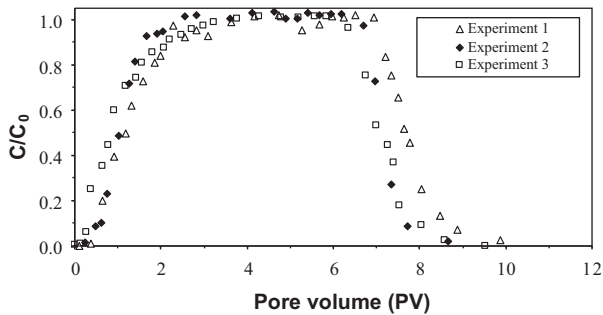


Fig. 1. Experimental breakthrough curves of bromide.

3. Results and discussion

3.1. Heavy metal transport – experimental results

3.1.1. Bromide breakthrough curves

Prior to heavy metal transport experiments, non-reactive tracer (bromide) tests were conducted to characterize the hydrodynamic properties of the lateritic soil columns. The results of these experiments are shown in Fig. 1. Under saturated steady state-flow conditions, the breakthrough curves (BTCs) of bromide were symmetrical, indicating ideal transport behavior in the lateritic soil columns [12].

3.1.2. Effect of secondary metals concentrations on mobility of Pb²⁺

Figs. 2–4 show experimental BTCs of Pb²⁺ in single, binary and multi-metal systems at pH 5. Table 3 shows some of the physical properties of the soil columns used in heavy metal column studies. The column experiments with Pb²⁺ at 5 mmol and Ni²⁺ at 3 mmol and Pb²⁺ at 5 mmol and Zn²⁺ at 10 mmol were repeated since these two column experiments gave the lowest (~30% decrease) and highest (~60% decrease) effects of the secondary metals (Ni²⁺ and Zn²⁺) on the retardation factors of Pb²⁺ (see Table 3). Over the experiment duration of about three weeks, a complete BTC of heavy metals was not achieved as seen by the extended tailing. It was observed that the BTCs for Pb²⁺ in a single metal system were longer than the BTCs for Pb²⁺ in binary systems for different initial

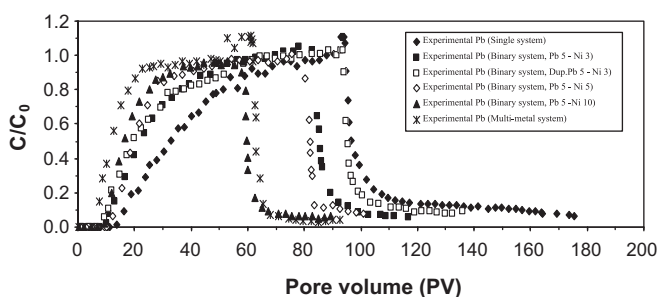


Fig. 2. Effect of Ni²⁺ on Pb²⁺ retention onto lateritic soil at pH 5.

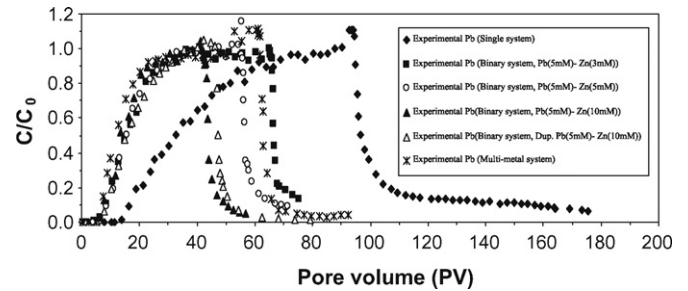


Fig. 3. Effect of Zn²⁺ on Pb²⁺ retention onto lateritic soil at pH 5.

concentrations of secondary metals. For example, the initial breakthrough time for Pb²⁺ was about 9 PVs in the Pb²⁺ (5 mmol)–Ni²⁺ (3 mmol) system while the breakthrough time was about 14 PVs in a single Pb²⁺ system (Fig. 2). The BTCs of Pb²⁺ in binary systems with increasing concentrations of secondary metal were found to be shorter than the BTCs in a single Pb²⁺ system (Figs. 2–4).

