Study on Retardation Effect of a Heavy Metal in Sandy Soils

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Abstract

Retardation effect of heavy metals in soils caused by adsorption onto the surfaces of solids particles is well known phenomena. The adsorption of metal ions has been recognized more strong in clay mineral and organic matter contents rather than sands and gravels. In this study, we investigated the retardation effect in two sandy soils by conducting batch and column tests. The column tests were conducted to obtain the relationship between concentration and time known as breakthrough curve (BTC). We applied pulse type injection of $ZnCl_2$ solution on the inlet boundary and monitored the effluent concentration at the exit boundary under steady state condition using EC-meter and ICP-AES. Batch test consisted of an equilibrium procedure for fine fractions collected from two sandy soils for various initial $ZnCl_2$ concentrations, and analysis of Zn ions in equilibrated solution using ICP-AES. The results of column test showed that i) the peak concentration of Zn analyzed by ICP was far less than that detected by EC-meter for both soils and ii) travel times for peak concentration were more less identical for two different monitoring techniques. The first result can be explained by ion exchange between Zn and other cations initially present in the soil particles since ICP analysis showed a significant amount of Ca, Mg ions in the effluent. From the second result, we found that retardation effect was not present in these soils due to strong cation exchange capacity of Zn ion over other cations since we did not apply a solution containing more adsorptive cations such as Al. The result of batch test also showed high distribution coefficients (K_d) for two soils supporting the dominant ion exchange phenomena. Based on the retardation factor obtained from the K_d, we predicted the BTC using CDE model and compared with the BTC of Zn concentration obtained from ICP. The predicted BTC, however, disagreed with the monitored in terms of travel time and magnitude of the peak concentrations. The only way to describe the prominent decrease of Zn ion was to introduce decay or sink coefficient in the CDE model to account for irreversible decrease of Zn ions in liquid phase.

I. Introduction

Ion exchange is a specific category of adsorption that is referred to as adsorbent-motivated sorption (Knox et al., 1993); that is, the accumulation occurs due to an affinity of the solid surface for the chemical. Among soil particles, the clay fraction is the most contributing mineral for adsorption. Adsorption of divalent cations originating from heavy metal ions onto fine fractions is well known and brings about retardation effect which slows down the mobility of chemicals in a porous medium. Amount of adsorption from liquid phase to solid surface is commonly given by partitioning coefficient or distribution coefficient that defines the ratio between amount of adsorbed and changes in solute concentration equilibrated between a specific cation and dry soil mass. Roy et al. (1987) studied lead adsorption by Cecil clay loam at pH 4.5 and they found the distribution coefficient to be 232 mL/g. Valocchi (1980) and Valocchi et al. (1981) evaluated the transport of ion exchanging solutes during groundwater recharge (Knox et al., 1993). Valocchi (1984) also discussed the use of an "effective" partitioning coefficient approach for describing the transport of ion-exchanging contaminants. Ceazan et al. (1989) conducted field studies with respect to the exchange and transport of ammonium and potassium in the sand and gravel aquifer and they found that adsorption (exchange) was responsible for the retardation of ammonium. Perillo et al. (1998) recently studied the retardation of FD&C blue no. 1 food dye in leaching experiments and reported that due to adsorption characteristic the dye retarded relative to the wetting front.

The objective of this study is to investigate the retardation effect of Zn in two sandy soils by conducting batch and column tests. The batch tests were conducted to obtain the distribution coefficient and the column tests to obtain the relationship between effluent concentration and time known as breakthrough curve (BTC) using an EC-meter and ICP.

II. Theory

Transport of reactive chemicals showing retardation and decay or degradation in a soil can be described by the following equation (Parker and van Genuchten, 1984):

$$R\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - V\frac{\partial C}{\partial x} - \mu C \qquad \text{Eq. (1)}$$

$$R = 1 + \frac{\rho_b}{\theta} K_d$$

where C is the concentration of the solute in the liquid phase, t is time, R is retardation factor, D is dispersion coefficient, V is pore water velocity, x is distance, ρ_b is bulk density, θ is porosity and K_d is distribution coefficient.

The analytical solution of Eq. (1) for flux concentration was given by van Genuchten and Alves (1982) using appropriate initial and boundary conditions for finite length of a porous medium:

    i) $C(x,t) = C_0 \cdot B(x,t)$ $(0 < t < t_0)$ Eq. (2)

$$B(x,t) = \frac{1}{2} \, EXP \left[\frac{(V-u)x}{2D} \right] Erfc \left[\frac{Rx - ut}{2(DRt)^{1/2}} \right] + \frac{1}{2} \, EXP \left[\frac{(V+u)x}{2D} \right] Erfc \left[\frac{Rx + ut}{2(DRt)^{1/2}} \right]$$

$$u = V(1 + \frac{4\mu D}{V^2})^{1/2}$$

    ii) $C(x,t) = C_0 B(x,t) - C_0 B(x, t - t_0)$ $(t > t_0)$ Eq. (3)

where C_0 is the concentration of the injected fluid and μ is decay coeffieicnt.

