Electrokinetic remediation of clayey soils containing copper(II)-oxinate using humic acid as a surfactant

Akira Sawada [a,b,c], Shunitz Tanaka [a],
Masami Fukushima [c,*], Kenji Tatsumi [c]

[a] *Division of Material Science, Graduate School of Environmental Earth Science, Hokkaido University, Kita-10, Nishi-5, Kita-ku, Sapporo 060-0810, Hokkaido, Japan*
[b] *New Energy and Industrial Technology Development Organization (NEDO), Sunshine 60 Bldg., Higashi Ikebukuro 3-1-1, Toshima-ku, Tokyo 170-6028, Japan*
[c] *National Institute of Advanced Industrial Science and Technology (AIST), Onogawa 16-1, Tsukuba West, Tsukuba, Ibaraki 305-8569, Japan*

Abstract

The utility of humic acid (HA) as a surfactant for use in the electrokinetic remediation (ER) of the clayey soils containing copper(II)-oxinate ($Cu(OX)_2$) was examined. A small simulator of ER was devised, which consisted of three types of artificial soils on the basis of the commercial kaolin: kaolin, kaolin + HA and kaolin + $Cu(OX)_2$. The layers of kaolin containing HA and $Cu(OX)_2$ were sandwiched between two kaolin layers. In all experiments, a constant dc voltage gradient of 2.2 V/cm was applied through the soil for 30 h, and the pH of the solution in the anodic chamber was maintained at 7.0. Generally, HA has a negative charge at a neutral pH. However, the HA was mainly transferred to the cathodic chamber. This shows that the driving force of the HA in the system used herein is predominantly due to electroosmotic flow. Moreover, the amount of $Cu(OX)_2$ removed from the clayey soils in the presence of HA was three times larger than those in the absence of HA. This can be attributed to the fact that the water solubility of $Cu(OX)_2$ is enhanced by the presence of HA. Thus, we conclude that HA has a potential for use as an amendment for the ER of hydrophobic chemicals, such as $Cu(OX)_2$.
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* Corresponding author. Tel.: +81-298-61-8328; fax: +81-298-61-8326.
E-mail address: m-fukushima@aist.go.jp (M. Fukushima).

1. Introduction

Contaminated soils, when left in an untreated state, lead to the subsequent contaminations of river and ground waters [1,2]. Hence, the development of technologies for cleaning up the soils, which are contaminated with hazardous chemicals, are important from the point of view of environmental protection. A variety of innovative methods for soil remediation have been examined and can be classified into in situ or ex situ technologies. Based on currently available information, in situ methods have some advantages over ex situ ones. Since the excavation and the transportation of the soils are not needed in the case of in situ methods, levels of the pollutant diffusion can be reduced. As a result, a variety of in situ technologies have been devised and developed [3–6].

Electrokinetic remediation (ER), a process for removing pollutants from clayey soils on the basis of electrokinetic phenomena, represents one such in situ technologies [7,8]. This is performed under a low-level dc current (in the order of mA per the cross-sectional area (cm^2)) through electrodes, which are placed into the contaminated sites. In the case of ER method, if the pollutants are ionic compounds, they can be transferred to the oppositely charged electrode by electromigration (EM). In addition, electroosmotic flow (EOF) is another important driving force for the movement of pollutants in the ER method. This is defined as the movement of an electrolyte solution by an electric field applied to a porous stationary solid that has negative surface charge. Therefore, electrically neutral pollutants, if they are water soluble, may be removed by EOF. The advantages of the ER method can be summarized as follows: (1) the movement of pollutants is limited only by the electrical field and (2) a relatively short time is required to remove pollutants from clayey soils [9]. As this writing, a number of studies of the ER method have been reported and adapted to a variety of sites contaminated with pollutants [10–13]. Nevertheless, it is difficult to apply the ER method to the removal of water insoluble pollutants. The use of solubilizing agents, such as surfactants, is one of the possible approaches to enhance the efficiency of removing water insoluble pollutants from the contaminated soils. Although several artificial surfactants have been examined for possible use in the ER method [14,15], this use may cause secondary contamination to the environment.

It is well known that humic substances (HSs), such as humic acid (HA) and fulvic acid, are weak-acid polyelectrolytes and are widely distributed in the environment [16]. The major source of organic carbon in natural soils consists of HSs, of which HA is a major component [17]. A number of studies have reported that HA contains both hydrophobic and hydrophilic moieties [18–20]. Thus, the hydrophobic portions of HA may serve as surfactants in aiding the dissolution of a variety of hydrophobic organic chemicals, such as herbicides and pesticides [21–23].

