Sorption and Desorption Characteristics of Cobalt in Clay: Effect of Humic Acids

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Abstract−The effect of humic acid (HA) on the sorption and desorption of Co(II) on kaolin was investigated. Cobalt ions interact with carboxylic and phenolic groups in HA and form HA-cobalt complex. The solubility of HA was affected by the surrounding pH. The presence of HA reduced the equilibrium time for the Co(II) sorption on kaolin compared to the absence of HA. Solution pH, not HA concentration, was a main factor to affect sorption of Co(II) on kaolin in the presence of HA. In the kinetic sorption and desorption of Co(II) on kaolin, the presence of HA shortened the breakthrough of Co(II) sorption on kaolin compared to bare kaolin, and HA solution enhanced the displacement of Co(II) from kaolin compared with deionized water.

Key words: Clay, Cobalt, Desorption, Sorption, Humic Acid

INTRODUCTION

The discharge of various cobalt radionuclides from nuclear reactors to surface water and their accumulation by aquatic organisms and sediments are drawing attention to the cycling and fate of this element in aquatic systems [Qian et al., 1998]. Cobalt, an essential element that plays a very specific role in vitamin B12, is rare, available only at low concentrations in aquatic systems. With regard to the fate of Co in natural waters, it is important to understand whether dissolved Co inputs will be easily bound to particles and retained in sediments or, in contrast, will be strongly complexed in solution and transported with the water phase [Qian et al., 1998].

The sorption and desorption characteristics of cobalt in soil and/ or groundwater systems are very important with respect to environmental pollution, and these processes are influenced by the presence of organic matter [Laszak and Choppin, 2001; Prado and Airoldi, 2003]. The organic matter of a soil system is difficult to define chemically as it represents a continuum from living root fibers and plant detritus to simple molecules such as carbon dioxide and methane which are the end products of humic degradation [Kim et al., 2002]. Because of its great complexity, the organic fraction has been classified operationally rather than chemically into 3 fractions: humin, which is insoluble in both acid and alkaline solutions; HA, which is soluble in alkaline solution but insoluble in strong acid; and fulvic acid, which is soluble in both strongly acid and alkaline solutions [Spark et al., 1997]. The main functional groups present in a sample of HA are carboxylic acids, alcohols, phenols, carbonyls, phosphates, sulfates, amides, and sulfides, and all of these groups are able to interact with metal species in solution. Humic substances are ubiquitous in the environment and they can play a role in nature. Generally, it has been found that the interaction of HA with metal cations in solution increases with pH, decreases with metal concen-

tration, and increases with HA concentration. The transport of cobalt released from a nuclear reactor in the subsurface including soil and groundwater is significantly influenced by the sorption and desorption characteristics of cobalt on soil particles [Park and Hahn, 2002; Park et al., 1999]. Soil organic matter is a dominant factor to govern the sorption and desorption characteristics of cobalt on soil particles. However, the sorption and desorption of cobalt in soil environments in the presence of humic acid and the feasibility of humic acid as a washing reagent for the removal of cobalt-contaminated soil has not studied in detail.

In this study, the sorption characteristics of cobalt including sorption capacity and sorption kinetics were investigated in the presence of various HAs. Transport characteristics of cobalt and dynamic sorption and desorption in a column were also investigated.

MATERIALS AND METHODS

1. Materials

All chemicals used were of analytical grade. $CoCl_2 \cdot 6H_2O$ obtained from Sigma (USA) was used in the preparation of synthetic contaminant bearing solution. The pH of the system was adjusted by using standard 0.1 N NaOH and 0.1 N HCl. Kaolin was obtained from Sigma (USA) with the diameter of 0.1-4.0 μm.

The HAs were selected from three different origins: (a) commercial product from Aldrich (ALHA), (b) extracted from Canadian peat moss (PMHA), and (c) separated from humus soil in a Korean mountain (HSHA). PMHA and HSHA were separated and purified following the standard international humic substance society (IHSS) procedure for the extraction of HA [Milne et al., 1995].