Another observation for binary systems was that the breakthrough times for secondary metals were earlier than that for Pb²⁺. For example, the breakthrough time for Ni²⁺ was about 5 PVs, which was less than the 9 PVs for Pb²⁺ in a Pb²⁺ (5 mmol)–Ni²⁺ (3 mmol) system (Fig. 2).

The longer breakthrough time for Pb²⁺ is most likely due to adsorption. Pb²⁺ has a smaller hydrated radius of 0.187 nm than Ni²⁺ (0.232 nm), Zn²⁺ (0.233 nm), and Mn²⁺ (0.235 nm) leading to higher coulombic or ionic forces of attraction of Pb²⁺ to the soil surfaces than the other metals. Work done by Rodríguez-Maroto et al. [10] showed similar trends to this study where Pb²⁺ was preferably retained as compared to Cd²⁺, suggesting that the hydrated radius may play a role (Cd²⁺ hydrated radius is 0.23 nm which is larger than that of Pb²⁺). In addition, Pb sorption was observed to be positively correlated with aluminum oxide, iron oxide and CEC as compared to other metals in competitive systems of Cd, Cr, Cu, Ni, Pb and Zn [6,30,31]. Due to the presence of other metals in the systems, the retardation factors of Pb²⁺ in such systems were lower than that for single Pb²⁺ system (Table 3). For example, for the Pb²⁺–Ni²⁺ system with 3, 5, and 10 mmol of Ni²⁺, the retardation factors of Pb²⁺ changed from 37.0 in single metal system to 25.5 (~30% decrease), 22.7 (~40% decrease), and 18.7 (~50% decrease) for the different

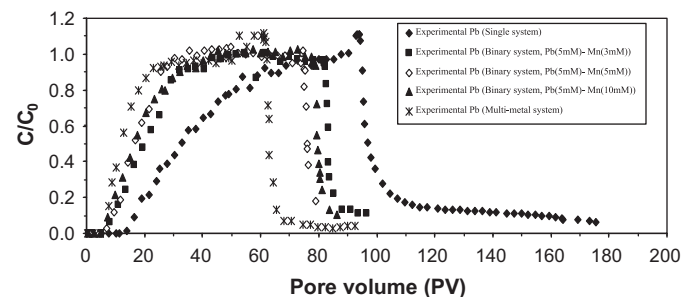


Fig. 4. Effect of Mn²⁺ on Pb²⁺ retention onto lateritic soil at pH 5.

Table 3
Summary of parameters of the lateritic column studies with binary and multi-metal systems at 5. C_0 initial concentration, L column length, ρ bulk density were determined experimentally, η porosity, q flow rate, ν average pore-water velocity, R retardation factor, R_{area} retardation factor, PV pore volume of the soil.

