중금속으로 오염된 점성토에서 동전기프로세스에 의한 탈착 특성

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Electrokinetic Extraction of Heavy Metal from Clayey Soil : Desorption Characteristics During Electrical Treatment

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ABSTRACT

A number of batch isotherm and electrokinetic experiments were conducted in order to investigate the migration of zinc and its removal efficiency during electrokinetic soil processing. Sorption and desorption characteristics of zinc spiked kaolin clay have been examined by comparison with electrically induced desorption and precipitation occurring in the anode and cathode regions, respectively. The removal efficiency of zinc under the applied voltage gradient of 300 V/m was found to be up to approximately 80 % within 4 hours of the electrokinetic treatment. The study is significant with respect to the remediation of contaminated areas.

   Key words : clayey soil, electrokinetic remediation, pH, precipitation, sorption/desorption

요 약 문

동전기적 처리에 의한 무기 오염 물질의 이동 및 제거율을 조사하기 위해 일련의 흡착/탈착 실험 및 동전기 정화 실험을 실시하였다. 동전기적 효과로 인해 발생된 양극 부근에서의 탈착 현상 및 음극 부근에서의 침전 현상을 중금속으로 오염된 점토 시료의 흡착 및 탈착 특성과 비교하여 분석하였다. 제거 효율은 300 V/m의 전압구배로 약 4시간의 동전기적 처리 결과 80% 정도의 높은 제거 효율을 확인할 수 있었다.

   주제어 : 점성토, 동전기 정화, pH, 침전, 흡착/탈착

1. Introduction

   Electrokinetic (EK) remediation is an innovative tech- nology for the removal of pollutants from contaminated ground. The EK technique involves passage of a low electric current through soil between electrode pairs, which can be applied in situ directly with the advantage of being effective for low hydraulic conductivity soils (Yeung, 1994). The fundamental processes of EK remediation are transportation of water and solute through porous media based on the phenomena known as electroosmosis (EO) and electromigration (EM) together with other related effects including sorption/desorption, electrolysis, and precipitation (Mitchell, 1993).

   Sorption isotherms and ion exchange capacities have been examined in some EK experiments (Puppala et al., 1997; Sah and Chen, 1998). Soils with strong

sorption capacities are much more difficult to clean up than clayey soils with low cation exchange capacities (Page and Page, 2002). Thus, the ionic pollutants must be desorbed first and removed for rapid and effective decontamination of soils at concentrations above the ion exchange capacity.

In general, changes in pH affect the sorption characteristics of the soil (Hicks and Tondorf, 1994). For example, metals tend to desorb from the soil at low pH and will be present in solution as positively charged ions. At higher pH, metal solubility is reduced by the formation of hydroxides (Sposito, 1984). The hydrogen ions generated by electrolytic reactions are effective for desorbing metal cations as the acid front passes through the soil (Weng et al., 1994). The main objective of this research is to examine the characteristic features of zinc sorption/desorption in the presence of kaolin clay with and without the EK treatment.

2. Experimental Programme

2.1. Testing Materials

The soil used in this study is kaolin clay (ASP-170, Tsuchiya Kaolin Co.). The elemental composition of kaolin expressed in mass percentage was Al_2O_3 38.5%, SiO_2 45.4%, Na_2O 0.2%, TiO_2 1.6%, CaO 0.03%, Fe_2O_3 0.5%, MgO 0.02%, K_2O 0.1%, and ignition loss 13.6%. Sodium chloride (NaCl) and zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$) were purchased from Nacalai Tesque to produce model contaminated soil samples. Details of the soil properties are shown in Table 1.

2.2. Sorption Experiments

Sorption studies were carried out using a batch equilibrium method, the magnitude of solid-liquid ratio (1 : 2) greater than the ratio used in standard batch test (1 : 10), in order to simulate the similar condition as the EK experiments. The background solution (0.01 M NaCl) was prepared with distilled water. Precise volume of zinc nitrate powder was added to the background solution to produce zinc concentrations of 100, 200, 300, 400, 500, 600, 700, and 800 mg/L. Solution pH adjustment was made using hydrochloric acid (HCl) and Sodium hydroxide (NaOH).