2. Methods

The equilibration time for Co(II) sorption on kaolin was measured by kinetic experiments in the presence of HA or in the absence of HA. Uptake of cobalt ion from aqueous solution by kaolin in the presence of HAs was measured by placing 25 ml of 0.5 mM cobalt solution into contact with 1 g of kaolin containing various

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HAs concentration in 50 ml plastic bottles. Samples were shaken in an over-end shaker at the speed to maintain the contents completely mixed, and the kaolin particles were suspended throughout the vessel. The solution's pH and ionic strength were adjusted before the sorption experiments were started. After equilibrium was reached, the mixtures were centrifuged and the supernatants were analyzed for cobalt. The quantity of cobalt ion sorbed on kaolin was calculated as the difference between initial concentration and concentration at equilibrium. Each experiment was repeated in triple to check the reproducibility.

The experimental procedures for Co(II) sorption and desorption of column experiments were employed in the Wang et al.'s experiments [Wang et al., 2002]. 30 g of air-dried kaolin was packed into the glass column with 220 mm in length and 18 mm in diameter. An HPLC pump was used to maintain a steady flow rate. 0.1 mol NaCl/l solution (pH 6.0) containing 10 mg/l Co(II) was introduced into the kaolin column for sorption experiments, while 0.1 mol NaCl/l adjusted to pH 6.0 with or without 0.01 g HA/l was introduced for desorption experiments. The effluent samples were collected and the breakthrough curves and the displacement curves of Co(II) were obtained.

FTIR (Bomem DA-8, Canada) was used to analyze the functional groups of HAs. Atomic adsorption spectroscopy (AAS, Perkin Elmer 3300, USA) was used for the analysis of cobalt in the aqueous phase.

In the present study, the following expression has been applied to calculate the distribution coefficient, K_d (ml/g) for Co(II) in the absence and presence of HA on kaolin:
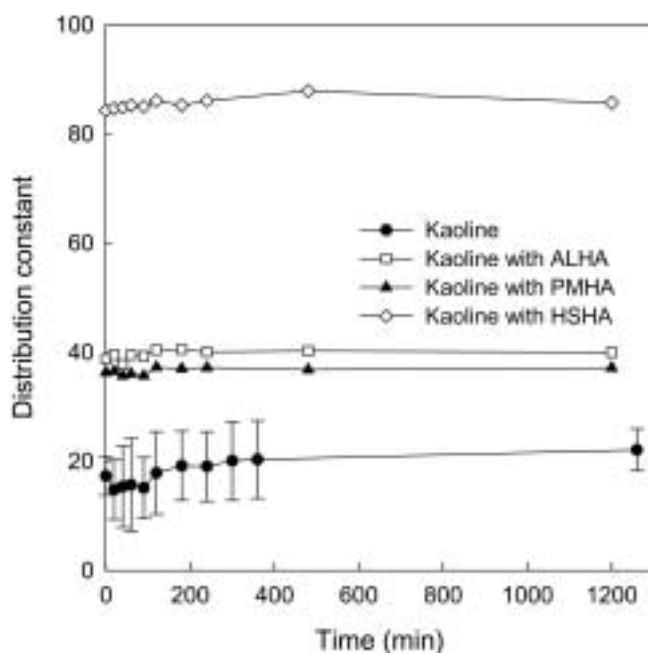
$$K_d = \frac{W(C_0 - C)}{CS}$$

Fig. 1. Sorption kinetics of Co(II) on kaolin in the presence or absence of HA, initial concentration of Co(II): 5.0×10⁻⁴ mol/l, V/S: 50/1 ml/g, ionic strength: 0.1 mol NaCl/l, HA concentration: 0.1 g/l, initial pH: 6.0, 25 ℃.
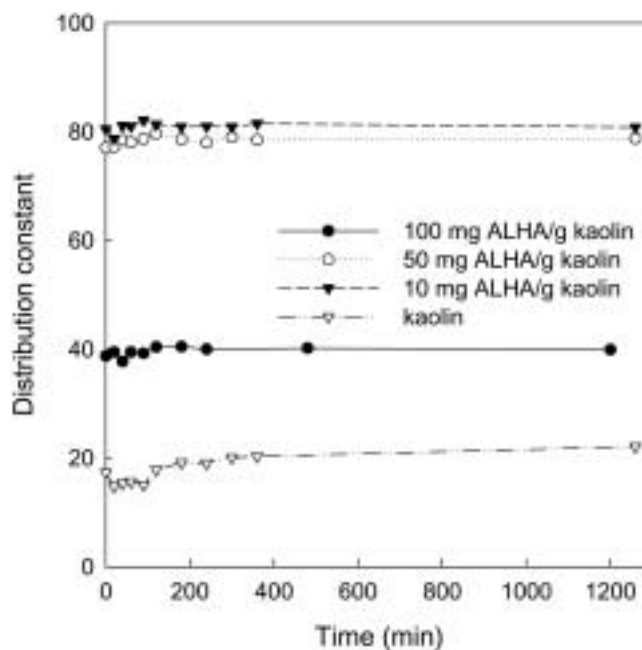
Fig. 2. Effect of HA concentration on the sorption kinetics of Co (II), initial concentration of Co(II): 5.0×10⁻⁴ mol/l, V/S: 50/1 ml/g, ionic strength: 0.1 mol NaCl/l, initial pH: 6.0, 25 ℃.