The purpose of the present study was to develop an effective ER system for the removal of hydrophobic chemicals from clayey soils. In particular, the surface-active functions of HA were examined for their potential use in the removal of hydrophobic chemicals. In the present study, copper(II)-oxinate ($Cu(OX)_2$) was selected as model hydrophobic pollutants. $Cu(OX)_2$, which is used as a fungicide, has widely been used at golf links in Japan, and this use led to water pollution via runoff and leaching of $Cu(OX)_2$ from golf links in Hokkaido, Japan in 1989. Thus, $Cu(OX)_2$ can be regarded as a pollutant in soils and aquatic environments [24,25].

Although, $Cu(OX)_2$ can be slightly soluble in water, its water solubility is increased by several folds in the presence of HA [26]. Therefore, in the present study, the moving behavior of HA and its effect on the solubilization of $Cu(OX)_2$ were investigated by using a laboratory-scale simulator (ER simulator), which was constructed.

2. Materials and methods

2.1. Materials

HA (sodium salt) was obtained from Aldrich Chemical Co. Inc. (Tokyo, Japan) and was used without further pretreatment. bis(2-hydroxyethyl)Iminotris (hydroxymethyl) methane (bis-Tris) was purchased from Dojindo Laboratories (Kumamoto, Japan). A commercial kaolin (kaolin) (chemical grade) was purchased from Wako Pure Chemicals Ltd. (Osaka, Japan). The kaolin, used in the present study, contained 42–46% of SiO_2, 37–40% of Al_2O_3, trace amounts of Fe_2O_3 and TiO_2. The particle size distribution is in the range of 2–15 μm. The pH of the kaolin slurry is 4.3 at the kaolin:water ratio of 1:2.5 (w/w). $Cu(OX)_2$ and other chemicals (analytical grade) were purchased from Wako Pure Chemicals Ltd. (Osaka, Japan). Doubly distilled water was used to prepare the stock and the buffer solutions.

2.2. Preliminary experiment

In preliminary experiments, we determined the apparent water solubility of $Cu(OX)_2$ (S_w) at a variety of HA concentrations according to a method described by Fukushima et al. [26]. The stock solution of $Cu(OX)_2$ was prepared by dissolving $Cu(OX)_2$ in the ethanol (0.30 mM). An 1 ml aliquot of the stock solution was then added into 19 ml of 10 mM bis-Tris–HCl buffer solution containing HA at pH 6.0. This mixture, in a 50 ml centrifuge tube, was shaken for 4 h at room temperature, and was then filtered through a nitrocellulose membrane filter (pore size: 0.45 μm; Toyo Roshi Kaisha Ltd.). It was confirmed that HA was completely dissoluted under the experimental condition and there was no loss of HA. The concentrations of $Cu(OX)_2$ in the filtrate were equal to the S_w.

2.3. Preparation of artificial soils

When the clayey soil was prepared from the kaolin with the buffer solution at pH 7, the pH of the soil slurry was lowered to 4–5 at the ratio of 1:2.5 (soil:water, w/w). This is due to the strong buffering capacity of kaolin. Thus, pretreatment procedures of kaolin were carried out: kaolin and doubly distilled water (0.25, w/w) were placed in a plastic bottle, and this mixture was then shaken for 24 h. The slurry was transferred to a beaker, and the pH of the slurry was adjusted to 7 by the addition of aqueous 0.1 M NaOH. The slurry was filtered through 5B filter paper and the kaolin on the filter was dried in an oven at 313 K for several days.

The kaolin containing HA (kaolin + HA) was prepared by mixing 11 g of the pretreated kaolin and 1 g of HA. The kaolin containing $Cu(OX)_2$ (kaolin + $Cu(OX)_2$) was prepared by mixing 12 g of the pretreated kaolin and 4 mg of $Cu(OX)_2$. The water content of each artificial soil was set at 31% using a buffer solution (pH 7.0, 0.1 M NaH_2PO_4/NaOH). Each
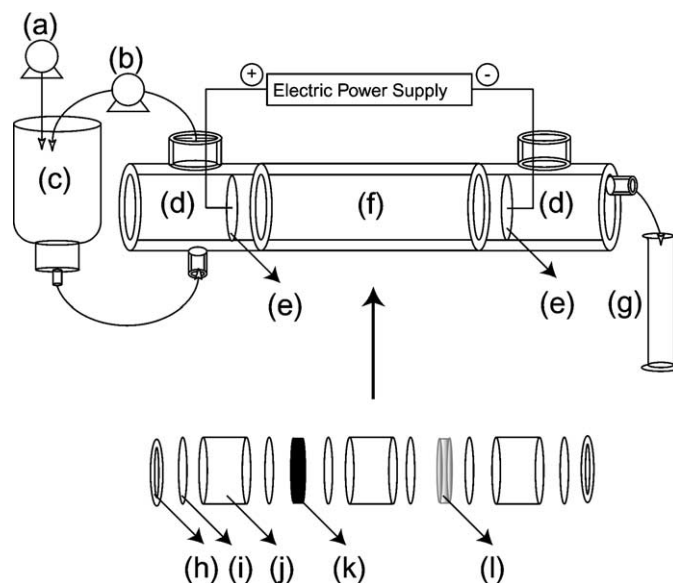
Fig. 1. Construction of ER simulator: (a) peristaltic pump, (b) circulation pump, (c) pH control chamber, (d) electrode chamber, (e) Pt–Ti electrode, (f) migration chamber, (g) measuring cylinder, (h) O-ring, (i) 5B filter paper, (j) kaolin, (k) kaolin + HA (l) kaolin + $Cu(OX)_2$.