System	C_0 (mmol)	L (cm)		ρ (g cm ⁻³)	n (cm ³ cm ⁻³)	q (mL h ⁻¹)	ν (cm h ⁻¹)	PV	R_{area} ^b		Sorbbed/g soil (mmol g ⁻¹)		Mass recovery (%)	
		1st metal (Pb ²⁺)	2nd metal						1st metal (Pb ²⁺)	2nd metal	1st metal (Pb ²⁺)	2nd metal		
Pb ²⁺ -Ni ²⁺	0	4.89	10	0.92	0.66	7.57	2.40	30.90	-	28.65	-	0.108	-	74.06
	5.05 ^a	0	10	1.03	0.62	7.76	2.55	31.5	35.35	-	0.117	-	73.45	-
	5.01 ^c	0	10	1.00	0.63	7.92	2.55	31.2	38.71	-	0.134	-	73.17	-
	4.86	3.01	10	1.00	0.63	8.45	2.72	31.5	25.53	17.68	0.082	0.037	78.03	86.64
	4.85 ^c	3.17	10	1.00	0.63	8.20	2.64	31.5	25.02	15.92	0.083	0.035	82.46	87.53
Pb ²⁺ -Zn ²⁺	4.93	5.13	10	1.04	0.62	8.21	2.71	32.1	22.74	13.77	0.076	0.048	76.88	87.18
	4.88	10.06	10	0.99	0.64	7.76	2.49	34.2	18.47	9.31	0.057	0.067	81.53	94.55
	0	4.61	10	0.92	0.66	8.43	2.61	29.54	-	30.15	-	0.095	-	68.49
	5.26	2.91	10	1.04	0.62	8.16	2.69	36.5	17.02	10.61	0.087	0.024	79.67	88.53
	5.22	5.36	10	1.04	0.62	8.19	2.71	36.4	16.81	9.50	0.067	0.039	79.97	91.91
Pb ²⁺ -Mn ²⁺	5.41	9.67	10	0.94	0.65	7.97	2.49	32.5	15.07	8.50	0.055	0.055	79.13	98.10
	4.33 ^b	9.48	10	0.92	0.66	7.63	2.35	29.9	17.41	9.61	0.056	0.068	72.45	93.11
	0	4.81	10	0.93	0.66	8.19	2.54	29.97	-	19.22	-	0.069	-	81.86
	5.31	2.73	10	1.04	0.62	8.58	2.84	30.5	20.90	13.92	0.079	0.024	81.12	88.99
	5.14	4.47	10	1.00	0.63	7.62	2.46	30.2	17.31	10.40	0.067	0.038	86.39	94.98
Pb ²⁺ -Zn ²⁺ -Ni ²⁺ -Mn ²⁺	4.85	8.66	10	1.02	0.62	8.28	2.70	32.3	16.98	8.52	0.057	0.066	86.48	94.12
	4.56	Zn ²⁺ = 4.73 Ni ²⁺ = 5.19 Mn ²⁺ = 4.38	10	0.94	0.65	8.33	2.60	32.5	13.68	8.10	0.047	0.028	86.18	96.58
									6.95	8.05	0.032	0.023	86.18	100.03

^a Pb's.

^b Estimated from area method [19,20].

^c Duplicated column.

Ni²⁺ concentrations, respectively. On the other hand, the retardation factors of Ni²⁺ decreased to 17.7 (~40% decrease), 13.8 (~50% decrease), and 9.3 (~70% decrease) when the concentrations of Ni²⁺ increased from 3 mmol, 5 mmol, and 10 mmol, respectively. These results were similar to Leitão and Zakharova [32] who observed the absence of sorption of Ni²⁺ at an initial concentration above 0.32 mmol (for Sertã soil) and 0.16 mmol (for Mortague soil) and a decrease of retardation factors of Ni²⁺ in the presence of Zn²⁺, and Cu²⁺ in column experiments. This is probably due to competition for sorption sites related to the presence of other two metals. Similarly, Bajrachaya et al. [33] found that the sorption coefficients of Cd²⁺ determined from column experiments was dependent on the influent concentration. For lower influent concentration, the sorption coefficient was found to be higher. As seen in Table 3, the sorption capacity and retardation factors of Pb²⁺ reduced with increasing concentrations of secondary metals in both binary and multi-metal systems. However, no significant differences in retardation factors of Pb²⁺ were found for an increase in the concentrations of Zn²⁺ of more than 3 mmol and concentration of Mn²⁺ of more than 5 mmol in Pb²⁺-Zn²⁺ and Pb²⁺-Mn²⁺ systems, respectively. A probable reason is that Pb²⁺ was more preferably sorbed than Zn²⁺ and Mn²⁺ since the hydrated radius of Pb²⁺ (0.187 nm) was smaller than of Zn²⁺ (0.233 nm) and Mn²⁺ (0.235). Consequently, the soil surface could be saturated with Pb²⁺, resulting in limited Zn²⁺ and Mn²⁺ access to the sorption sites.