where C_0 and C are concentration of cobalt (mg/l) before and after contact with the adsorbent phase, respectively. V (ml) and S (g) are the volume of solution and the weight of kaolin, respectively [Wang et al., 2000].

RESULTS AND DISCUSSIONS

1. Sorption Kinetics

The sorption kinetics of Co(II) on kaolin containing HA are presented in Fig. 1 and Fig. 2. Fig. 1 shows the result of sorption kinetics of Co(II) on kaolin at pH 6.0 in the presence or absence of various HAs. It is shown that the steady state was reached within 420 min approximately. As compared with the sorption kinetics in the presence of HAs (equilibration time of 200 min), the sorption rate of Co(II) on kaolin was a much slower kinetic process. The presence of HA enhanced the adsorption of Co(II) on kaolin, and HSHA increased the sorption of Co(II) 4 times compared to the bare kaolin. Fig. 2 shows the effect of ALHA content on Co(II) sorption on kaolin. Although the presence of HA enhanced the sorption, the sorption did not increase with the HA content. At 10 mg ALHA/g kaolin, the sorption showed the highest value, while the sorption was a half of the value at the 100 mg ALHA/g kaolin because the HA in the aqueous phase increased the aqueous Co(II) concentrations due to the interaction between carboxylic or phenolic groups and Co(II).

2. FTIR for Functional Groups Analysis of HAs

The functional groups of ALHA have been compared with that of HSHA and PMHA by FTIR spectroscopy (Fig. 3). The spectra from this analysis have been interpreted by using the peak assignment reported by Spark and his colleagues [Spark et al., 1997]. Although FTIR spectra are unsuitable for estimating concentrations of organic matter, they can be used to determine the relative concen-
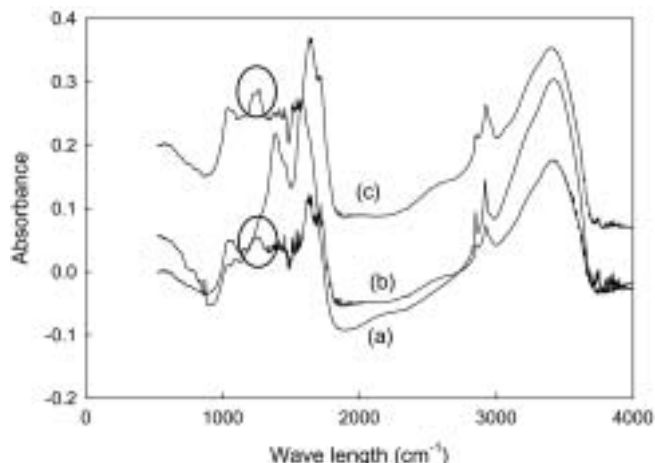
Fig. 3. FTIR spectra of (a) Aldrich HA (ALHA), (b) a humus soil HA (HSHA), and (c) peat moss HA (PMHA). The circle means phenolic peak.

trations of functional groups within a sample [Spark et al., 1997].

The content of -COOH (1,720 cm^{-1}), -CH$_2$ (2,840-2,940 cm^{-1}) and aromatic group (750-900 cm^{-1}) is similar for all 3 HAs. The major difference between ALHA and the others is in the region associated with phenolic groups (1,270 cm^{-1}). The PMHA and HSHA showed clearly a phenolic peak, while the peak was not clearly observed in the case of ALHA. However, the carboxylic peak of ALHA was greater than others. Thus, some difference in sorption and desorption characteristics of cobalt at the presence of HAs are expected because the binding of Co(II) onto HA is dominated at the carboxylic and phenolic groups.