soil was packed into the migration chamber as shown in Fig. 1. The total weight of the soils in the migration chamber was 118 ± 4 g. The amounts of $Cu(OX)_2$ or HA in the soil could be calculated from the mixing ratio of kaolin + $Cu(OX)_2$ or kaolin + HA to kaolin only ($Cu(OX)_2$, 1.4 mg; HA, 0.4 g).

2.4. Construction of ER simulator

The ER simulator, as shown in a previous paper [27], was modified for the purpose of the present study. The construction of the simulator is illustrated in Fig. 1. The simulator consisted of three parts that were made of acrylic resin: one migration chamber and two electrode chambers. The size of migration chamber was 3.0 cm i.d. × 10.0 cm (approximately 70 cm^3). Each end of the migration chamber was connected with the electrode chambers by partitioning with 5B filter paper and an O-ring. The migration chamber was packed with three types of artificial soil: kaolin only, kaolin + HA, and kaolin + $Cu(OX)_2$. As shown in Fig. 1, the arrangement of the soil samples in the migration chamber was kaolin/kaolin + HA/kaolin/kaolin + $Cu(OX)_2$/kaolin, and the kaolin + HA or $Cu(OX)_2$ layers were separated by 5B filter paper. $Cu(OX)_2$ is moved to the cathode by EOF, HA is also moved to the same direction. Because the velocity of $Cu(OX)_2$ is much smaller than that of HA, the layer containing HA was placed near the anodic chamber compared to the layer containing $Cu(OX)_2$.

The size of the electrode chamber was 3.0 cm i.d. × 5.5 cm (approximately 22 cm^3). As shown in Fig. 1(d) and (e), meshed Pt–Ti electrodes were inserted into each chamber, and

the chambers were filled with a buffer solution (pH 7.0, 0.1 M NaH_2PO_4/NaOH buffer). The anodic chamber was connected with a pH control system (Fig. 1(a)–(c)). The pH of anodic solution was maintained at pH 7 by circulating the buffer solution in the anodic chamber with a buffer circulator (Fig. 1(b)) (AE-6380, Atto Co. Ltd., Tokyo, Japan). The acidic solution from the anodic chamber was neutralized with an aqueous NaOH by means of a peristaltic pump (P-1, Pharmacia Biotech Inc., Tokyo, Japan) (Fig. 1(a)). The water level of each chamber was maintained at the same level to prevent natural water flow, generated by the difference of hydrostatic pressure between the two chambers.

In the migration chamber, a constant dc voltage (22 V) was applied between two electrodes by means of a dc power supply (HP-7612D, Marysol Co. Ltd., Tokyo, Japan). As shown in Fig. 1(g), the effluent by EOF was collected in a measuring cylinder and stored for analysis. In all experiments, a constant dc voltage gradient (2.2 V/cm across the soils) was applied for 30 h.

2.5. Analyses

After applying the voltage, the analyses of HA and $Cu(OX)_2$ were performed with respect to the solutions in the cathodic chamber and the effluent in the measuring cylinder. The concentrations of HA were determined by means of an ultraviolet–visible absorption spectrophotometer (V-550, Japan Spectroscopic Co. Ltd., Tokyo, Japan) at a wavelength of 450 nm. The concentrations of $Cu(OX)_2$ were determined by measuring copper in the solutions by means of an atomic absorption spectrophotometer (170-50, Hitachi Co. Ltd., Tokyo, Japan).

3. Results and discussion

3.1. S_w in the presence of HA

Firstly, S_w was checked in the presence of the HA and this can be expressed as

$$S_w = S_{w_0} + K[HA] \tag{1}$$

where S_{w_0} and K represent the water solubility of $Cu(OX)_2$ in the absence of HA and the distribution coefficient, respectively.

Fig. 2 shows the relationship between S_w and HA concentration ([HA]). The value of S_w linearly increased with increasing [HA]. The slope of the line corresponds to the distribution coefficient, which was determined to be 0.17. Moreover, the value of S_w at [HA] = 1.3 mg/l (6.00 μM) was eight times larger than that in the absence of HA (0.75 μM). These results show that the presence of HA results in an enhancement in the water solubility enhancement of $Cu(OX)_2$.