Mohan and Singh [34] used batch studies to investigate the mutual effects of metals in the multi-metals system by measuring the ratio of the sorption capacity of one metal in multi-metals systems, q_i^{mix}/q_i^0 , to the sorption capacity of given metal in single-metal system, q_i^0 . If $q_i^{\text{mix}}/q_i^0 > 1$, sorption of metal i is enhanced by other metals ions. If $q_i^{\text{mix}}/q_i^0 = 1$, metals had no effects on each other. If $q_i^{\text{mix}}/q_i^0 < 1$, metal i competed with other metals for sorption sites of soil. In our study using the average sorption capacity as shown in Table 3, the values of q_i^{mix}/q_i^0 were less than 1, indicating competitive sorption of metals in binary and multi-metal systems. The batch studies conducted by Mohan and Chander [35] showed competition of Fe with other metals (Mn, Zn, and Ca) for lignite sorption sites as evident by the $q^{\text{mix}}/q^{\text{Fe}}$ being lower than 1. Similarly, Serrano et al. [8] found that $q^{\text{mix}}/q^{\text{Pb}}$ and $q^{\text{mix}}/q^{\text{Cd}}$ were lower than 1, suggesting that the presence of Pb²⁺ and Cd²⁺ reduced sorption through competition for sorption sites on acid soils from Spain. As presented in Table 3, sorption capacities of Pb²⁺ in the presence of secondary metals were reduced in comparison with that in the single component system. For example, the average sorption capacity of Pb²⁺ was about 0.126 mmol g⁻¹, but this was reduced by ~35%, ~40%, and ~55% when the Ni²⁺ solution were 3, 5, and 10 mmol, respectively. On the other hand, the sorption capacity of Ni²⁺ was reduced from approx. 0.11 mmol g⁻¹ (in single metal system) [16] by ~55% in the presence of Pb²⁺ at 4.93 mmol. As described above, the reduction percentages of sorption capacity of Pb²⁺ were similar to the reductions in retardation factors. Furthermore, for a 1:1 molar ratio at 5 mmol in binary systems, the presence of Pb²⁺ reduced the sorption capacity of Zn²⁺ (~60% decrease) the most in comparison to the other metals. Similarly, based on a 1:1 molar ratio in binary system, the percentage reduction of sorption capacities of Pb²⁺ (~40% for Ni²⁺, 50% for Zn²⁺, 50% for Mn²⁺) caused by secondary metals were lower than those of the secondary metals caused from Pb²⁺ (~50% for Ni²⁺, ~60% for Zn²⁺, 50% for Mn²⁺).

For multi-metal systems, the sorption capacity of Pb²⁺ (Fig. 5) was reduced from approx. 0.13 mmol g⁻¹ in single metal system to 0.047 mmol g⁻¹ (~60% decrease). On the other hand, the sorption capacities of Zn²⁺ (0.095 mmol g⁻¹), Ni²⁺ (0.108 mmol g⁻¹), and Mn²⁺ (0.069 mmol g⁻¹) in single metal systems were reduced to 0.028 (~70% decrease), 0.032 (~70% decrease), and 0.023 (~60% decrease) mmol g⁻¹, respectively. Pb²⁺ caused the highest percentage reduction of the sorption capacities of other