Nine replicate tubes were prepared for each treatment by adding 40 g of dry soil and 80 ml of target zinc solution. The slurries were then shaken on a reciprocating shaker (SR-1 Taitec) operated at 2000 ± 2 rpm at a room temperature for 3 hours to achieve chemical equilibrium. Preliminary experiments of sorption kinetics indicated that a period of 2 hours was sufficient to attain equilibrium as shown in Fig. 1. At the end of desired contact time, sample tubes were removed from the shaker and centrifuged for 30 minutes at 3000 ± 1 rpm. Zinc concentration and soil pH were measured before and after sorption experiments by ICP (ICPS-8000 Shimadzu) and pH meter (F-14 Horiba), respectively. Each test was

Table 1. Specification of kaolin clay

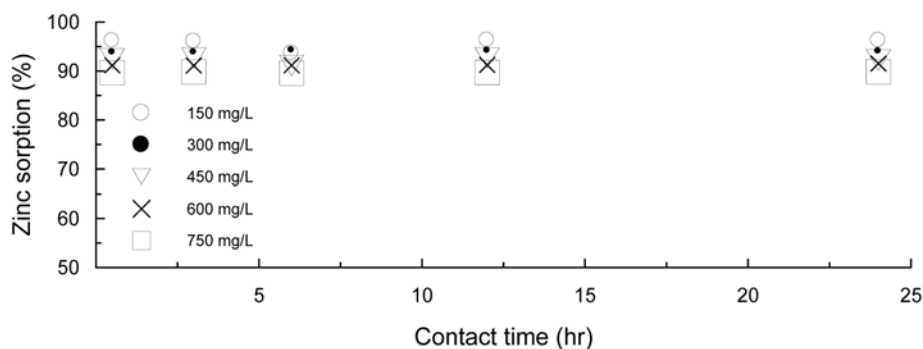| Typical properties	Value
Average particle size	0.4 μm
325 mesh residue	0.01%
Specific gravity	2.58
pH	6.0~8.0
CEC	3~15 meq/100 g

Fig. 1. Zinc sorption onto kaolin clay.

repeated in duplicate runs, both producing reliable results.

Solid-phase zinc concentrations, q_t, were determined according to Eq. (1);

$$q_t = \frac{(C_0 - C_t)L}{S}$$
(1)

where C_0 is the zinc concentration in the blank solution, C_t is the zinc concentration in the solution in sorption equilibrium, and L/S is the liquid to solid ratio.

2.3. pH-Controlled Sorption Experiments

A number of pH-controlled sorption tests was also undertaken in order to determine the effect of pH on zinc sorption in kaolin clay. All the pH-controlled sorption experiments followed the same procedures as the batch equilibrium test described in the previous section. Distilled water was mixed with sodium chloride and zinc nitrate powder to prepare background solution (i.e. 0.01 M NaCl and 500 mg/L zinc). Two sets of soil specimen (i.e. 10 g of kaolin clay mixed with 20 ml background solution) were prepared: each set consisting of ten kaolin samples. The soil pH was adjusted using dilute acetic acid (CH_3COOH) and sodium hydroxide (NaOH).

2.4. Desorption Experiments

The solid samples after batch sorption tests were used for desorption studies. The remainder of the supernatant of the sorption test was removed from the tube and thereafter fresh distilled water was added to the sediment residue. Desorption was processed for 5, 10, 15, 20, and 24 hours, respectively. The desorbed zinc concentration was determined from the collected supernatant after centrifuge.

