Enhancement Effect of Humic Acid on Removal of Lead from Soil by Electrokinetic Process

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The environmentally friendly electrokinetic process was investigated using model contaminated soil with Pb and humic acid. Although humic acid has a negative charge, it moved toward the cathode side by electroosmotic flow. The removal efficiency of Pb from model contaminated soil was 48.0% under 1 V/cm of the potential gradient after 72 h of operation, while it improved to 72.6% with humic acid. These results indicated that humic acid has high potential for application in the environmentally friendly remediation of soil.

Keywords Soil treatment, electrokinetic process, lead, humic acid, pyrophyllite, electroosmotic flow

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Introduction

Contaminated soils with inorganic substances exceeding the legal standards were reported more than 1800 times in Japan in 2017.¹ If these contaminated soils containing pollutants, such as heavy metals, are left unattended, the pollutants will continue to be discharged for a long time. Therefore, on-site soil remediation is required to avoid the spread of the pollutants and secondary pollution.

The electrokinetic (EK) process is one of the on-site remediation technologies for soil, in which electromigration and electroosmotic flow (EOF) are used to transport pollutants in soil.² The remediation of contaminated soil with heavy metals and harmful organic substances by the EK process has been investigated.³⁻⁷ Recently, the application of the EK process to soil contaminated with radioactive Cs has been performed.⁸⁻¹² To enhance the removal efficiency of heavy metals from soil, a strong inorganic acid or artificial chelating reagent such as EDTA was used.^{13,14} However, the use of these substances may cause secondary pollution.

Humic acid (HA) is one of the organic substances in soil, which is produced by the degradation of dead plants chemically and biologically. HA has an interaction with various heavy metals and organic substances to solubilize these substances.¹⁵⁻¹⁸ The migrating behaviors of heavy metals in soil by the EK

process are also affected by the presence of HA, and the applications of HA to the remediation of contaminated soil by the EK process have been investigated.¹⁹⁻²²

In this study, the migrating behavior of HA in the EK process was investigated at first and then the enhancement effect of HA on the removal of Pb was demonstrated. Finally, the roles of HA for the removal of heavy metals in soil by the EK process were discussed for the development of an environmentally friendly soil remediation method.

Experimental

Reagents and chemicals

White clay (Practical Grade, Wako Pure Chemical Industries, Ltd.) was used as the model soil. This material includes pyrophyllite (one of the clay mineral) and quartz.¹² In this paper, white clay was expressed as “pyrophyllite”. Pb(NO₃)₂, NaOH and HCl were purchased from Wako Pure Chemical Industries, Ltd. HA was purchased from Sigma Aldrich Co. Distilled water (DW) was used for the preparation of the sample solutions.

Preparation of model soil

The model soil containing HA was prepared by the following procedure. Powdery HA was added to pyrophyllite to achieve 5 wt%, and four times as much DW as the soil by weight was added to the mixture of HA and pyrophyllite. The mixture was horizontally shaken for 24 h at 170 rpm by Multi Shaker (MMS-3010, EYELA). Then it was dried at 80°C in a dry oven DK-62 (Yamato Scientific Co., Ltd.) until complete dryness. The dried soil was crushed by a mortar and used as the model soil containing HA. The model contaminated soil containing lead

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Fig. 1 Schematic diagrams of equipment for the electrokinetic (EK) process in this study.

(0.3 mg Pb^{2+}/g) was prepared by the following procedure. Powdery $\text{Pb}(\text{NO}_3)_2$ was added to pyrophyllite and DW was added to adjust the soil moisture (30 wt%). The soil sample was mixed well and used as the model contaminated soil. The equipment for the EK process as shown in Fig. 1 is the same as that used in our previous study.¹²

Analytical procedure

The soil sample in the migration chamber was divided into five sections after the EK process and each soil sample was dried at 80°C for 12 h. Then, 0.1 mol/L NaOH solution was added to the dried soil sample (solid:liquid ratio was 1:10), and it was mixed for 4 h at 1500 rpm by a Cute Mixer (CM-1000, EYELA). The mixture was separated by centrifugation for 15 min at 4000 rpm (2410, Kubota Corp.). The concentration of HA in the supernatant was estimated as the total organic carbon measured by TOC equipment (5000A, Shimadzu Corp.).

The extraction procedure of Pb in soil after the EK process was performed according to the following procedure. First, 1 mol/L HCl was added to the dried soil sample (solid:liquid ratio was 1:10) after the EK process. The mixture was shaken for 12 h at 1500 rpm and then centrifuged for 15 min at 4000 rpm. The concentration of Pb in the supernatant was measured by atomic absorption spectrophotometer (AAS) (A-2000, Hitachi Ltd.) at 217.0 nm.⁴ Adding DW to the dried sample after the EK process (solid:liquid ratio was 1:5) and mixing it for 1 h at 1500 rpm, pH of the mixture was measured using a pH meter (M-13, Horiba Ltd.). The solutions in anode, cathode chambers and a cylinder receiving the overflow of the EOF were used for the measurement of HA and Pb. The removal efficiency of Pb in the sample soil was calculated by the following Eq. (1).

$$\text{Removal efficiency (\%)} = C_{\text{before}}/C_{\text{after}} \times 100 \quad (1)$$

Here, C_{before} and C_{after} indicate the concentration of Pb in soil before and after the EK process at section 3 (mg/g).