3. HA Effect on the Sorption of Co(II)

Figs. 4(a)-4(c) show the effect of solution pH and concentration of HAs on sorption characteristics of Co(II). The effect of HA concentration on Co(II) sorption was negligible except at pH 10. Major factor affecting Co(II) sorption was solution pH. Co(II) can be sorbed on both kaolin and HAs. Two types of binding sites on kaolin are available: weakly acidic groups, which undergo ion exchange, and amphotoric surface hydroxyl groups, which form inner sphere complex. With increasing pH, the surface charge becomes more negative and thereby increases the sorption of Co(II). The sorption of Co(II) to ion exchange sites is dominated by attractive electrostatic interactions [Sen et al., 2002]. Also Co(II) can be bound to the carboxylic group and phenolic group of HAs sorbed on clay and in the aqueous phase. With increasing pH, the carboxyl and phenolic group become negative due to deprotonation, thereby increasing the sorption of Co(II). On the other hand, the solubility of HA was enhanced with increasing pH, which caused a decrease in the sorption of HA on kaolin. As a result, most of HA existed not on the kaolin particles but in the solution, also cobalt-humate complexes were present in the solution. The increase of pH caused the precipitation of Co(II) as a form of Co(OH)$_2$ or decrease in valence due to the formation of Co(OH)$^+$ (Fig. 5) [Choo et al., 2002]. Kaolin with HAs showed the maximum sorption capacity at the slightly acidic conditions (pH 4 or pH 6) because the increase of pH caused the multiple phenomena mentioned above.

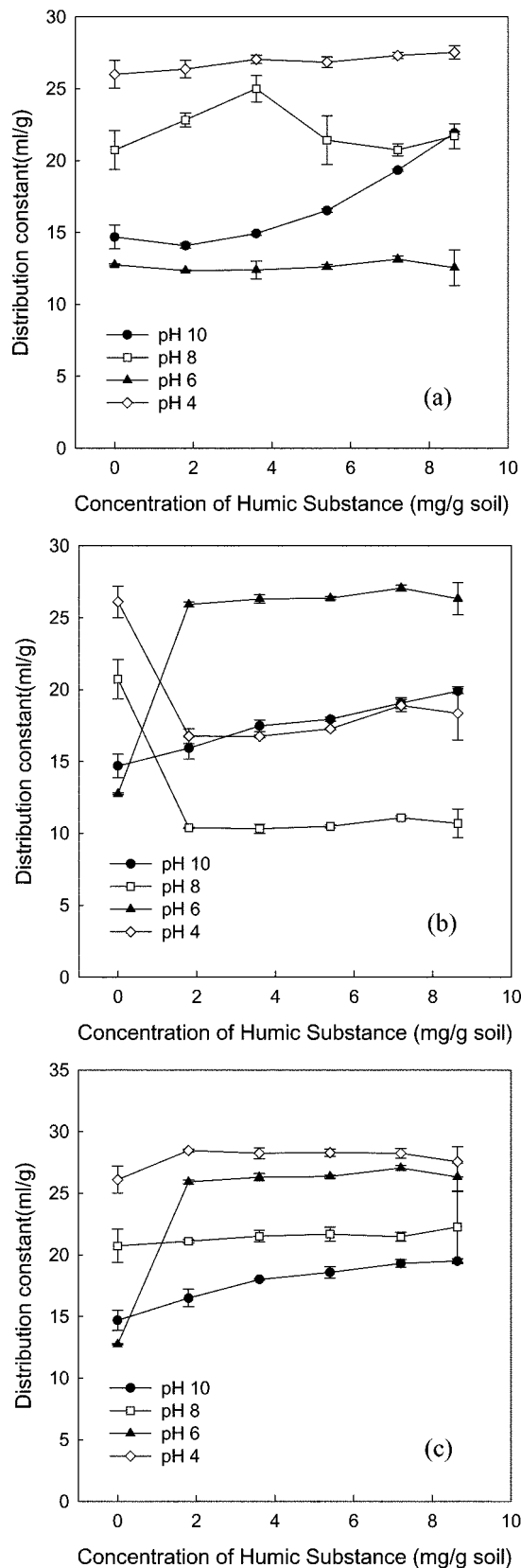## 4. Breakthrough Curves and Displacement Curves of Co(II) Transport