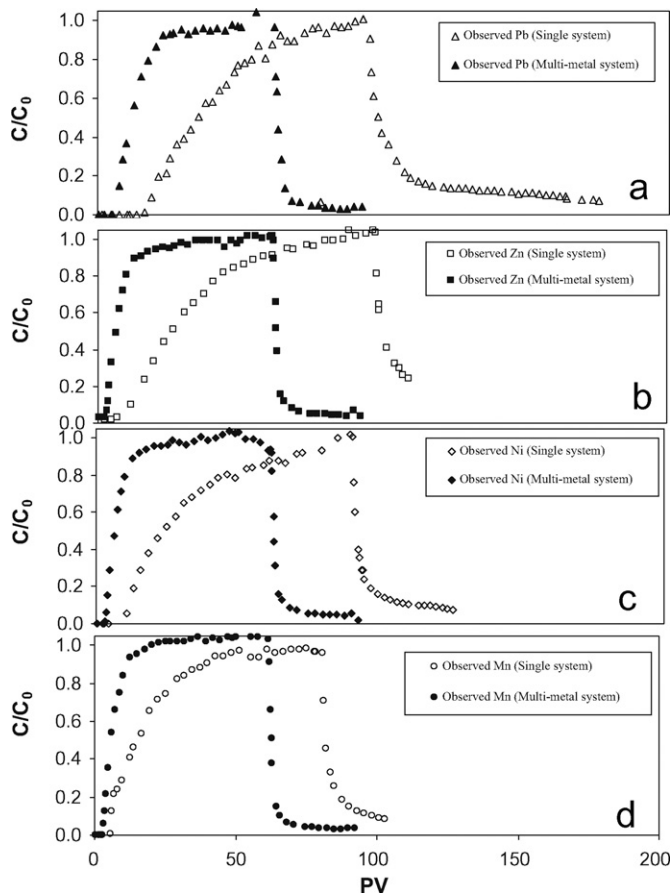


Fig. 5. Heavy metal breakthrough data in lateritic soil column for multi-metal systems (Pb^{2+} 5 mmol– Zn^{2+} 5 mmol– Ni^{2+} 5 mmol– Mn^{2+} 5 mmol) at pH 5.

metals. The preferred selectivity of one heavy metal ions over another is called selective sorption [36]. The selectivity order is assumed to be inversely proportional to the hydrated radius of the metal with smaller radius being more favorable [30]. Thus, the expected order of selectivity is Pb^{2+} (0.187 nm radius) > Ni^{2+} (0.232 nm radius) > Zn^{2+} (0.233 nm radius) > Mn^{2+} (0.235 nm radius). As shown in the results, the sorption capacities in multi-metal systems (for the same initial concentration) were in the order: Pb^{2+} (0.047 mmol g^{-1}) > Ni^{2+} (0.032 mmol g^{-1}) > Zn^{2+} (0.028 mmol g^{-1}) > Mn^{2+} (0.023 mmol g^{-1}), which was in agreement with the order of selectivity of metals. Aqueous speciation modeling using MINEQL+ version 4.5 [37] showed that at or below pH 5.0, most of the Pb (~80%) was in the form of Pb^{2+} while less than 20% were $\text{Pb}(\text{OH})^+$. Zn^{2+} , Mn^{2+} , and Ni^{2+} were the predominated species (almost ~100%) for Zn, Mn and Ni. To clarify this further, the first hydrolysis constants of the metal have been provided [38], $K_1 = (\text{MOH}^+)/(\text{M}^{2+})(\text{OH}^-)$, ($\log K_{\text{Pb}} = -7.71 > \log K_{\text{Zn}} = -8.96 > \log K_{\text{Ni}} = -9.86 > \log K_{\text{Mn}} = -10.59$) which shows that the species present for the pH in our experiments were dominantly metal ions species.

The physical–chemical properties of the surface play an important role in the sorption. Although acidity of the surface can be used, a common property used to describe preferential sorption is the point of zero charge (PZC) [39] of the sorbent. For our simultaneous systems at a pH of approximately 5 which was higher than point of zero charge of lateritic soil (~2), the net charge on the surface was negative which would result in Pb being sorbed stronger onto the lateritic soil than other metals. This is in agreement with the study by Elliot et al. [40] using Christiana soil. Furthermore, the presence of Fe oxides and Al oxides which are generally found in

lateritic soils may preferentially sorbed metals such as Pb relative to other metals such as Ni, Zn and Mn as shown by results of others [5,41]. Consequently, the magnitude of the retardation factors would follow the trend: $\text{Pb}^{2+} > \text{Zn}^{2+} \sim \text{Ni}^{2+} > \text{Mn}^{2+}$ for multi-metal system. This would infer that the mobility of multi-metal through lateritic soil, would be in the reverse order as written above.