III. Materials and Methods

We used two sandy soils having different soil texture and the particle size analysis is given in Fig. 1. Fine fractions less than 23 μm of sandy and loamy sandy soil was 1.45 and 12.5 % respectively. These fractions were used for batch test to obtain distribution coefficient. The initial concentrations of $ZnCl_2$ was 10, 100, 1000, 5000 ppm. We allowed shaking of 50 mL solution containing 5 g of dry soil mass for equilibration about 48 hrs. The Zn ion in the equilibrated solution were analyzed using ICP-AES. The pH of the equilibrium solution ranged from 6.95 to 8.32. The distribution coefficient (K_d) was obtained using linear adsorption isotherm. Parallel to the
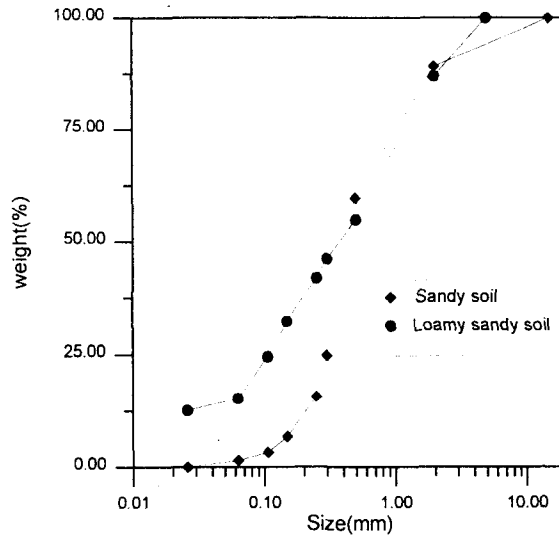

Fig. 1. Partlcle size distribution of sandy and loamy sandy soils.

batch test, we conducted also column test for the two soils uniformly packed into PVC cylinder with 20 cm of both diameter and height to obtain BTC of $ZnCl_2$ and to investigate the retardation effect under steady state condition. Volume of 314 mL solution with input concentration of 10 and 20 g/l was respectively injected onto the inlet boundary of two soil samples as pulse type and subsequent monitoring of effluent concentration with time was conducted using an EC-meter and ICP. Parameters of V and D for the effluent concentration monitored by the EC-meter were first estimated neglecting R and μ in Eq.(2) and then Zn concentration was simulated using Eq.(2) with R calculated from K_d factor and compared with the measured Zn BTC. In addition, with the parameters of V and D obtained for effluent concentrations, we estimated only the decay coefficient in Eq. (2) for Zn BTCs.

IV. Results and Discussions

Fig. 2 and Fig. 3 show the results of BTCs for effluent concentrations monitored using EC-meter and ICP for two sandy soils. The peak of Zn BTC data detected by ICP was far less than that of BTC data measured by EC-meter but the travel time of the peak concentration was more less the same. Inclusion of other cations (Ca, Mg) concentration approached nearly 75 % of the BTC measured by EC-meter. This indicates that large difference in effluent concentration between two different monitoring techniques are due to the ion exchange as also observed by Ceazan et al. (1989) since Zn ion has higher exchange capacity than other divalent cations present in the soils. The Zn concentration in loamy sandy soil as can be seen in Fig. 3 was very low with
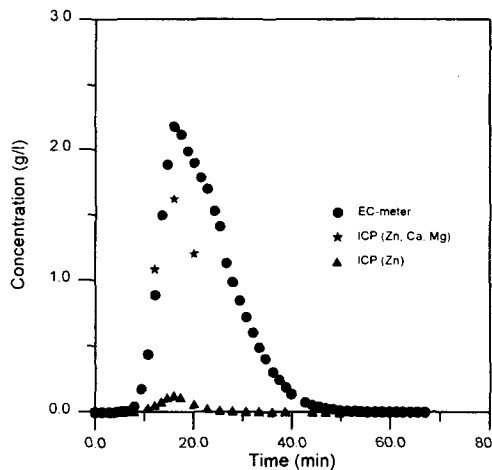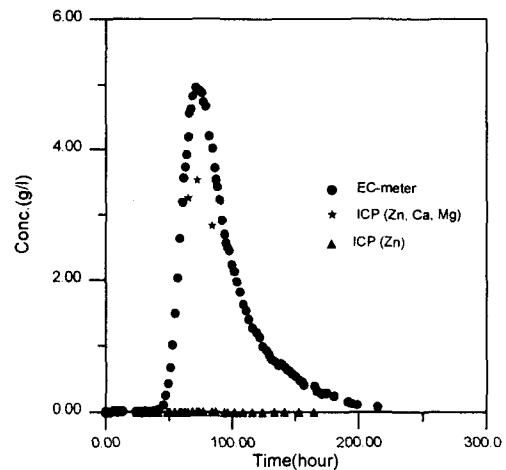

Fig. 2 BTC of sandy soil.