Solid-phase zinc concentration after desorption processes, $q_t^{(d)}$, was determined according to Eq. (2);

$$q_t^{(d)} = q_t + \frac{C_t m}{S} - \frac{C_t^{(d)} L'}{S}$$
(2)

where m is the volume of solution remaining after removal of supernatant, $C_t^{(d)}$ is the aqueous phase zinc concentration after desorption, and L' is the sum of the volume of the residual solution phase (m) and the zinc-free solution added for aqueous desorption.
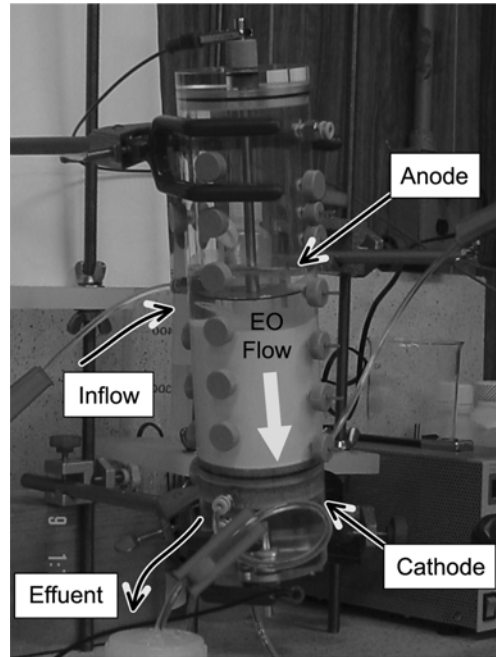

Fig. 2. Electrokinetic column in use.

2.5. Electrokinetic Extraction Experiments

The EK column used in this study is shown in Fig. 2. The contaminated soil sample is contained in the acrylic tube of 60 mm diameter and 300 mm long, equi- pped with each of 5 voltage probes and pH ports along the side of the wall, that is connected on each end to a 50 mm long electrode chamber containing a disc shape stainless steel electrode.

The voltage probes and pH ports are embedded in contact with the slurry sample at regular intervals in order to measure local voltage gradient and pH within the soil sample. Pressure-induced flow is prevented by equalising the static heads in a hydraulic head control device. Ports in the bottom chamber vent the oxygen and hydrogen produced by the electrolytic reactions. The preparation of zinc spiked samples for all EK extraction tests followed the same procedures as the batch sorption equilibrium test described in Sec. 2.2.

During the test, the volume of effluent collected from the cathode reservoir is monitored as well as the current through the cell. At the end of each run, the sample was divided into two sections (e.g., anode region vs. cathode region), and each section was analysed for total and dissolved concentrations of zinc by ICP. In

order to determine the average dissolved zinc concent-ration, the pore solution was separated from a portion of a clay section by centrifuge and another portion of sample was acidified with hydrochloric acid before centrifuge for determining total zinc concentration.

3. Results and Discussion

3.1. Sorption Experiments

Fig. 3 shows typical sorption isotherms of zinc ions adsorbed onto kaolin clay with their concentrations in

solution at pH 5 and moisture content of 200 %. In general, sorption isotherms can be described by mathe-matical expressions such as the Langmuir and Freundlich equations (Atkins, 1978).

The sorption data were fitted well to the following Langmuir equation;

$$q_t = \frac{abC_e}{1 + bC_e} \tag{3}$$

where q_t is the solid-phase zinc concentrations, a and b are constants, and C_e is the final concentration in solution.
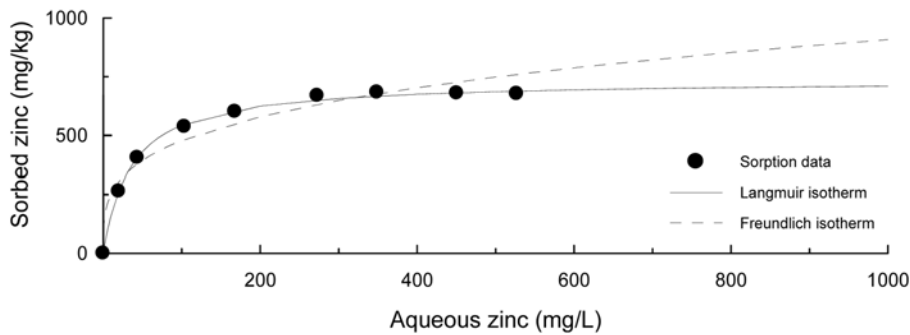

