Transport Mechanism of Heavy Metal Ions through Saturated Soils

(a)

10

10

(mg/mg)

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1. Introduction

Heavy metals contaminants are commonly found in several kinds of wastes, including sludge and landfill leachates, and are highly toxic to humans. Concentrations of heavy metals are typically 100-10,000 ppm in sewage sludges, mining wastes, and various industrial wastes, such as those originating from the electroplating, pulp and paper, and chemical industries¹. In this study, batch equilibrium and column leaching tests are performed to investigate the transport characteristics of heavy metal ions in soils. Three divalent cations, lead (Pb²⁺), copper (Cu²⁺), and cadmium (Cd²⁺), and four different types of soils, loam, bentonite clay, kaolinite clay, and sand, are used. The selectivity order of heavy metals to soils and the transport mechanism of heavy metals through saturated soil are discussed.

2. Adsorption of Heavy Metals in Soils

Batch equilibrium test was performed first to investigate the adsorption characteristics of heavy metals to four different type of soils, Kanto loam (a common Japanese volcanic soil), bentonite clay (main component montmorillonite), kaolinite clay (typical clay mineral consisting of silica andalumina sheet) and hill sand. Air-dried soils (0.5-5.0g) were added to distilled water (100mL), and agitated with a magnetic stirrer to produce homogeneous mixtures. Then metal ions, lead (Pb²⁺), copper (Cu²⁺), and cadmium (Cd²⁺) of different initial concentration ($C_0 = 20-200 \text{ mg/L}$) were added to the suspensions. The change in concentration of solution with time was measured using the an electrochemical ion meter (IOL-40, TOA-DKK). All of the tests were conducted at pH=6.

Fig.1 shows, for example, the change in ion concentration for the suspensions of Pb^{2+} and Kanto loam. The concentrations gradually decrease because of the adsorption of metal ions on the soil particles, and the mass ratio *S* of adsorption on soil particles is computed for each suspension with Tokai Univ. Student MemberOAbidullah ARABZAITokai Univ. Regular MemberShigeo HONMA

where C_0 is the initial ion concentration of solution (mg/L), V is the volume of liquid (mL), and m_s is the mass of soil (mg). Equilibrium is achieved from t =20 to 60 min, and the relationships between the equilibrium concentration C and equilibrium

S =

C (mg/L)

(1)

 $(C_0 - C)V$



equilibrium isotherms.

(2)

adsorption *S* are given by the following Freundlich equilibrium isotherm.

$$= k_1 C^{k_2}$$

The adsorption coefficients obtained from the Freundlich plots are listed in Table2.

Ion	Soils	Freundlich Coefficients	
		<i>k</i> ₁	k_2
Pb ²⁺	Loam	4.45×10^{-3}	0.345
	Bentonite Clay	1.36×10^{-3}	0.463
	Kaolinite Clay	1.77×10^{-4}	0.652
	Sand	1.13×10 ⁻⁵	0.842
Cu ²⁺	Loam	1.99×10^{-3}	0.479
	Bentonite Clay	4.59×10^{-4}	0.731
	Kaolinite Clay	1.36×10 ⁻⁵	0.871
	Sand	1.53×10^{-5}	0.933
Cd ²⁺	Loam	7.63×10 ⁻⁴	0.409
	Bentonite Clay	2.41×10^{-4}	0.660
	Kaolinite Clay	3.37×10 ⁻⁵	0.800
	Sand	1.54×10^{-5}	0.897

Table1 Coefficients for the Freundlich isotherm.



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Selective adsorption of heavy metals is observed from Fig.2 that the selectivity order of heavy metals is $Pb^{2+} > Cu^{2+} > Cd^{2+}$ for all soils. In the adsorption coefficient of Table1, k_1 represents the relative magnitude of adsorption, and k_2 is the degree of nonlinearity between *C* and *S*. The value of k_1 decreases rapidly in the order loam > bentonite > kaolinite > sand, and k_2 is between 0.35 and 0.48 for loam, 0.46 to 0.73 for bentonite, and for kaolinite and sand the values approach 1.