Interestingly, the data in Table 3 indicate that total sorption capacity of Pb^{2+} in single system, and the total sorption capacity of the metals in binary systems (Pb^{2+} – Ni^{2+} , Pb^{2+} – Zn^{2+} , Pb^{2+} – Mn^{2+}), and in a multi-metal system for equal molar concentration system were approx. 0.13, 0.12, 0.11, 0.11, and 0.13 mmol g^{-1} , respectively (addition of column 12 + 13). This implies that the maximum sorption capacity of lateritic soil was approx. 0.13 mmol g^{-1} . However, the total amounts of Pb^{2+} and secondary metals (i.e., Ni^{2+} , Zn^{2+} , and Mn^{2+}) retained in the binary metal systems (0.12, 0.11, and 0.11 mmol g^{-1} for Pb^{2+} – Ni^{2+} , Pb^{2+} – Zn^{2+} , and Pb^{2+} – Mn^{2+} , respectively) were smaller than the sum of the amounts of Pb^{2+} and secondary metals (0.23, 0.22, and 0.19 mmol g^{-1} for Pb^{2+} – Ni^{2+} , Pb^{2+} – Zn^{2+} , and Pb^{2+} – Mn^{2+} , respectively), which can be sorbed alone, indicating that competition exists and some sorption sites are common for both Pb^{2+} and secondary metal (i.e., Ni^{2+} , Zn^{2+} , and Mn^{2+}) sorption.

As mentioned above, the presence of secondary metal ions in the systems, resulted in a decrease in the sorption capacity and retardation factor of the primary metal (Pb^{2+}), indicating there was competitive sorption among metals for the available sorption site on the lateritic soil. As more metal ions were presented in the system, the competition among metal ions for available sites was more obvious.

Sorption linearity was evaluated by comparing the shapes of the arrival and elution portions of each metal breakthrough curve for single metal systems. A characteristic of nonlinear sorption is that the breakthrough curves are asymmetrical with a sharply rising front and a relatively more dispersed elution portion (Figs. 2–4). Consequently, the arrival and inverted elution portion of the breakthrough curves did not coincide. The results showed that sorption nonlinearity had a significant influence on the transport of Pb^{2+} , Mn^{2+} , Ni^{2+} and Zn^{2+} in the lateritic soil, especially for single metal systems. Comparison of arrival and inverted elution parts of the breakthrough curves of individual metals for binary and multi-metal systems showed that the arrival and inverted elution parts coincided more than those of single metal systems. This showed that sorption nonlinearity had a significant impact on the transport of heavy metals in the lateritic soil under the simultaneous presence of other metals. Furthermore, as compared to the metals in single metal systems, mass recovery of each metals in the column experiments tend to increase in binary and multi-metal systems, particularly for secondary metals (~98–100%), indicating that sorption behavior becomes more reversible under competitive multi-metals systems. However, Pb^{2+} exhibited a slightly greater degree of reversible transport (~78–86% recovery) under multi-metal systems as compared with other 3 metals (~86–100% recovery), indicating that the sorption of the metals in single metal systems may be relatively stronger than sorption of multi-metals in binary and multi-metal systems.

4. Conclusion

Based on the breakthrough time of Pb^{2+} in single metal system, Pb^{2+} was found to be retained in lateritic soil more than the other metals (Zn^{2+} , Ni^{2+} , and Mn^{2+}), resulting in retardation factors and averaged maximum sorption capacity that were higher than the other tested metals for single, binary and multi-metal systems. However, due to the presence of other metals (Zn^{2+} , Ni^{2+} , and Mn^{2+}) in the binary and multi-metal systems, competition for

available sorption sites resulted in a reduction in the maximum sorption capacity of individual metals for both binary and multi-metal systems. The values of q_i^{mix}/q_i^0 were found to be less than 1 for binary and multi-metal systems, indicating the presence of competitive sorption in these systems. The selectivity order is assumed to be inversely proportional to the hydrated radius of the metal with a smaller radius being more favorable to sorption. Hence, the mobility of multi-metals through lateritic soil, was in the order of $Mn^{2+} > Ni^{2+} \sim Zn^{2+} > Pb^{2+}$. Sorption was found to be more reversible under competitive multi-metal systems. Engineering implications of these findings show that Mn^{2+} may be transported further than the other metals under multi-metal systems due to a dramatic reduction of its retardation factor and a change to more reversible sorption, while Pb^{2+} may take a longer time to be released from soils as it is preferentially sorbed as compared to the other metals. The results obtained from this study suggest that presence of other metals in lateritic soil increase the mobility of certain metals through groundwater and the potential risk of groundwater contamination.

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