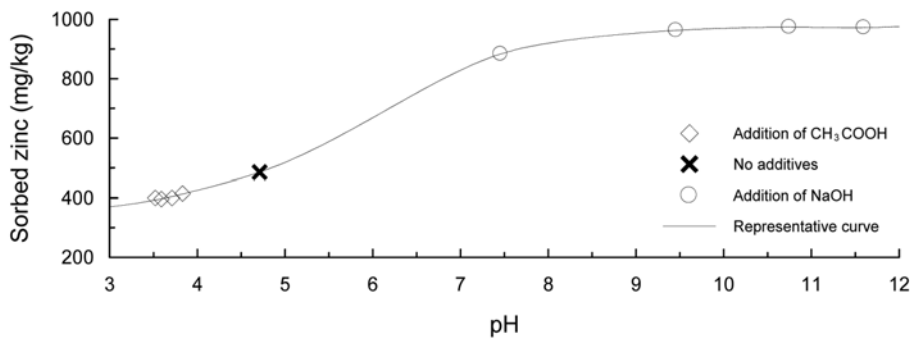**Fig. 3.** Zinc sorption isotherms at pH 5.

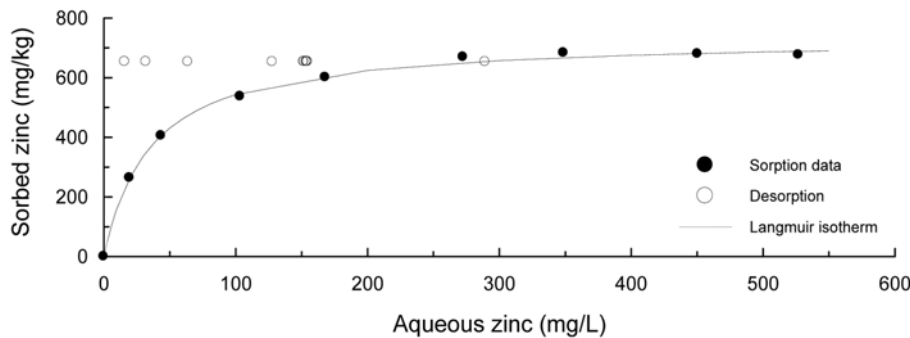**Fig. 4.** pH-dependent sorption-desorption of zinc onto kaolin clay.

Fig. 5. Sorption-desorption of zinc onto kaolin clay.

3.2. pH-Controlled Sorption Experiments

The pH-controlled sorption experiments allowed the evaluation of the pH dependence of zinc sorption onto kaolin clay. The effects of pH on the zinc sorption are shown in Fig. 4. It can be seen in general that the sorption of zinc increased with increasing pH. The test results clearly illustrate the significance of pH dependency of zinc sorption in kaolin.

3.3. Desorption Experiments

Fig. 5 shows typical desorption processes of zinc in kaolin clay. As seen, zinc adsorbed onto soil surface remains almost constant with the decreasing zinc concentrations in pore solution. It appears that batch desorption of zinc using clean distilled water can slowly remove the ionic form of zinc in pore solution only.

3.4. Electrokinetic Extraction Experiments

Fig. 6 shows EO flow rate and zinc removal efficiency with respect to time results. It can be seen that the pore fluid flow induced by EO rapidly increased with time after approximately 30 minutes of EK processes. The accumulated effluent was up to 190 ml for about 4 hours of EK treatment with the applied voltage gradient of 300 V/m.