Fig. 3 BTC of loamy sandy soil.

the peak equal to an order of 1.0 ppm (1x 10^{-3} g/l) in contrast to the input concentration of 20 g/l. This can be explained by the fact that the input amount of $ZnCl_2$ corresponding to 6.28 g in 314 mL was much less than the exchange capacity of the fine fractions given as approximately 17.2 g assuming that the CEC of fine fractions were 20 meq/100g. In the sandy soil, the exchange capacity of Zn was 2.41 g whereas the input amount was 3.14 g in 314mL.

Table 1. Distribution coefficients of sandy and loamy sandy soils.

		Lower range					Higher range	
Initial Conc. (ppm)		4.9	43.26	401.8	K_d (ml/g)	Initial Conc. (ppm)	2646	K_d (ml/g) (pH = 6.95-8.32)
Equilibrated Conc. (ppm)	Sandy Soil	0.2	1.55	11.91	332	Equilibrated Conc. (ppm)	858.9	17
	Loamy Soil	0.19	0.78	1.39	3332		682.5	22

Table 2. Transport parameters estimated from BTCs obtained by EC-meter for sandy and loamy sandy soils.

	V (cm/min)	D (cm^2/min)
Sandy soil	0.897	1.22
Loamy sandy soil	14.22	10.26

The results of K_d is shown in Table 1. It is noted that the relationship between adsorbed amount and equilibrium concentration consisted of two linear part for both soils; one for lower concentration range showing high K_d and the other for higher concentration range with relatively low K_d as also reported by Roy et al. (1987). Based on these K_d values, we calculated R and simulated Zn BTC with the V and D (table 2) estimated from the BTC measured by EC-meter. For sandy soil having a clear peak of $ZnCl_2$, the predicted BTC yielded a different shape from the measured BTC in terms of peak concentration and travel time of the peak concentration (Fig. 4). In this regard, the theory based on the retardation effect failed to describe the transport of Zn ion showing a high ion exchange capacity. Therefore we attempted to use the decay coefficient, μ, appeared in Eq. (1). The fitted curves to the measured data points are shown in Fig. 5 with the estimated parameters.
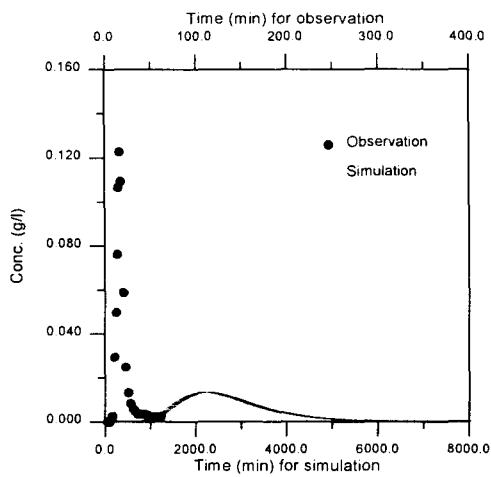

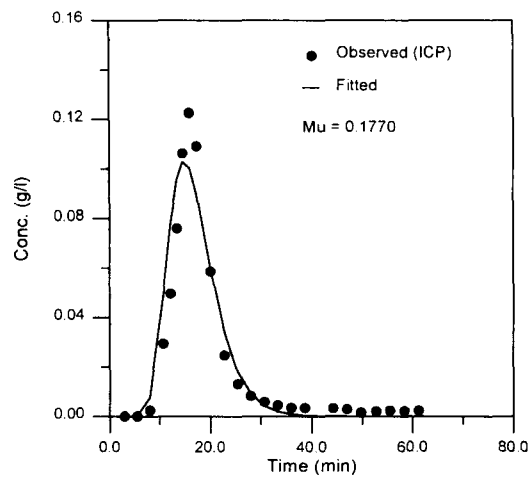그림 4. Predicted BTC of sandy soil with retardation effect (R=121.8).

Fig. 5 Parameter estimation result of sandy soil.

V. Conclusion

In order to investigate the retardation effect of Zn ion in two sandy soils, we conducted batch and column tests using a standard procedure and steady state condition. The BTC of Zn showed about 20 times low peak compared to the total cations concentration as measured by EC-meter. The large difference was due to the strong ion exchange capacity inherent in Zn ion over other cations such as Ca and Mg. Use of retardation factor calculated from the distribution coefficient determined by batch test could not describe the Zn concentration in terms of the peak concentration and travel

time of the peak concentration. Hence, the commonly accepted retardation effect caused by adsorption process of heavy metals could not describe the transport behaviour of Zn ion used in this study since desorption of Zn ion could not be realized under BTC condition. Rather, accommodation of decay coefficient was more appropriate to realize the transport behaviour of Zn.

VI. References

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