Fig. 4. Effect of HA concentration and solution pH on the sorption of Co(II), initial concentration of Co(II): 5.0×10^{-4} mol/l, V/S: 25/1 ml/g, ionic strength: 0.1 mol NaCl/l, 25 °C. (a) Aldrich HA (ALHA), (b) peat moss HA (PMHA), and (c) a humus soil HA (HSHA).
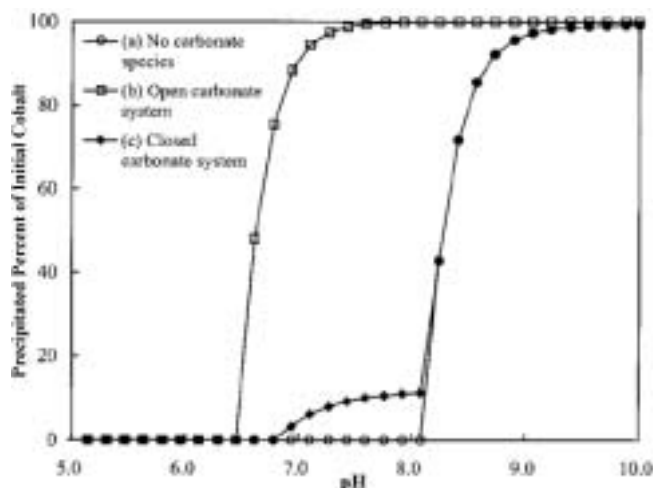
Fig. 5. Calculations of the percentage of precipitates of initial cobalt at various pH levels studied when different carbonate systems are involved in solution equilibria: (○) a system with no carbonate species; (□) an open system with an equilibrium dissolved CO_2 concentration of 10^{-5} M; (●) a closed system with a total carbonate concentration of 10^{-5} M. The total cobalt concentration is 0.0848 mM [Choo et al., 2002].

Fig. 7. Effect of HA concentration on breakthrough and displacement of Co(II) on kaolin, initial concentration of Co(II): 10 mg/l, ionic strength: 0.1 mol NaCl/l, initial pH: 6.0, 25 °C.
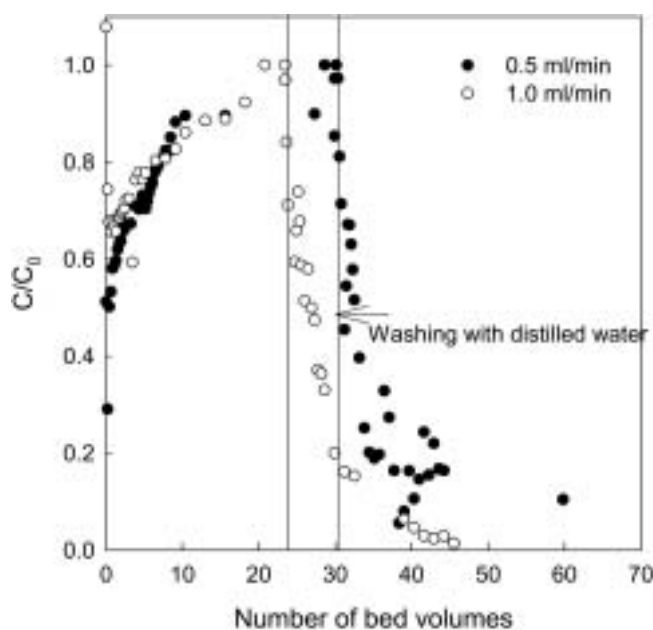

Fig. 6. Effect of flow rate on breakthrough and displacement of Co(II) on kaolin, initial concentration of Co(II): 10 mg/l, ionic strength: 0.1 mol NaCl/l, initial pH: 6.0, 25 °C.

Fig. 8. Displacement of Co(II) on kaolin by HA solution, initial concentration of Co(II): 10 mg/l, ionic strength: 0.1 mol NaCl/l, HA for washing: 50 mg/l, initial pH: 6.0, 25 °C.