3. Transport of Heavy Metals in Soils

Soil column leaching tests were performed next to investigate adsorption and diffusion of heavy metal ions through a soil column. Hill sand was packed in the column of the length L=30cm, the diameter D=3cm, and saturated with distilled water. The dry density ρ_d was 1.60 g/cm³, porosity *n* was 0.399, and the volume of void V_v was 81.7 cm³. A solution of heavy metal ions with a concentration C_0 is pumped up from the bottom of a column at a constant rate. The concentration *C* of the effluent collected from the top of the column is measured over time and the results are plotted as solute breakthrough curves, relative concentration C/C_0 versus pore volumes of flow (V_p) . V_p is the cumulative volume of flow through the soil divided by the volume of the void space in the soil.

The one-dimensional transport equation for leachate concentration *C* including retardation and decay caused by adsorption to a soil matrix is expressed as $^{2)}$

$$\frac{\partial C}{\partial t} = \frac{D_L}{R} \frac{\partial^2 C}{\partial z^2} - \frac{v_e}{R} \frac{\partial C}{\partial z} - \lambda C$$
(3)

where $D_L = a_L v_e$ is the longitudinal dispersion coefficient (cm²/s), a_L is the dispersivity of soil matrix (cm), v_e is the pore velocity (cm/s), R is the retardation factor, and λ is the decay constant (s⁻¹). The retardation factor R is given for linear adsorption as

$$R = 1 + \frac{\rho_d}{n} K_d \tag{4a}$$

and for non-linear adsorption process as

$$R = 1 + \frac{\rho_d}{n} \frac{\partial S}{\partial C} \tag{4b}$$

The analytical solution of Eq. (4) with initial and boundary conditions corresponding to the column leaching test is given by $^{3)}$

$$\frac{C}{C_0} = \frac{1}{2} \exp\left\{\frac{P_e}{2}(1-\gamma)\right\} \operatorname{erfc}\left(\frac{\sqrt{P_e}}{2}\frac{1-V_p\,\gamma/R}{\sqrt{V_p/R}}\right) \tag{5}$$

where $\gamma = \sqrt{1 + 4\lambda a_L R/v_e}$, $P_e = L/a_L$ is the particle Peclet number. The best fit curve was found by trial and error, through changing P_e , γ , and R in Eq.(5) to match the experimental results. The results are shown in Fig.3. The effluent concentrations did not reach C_0 after breakthrough, because of the adsorption of the ions to the soil. Since the adsorption characteristics of heavy metal ions on sand are



almost linear (Fig.2 and Table1), the retardation factor Rcan be calculated using Eq. (4a). It was found R = 46.4 for Pb, R = 62.8 for Cu and R = 63.2 for Cd. These values are very high, and inconsistent with the transport retardation observed in the column leaching tests. This is because in the batch equilibrium tests, the entire soil particle surface is exposed to the contaminants, but during the transport process, contaminants are not directly in contact with the soil particle surfaces and migrate through the center of the voids. Furthermore, the retardation coefficients evaluated from batch tests are measured at equilibrium, whereas equilibrium may not be achieved during transport in the column. Therefore, it is important not to confound the adsorption parameters between the two tests when we intend to asses a long term geoenvironmental contamination problem.

References: 1) Yong R.N., Mohamed A.M.O. and Warkentin B.P. : Principles of Contaminant Transport in Soils (Elsevier, 1992) p.1-22. 2) Kinzelbach W. : Groundwater Modeling, Development in Water Science 25 (Elsevier, 1986) p.188-220. 3) Abidullah ARABZAI, Shigeo HONMA: Adsorption of Heavy Metals Ions in Saturated Soils, Joint International Conference on Material & Environmental Science, ACCMES-1394, CD-ROM, p.-, (2014)