The removal efficiency was calculated from the ICP analysis based on the EO flow rate. In general, the removal efficiency of zinc increases with the increasing period of EK treatment. It is interesting to note that the zinc removal for the first 2 hours of EK processes was about 0 % with the pore fluid removal of approximately 70 ml; a noticeable increase of zinc removal can be seen after 2 hours of the EK treatment. It seems that both the soluble form of zinc ions in pore solution and those adsorbed onto soil surfaces were initially mobilised and transported through the soil matrix by the effects of EM resulting in the net pore fluid flow through the system. However, the introduction of hydroxyl ions (OH^-) from the cathode side due to the combined effects of electrolysis and EM may have prevented the advance of migrating zinc ions, and precipitations occurring in the cathode
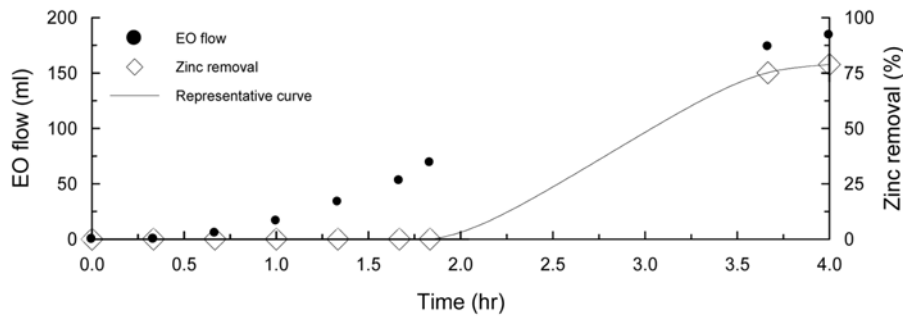

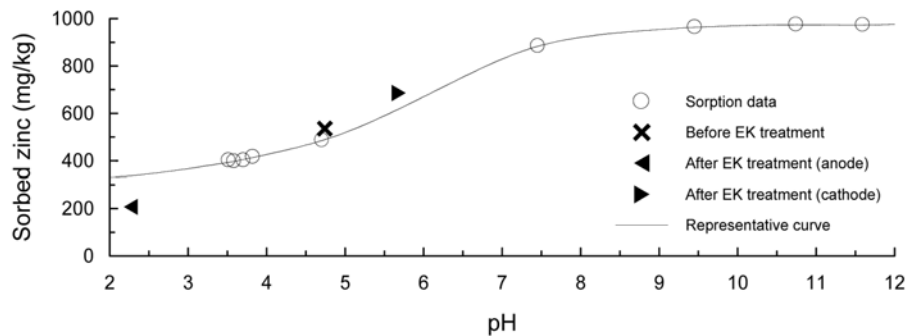**Fig. 6.** Electroosmotic flow and zinc removal with respect to time.

Fig. 7. Electrically induced sorption-desorption of zinc onto kaolin clay.

region. The sorption capacity of soil can be changed under different pH environment (see Fig. 4) and that capacity of soil containing the migrating zinc ions from the anode side appears to be exceeded after 2 hours of the EK processes. Since then, the migrating zinc ions from the anode side passing through the cathode region may have been increased with the enhancement by advancing acid front from the anode side. Thus, the zinc removed at the early stage of the EK processes could be the adsorbed zinc in the anode region, which means that the mobilisation of zinc from the soil matrix may be induced by the combined effects of cation exchange reactions and EK processes with time interval, especially, at the early stage of EK treatment.

Fig. 7 shows the results from pH-controlled sorption tests together with the zinc sorption/desorption observed during the EK experiments. Sorption and desorption by the EK treatment in both anode and cathode regions follow the pH-controlled sorption curve. The data point obtained from the anode region may imply that the removal of zinc ions under the EK processes could be enhanced by the effects of EM. On the other hand, in the cathode region, the zinc ions adsorbed onto soil surfaces are increased due to the continuous supply of zinc migrating from the anode side, which may have been precipitated onto soil surfaces.

4. Summary and Conclusions

The following conclusions can be drawn based on the experimental studies:

1. The pH of the soil plays an important role in sorption and desorption processes of et al ions. A sub- stantial metal sorption can be achieved in a high soil pH environment, while a low soil pH condition would cause less sorption of metal contaminants.

2. The migrating metal ions induced by the EK treatment can be precipitated in the cathode region, depending on the electrically changing pH condition and soil sorption capacity, resulting in a low efficiency of metal removal.

3. The key for the successful application of EK technique to extract heavy metal contaminants from fine-grained soils is to keep the target heavy metals in soluble forms.

A thorough understanding of the sorption and desorption processes occurring during the EK treatment is required for successful use of EK remediation technology in actual field application.

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