Results and Discussion

First, the migration behavior of HA in the EK process was investigated. Pyrophyllite soil without HA was used to fill in all sections of the migration chamber except section 3. The soil containing HA was located in section 3 and the movement of HA in the migration chamber was observed during the EK process. As shown in Figs. 2a and 2b, the brown color of

Fig. 2 (a) and (b) show the behavior of humic acid (HA) before and 72 h after the electrokinetic (EK) process, respectively. The potential gradient was 1 V/cm, and the migration solution was distilled water.

section 3 observed before the EK process faded after 72 h. On the contrary, the cathode chamber changed to a brown color after the EK process. Therefore, HA seems to be transported to the cathode side by the EK process. Usually, the transportation in soil by electromigration is faster than that by EOF. Therefore, anionic species such as chloride ion and acetic ion are transported to the anode side by electromigration.² HA has a large molecular weight and the electrophoretic mobility of HA in soil is small. Therefore, the effect of EOF, a water flow to the cathode side, was larger than that of electromigration, and consequently HA was transported to the cathode side. This result was similar to our previous research.²⁰

If HA could be transported to the cathode side by EOF, it would be possible to supply HA added as an electrolyte in the anode chamber to the soil. Some reagents such as EDTA, organic acids and inorganic acids were added to the electrode chamber and supplied to the part contaminated with heavy metal to facilitate the removal of the metals in soil.^{14,22} However, HA stayed in the anode chamber even after the 72 h of operation (Fig. S1, Supporting Information). It was impossible to have HA in the anode chamber penetrated into the migration chamber because EOF is generated only in solid media such as clay minerals but not in water. These results showed that HA should be located in soil of the anode side from pollutant to enhance the removal efficiency of pollutants in soil by using the complexing and solubilizing abilities.

To investigate the migration behavior of Pb by the EK process, the model contaminated soil with Pb was located in section 3 and other sections were filled with uncontaminated soil. Most natural soil contains organic matters, such as humic substances, therefore, the presence of HA might affect the migration behavior of Pb by the EK process. Figure 3 shows the distribution of Pb after the EK process with and without HA. Pb in section 3 was partially transported to section 2 of the cathode side by electromigration and EOF under the condition without HA. However, Pb was not found in section 1 and the cathode chamber, and the removal efficiency of Pb was 48.0%. Since the soil pH of section 1 increased to around 6 because of the generation of hydroxide by the electrolysis of water at the cathode, Pb began to precipitate in the hydroxide form around the interface between section 1 and 2. Therefore, Pb could not reach section 1. To investigate the effect of HA on the migration

Fig. 3 Distribution of (a) Pb, pH and (b) humic acid (HA) in soil 72 h after the electrokinetic (EK) process. The potential gradient was 1 V/cm, and the migration solution was distilled water.

behavior of Pb by the EK process, powdery HA was mixed with the dried model soil contaminated with Pb and the mixed contaminated soil was located in section 3. It was found that 72.6% of Pb in section 3 was transported to the cathode side with HA (the removal efficiency was 72.6%). Usually, Pb is transported to the cathode side by electromigration as ion-exchanging on the surface of clay mineral. However, when HA exists, Pb interacts more with HA than with the clay mineral.²³ Since HA is transported to the cathode side by EOF, as a result, the interaction between Pb and the clay mineral became weak and the removal efficiency of Pb was enhanced by the presence of HA. Moreover, Pb was not observed in section 1 without HA but observed in section 1 and the cathode chamber in the presence of HA after the EK process. The main interaction between Pb and HA was reported as a binding with two carboxylic groups, or with one carboxylic group and one phenolic group.²⁴ When pyrophyllite containing Pb and HA was prepared, the pH of the prepared pyrophyllite was 8.8. At this pH, the carboxylic group was almost completely deprotonated, but the phenolic group was not deprotonated.²⁵ Therefore, it was expected that Pb was mainly complexing with carboxylic groups on HA (Eq. (2)).

These results indicated that when HA is used as an additive to enhance the removal efficiency of soil contaminated with heavy metals, HA should be added to the contaminated place directly, and not be introduced from the electrolyte chamber.