In general, sorption plays an importance role on Co(II) breakthrough patterns in transport experiments. Fig. 6 presents the measured breakthrough curves and displacement curves of Co(II) on two different flow rates. Breakthrough curves are presented as plots of C/C_0 against number of bed volumes where C is cobalt concentration in the effluent aqueous phase, and C_0 is the influent cobalt concentration. At a slower flow, the breakthrough was delayed slightly because tardier flow caused slower transport of Co(II). Washing
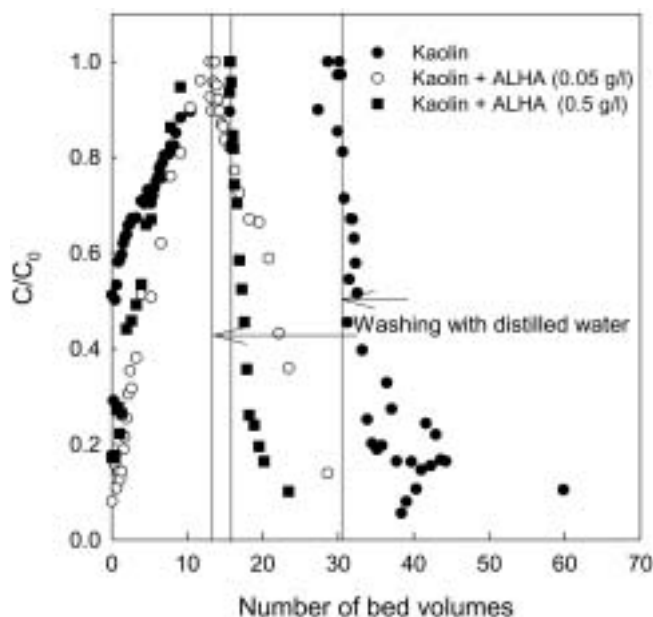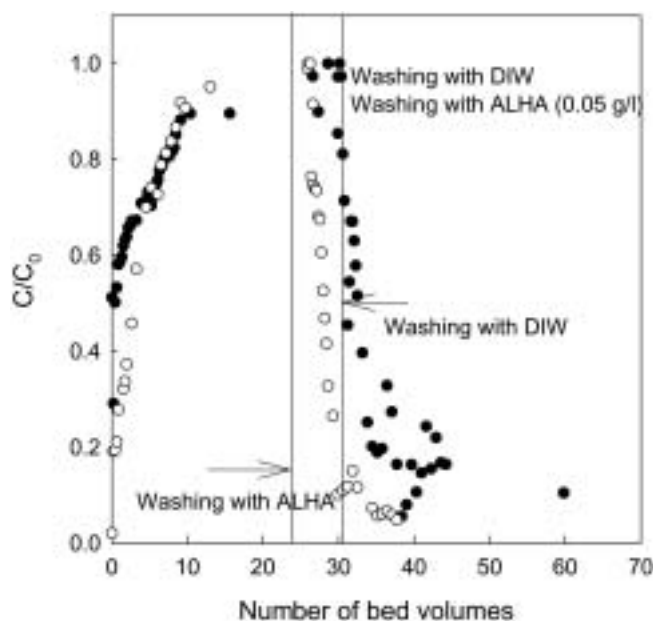
with faster flow exhibited more rapid displacement.

Fig. 7 shows the breakthrough curves and displacement curves of Co(II) on kaolin coated with HA. On the bare kaolin, the breakthrough was delayed compared to the kaolin coated with HA. The breakthrough on kaolin coated with higher concentration of HA was delayed slightly compared to the case of kaolin coated with lower amount of HA. At the initial stage of kinetic sorption, the flow transported Co(II) on kaolin and displaced HA from kaolin simultaneously because the sorption of HA on kaolin was a very weak

physical interaction. However, in the field, the opposite phenomenon is expected that higher concentration of HA can cause the delay in breakthrough of Co(II) due to the aging of humic acid on soil (strong sorption on soil particles). The plentiful HA on kaolin inhibited the displacement of Co(II) compared to the bare kaolin and less HA on kaolin. Tailing of displacement was not observed in the kaolin coated with HA, but observed in the bare kaolin.

Fig. 8 shows the breakthrough curves and displacement curves of Co(II) with HA solution. Washing using HA solution enhanced the displacement of Co(II) compared to deionized water.

CONCLUSIONS

The sorption of Co(II) reached an equilibrium state within 420 min for the kaolin in the absence of HA, while equilibrium was attained within 200 min in the presence of HA. The sorption characteristics, distribution coefficient of Co(II), were highly dependent on the solution pH, but were independent of HA concentration in the solution at the solution pH of <10. At the solution pH of 10, the sorption of Co(II) increased gradually with the HA concentration in the aqueous phase. In the kinetic sorption and desorption of Co(II) on kaolin, the presence of HA shortened the breakthrough of Co(II) on kaolin compared to bare kaolin, which was consistent with the shorter equilibrium time for sorption kinetics. HA solution enhanced the displacement of Co(II) from kaolin compared to deionized water, which meant that the HA solution could be used to remediate the soil contaminated with cobalt.

ACKNOWLEDGMENT

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