Conclusions

The environmentally friendly remediation process for Pb was investigated by combining the EK process with HA. The effect of EOF on the movement of HA was stronger than that of electromigration, and HA was transported to the cathode side. However, in the case that HA was put in the anode chamber, HA could not easily penetrate into the soil chamber. When the EK process was applied to the model soil contaminated with Pb, the removal efficiency of Pb was 48.0% without HA. The removal efficiency of Pb was enhanced to 72.6% by the addition of HA. The presence of HA might weaken the interaction between Pb ions and clay mineral to facilitate the movement in soil, and consequently HA enhanced removal efficiency of Pb.

The basic investigation on the migration behavior of Pb and

HA in soil by the EK process in this study will contribute to the development of environmentally friendly soil remediation. Especially, this study revealed newly how HA was transferred as interacting with heavy metals and how the migration behavior of heavy metals was affected by HA under the electric field. Since HA is widely distributed in soil and aqueous environments and affects the behavior of pollutants and nutrition in those environments, our findings that Pb was transported with HA to the cathode side in the EK process and the efficiency was enhanced by the presence of HA will also contribute to elucidate material circulation in clay soil.

Supporting Information

The behavior of HA before and 72 h after the EK process when HA was put in the anode chamber as electrolyte are shown in Fig. S1. This material is available free of charge on the Web at <http://www.jsac.or.jp/analsci/>.

References

1. Ministry of the Environment, Japan, "Report on Soil Contamination Surveys and Countermeasures", **2019**, <http://www.env.go.jp/press/files/jp/111308.pdf> (in Japanese).
2. Y. B. Acar and A. N. Alshawabkeh, *Environ. Sci. Technol.*, **1993**, 27, 2638.
3. A. Sawada, K. Mori, S. Tanaka, M. Fukushima, and K. Tatsumi, *Waste Manag.*, **2004**, 24, 483.
4. R. S. Putra, Y. Ohkawa, and S. Tanaka, *Sep. Purif. Technol.*, **2013**, 102, 34.
5. T. Suzuki, M. Niinae, T. Koga, T. Akita, M. Ohta, and T. Choso, *Colloids Surf., A*, **2014**, 440, 145.
6. E. Bocos, C. Fernandez-Costas, M. Pazos, and M. A. Sanroman, *Chemosphere*, **2015**, 125, 168.
7. G. C. C. Yang, *Sci. Total Environ.*, **2019**, 659, 963.
8. Y. Akemoto, C. Kitagawa, R. Miyamura, M. Kan, and S. Tanaka, The 13th International Symposium on Electrokinetic Remediation (EREM2014), ed. J. M. Rodríguez-Maroto, **2014**, Málaga, Spain, 134.
9. G.-N. Kim, S.-S. Kim, U.-R. Park, and J.-K. Moon, *Electrochim. Acta*, **2015**, 181, 233.
10. M. Igawa, K. Ishiyama, and B. Nanzai, *Bull. Soc. Sea Water Sci. Japan*, **2018**, 72, 88 (in Japanese).
11. M. Kabir, Y. Hatakeyama, and S. Nakajima, *Nat. Environ.*

- Pollut. Technol.*, **2018**, 17, 237.
12. Y. Akemoto, M. Kan, and S. Tanaka, *J. Chem. Eng. Japan*, **2019**, 52, 662.
 13. A. T. Yeung, C. Hsu, and R. M. Menon, *J. Geotech. Eng.*, **1996**, 122, 666.
 14. K.-J. Kim, D.-H. Kim, J.-C. Yoo, and K. Baek, *Sep. Purif. Technol.*, **2011**, 79, 164.
 15. H. Kerndorff and M. Schnitzer, *Geochim. Cosmochim. Acta*, **1980**, 44, 1701.
 16. M. Taga, S. Tanaka, and M. Fukushima, *Anal. Sci.*, **1989**, 5, 597.
 17. S. Tanaka, K. Oba, M. Fukushima, K. Nakayasu, and K. Hasebe, *Anal. Chim. Acta*, **1997**, 337, 351.
 18. R. Kodama, K. Sazawa, T. Miyamoto, Q. Zhu, M. Igarashi, K. Oda, H. Kuramitz, and M. Fukushima, *Chemosphere*, **2018**, 204, 63.
 19. K. R. Reddy and S. Chinthamreddy, *Waste Manag.*, **1999**, 19, 269.
 20. A. Sawada, S. Tanaka, M. Fukushima, and K. Tatsumi, *J. Hazard. Mater.*, **2003**, B96, 145.
 21. A. Giannis, E. Gidarakos, and A. Skouta, *Desalination*, **2007**, 211, 249.
 22. F. Rozas and M. Castellote, *Electrochim. Acta*, **2012**, 86, 102.
 23. I. Heidmann, I. Christl, and R. Kretzschmar, *Geochim. Cosmochim. Acta*, **2005**, 69, 1675.
 24. W. L. Yan and R. Bai, *Water Res.*, **2005**, 39, 688.
 25. D. E. Wilson and P. Kinney, *Limnol. Oceanogr.*, **1977**, 22, 281.
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