3.2. Electroosmotic flow and the pH profile of the anodic electrolyte

While the voltage was applied, hydrogen and hydroxide ions are generated by the electrolysis of water on the surfaces of anode and cathode, respectively. These ions permeate
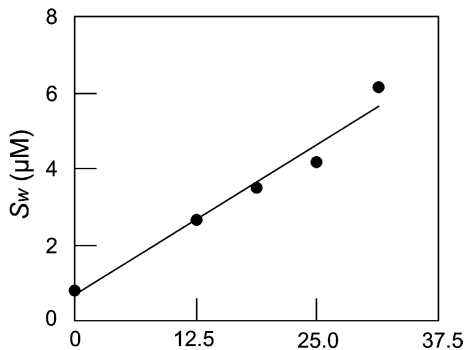
Fig. 2. S_w as a function of [HA].

into the soil by EM and/or EOF. Because the driving forces of hydrogen ions in the migration chamber are due to EOF and EM, the movement rate of hydrogen ions can be faster than that of hydroxide ions. Therefore, the soils can become acidic [7,8]. Generally, the zeta potential of kaolin can be lowered by acidification and this leads to a decrease of EOF. In addition, precipitation and aggregation of HA may occur at low pH. Thus, to obtain constant EOF and to allow the HA to remain in a soluble state, the pH of the solution in the anodic chamber was maintained at pH 7.

Fig. 3(a) and (b) show the volume of effluent and the pH of the solution in the anodic chamber in the presence of HA as a function of time. When the pH of the solution was maintained 7 by using the pH control chamber in Fig. 1(c), a constant pH of the solution in the anodic chamber could be obtained during most of the experimental period (Fig. 3(b)). Although the pH of the solution in the anodic chamber was lowered to 5.2 at 7 h (Fig. 3(b)), the volume of effluent increased in a linear manner to the EOF and this value was calculated to be 4.3 ml/h. This shows that a constant EOF can be obtained over the entire experimental period. However, in the absence of pH control, the pH of the anodic solution decreased
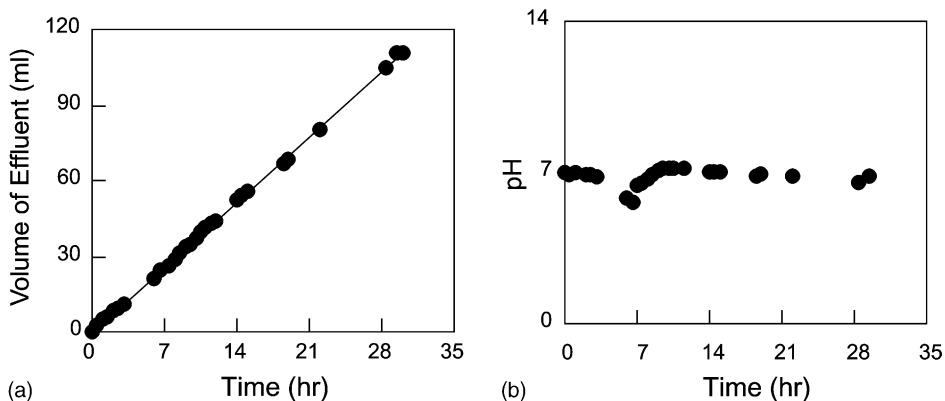

Fig. 3. (a) Volume of effluent as a function of time, (b) pH of the solution in the anodic chamber as a function of time.

rapidly, and the EOF gradually decreased (data not shown). These results demonstrate that the pH control in the anodic chamber is important in obtaining a constant rate of EOF.

In the present study, the pH of the solution was controlled in the anodic chamber but not in the cathodic chamber. Thus, the pH of the soil in the migration chamber increased to 10 after 30 h. The zeta potential of kaolinite is generally constant at pH values above 7, and the rate of EOF may also be constant [17,28]. Therefore, such an increase of the pH in the soil may have a negligible affect on the EOF in the present system.

3.3. Moving behavior of HA

Fig. 4 shows the mass of accumulated HA as a function of the volume of effluent that accumulated. The mass of accumulated HA at each sampling time could be calculated on the basis of the hypothesis that the [HA] in each effluent fraction was equal to the [HA] in the solution of the cathodic chamber at arbitrary sampling times (t_i). Therefore, the mass of accumulated HA at t_i can be written as

$$\text{(accumulated mass of HA)}_{t_i} = \sum_i \{[HA]_{t_i}(V_{t_i} + V_c)\} \tag{2}$$

where V_{t_i} and V_c represent each volume of the effluent at t_i and constant, respectively. As shown in Fig. 4, HA could be detected in the cathodic chamber after the retardation for 60 ml of volume accumulated, while corresponds to 17 h of applied voltage. The mass of accumulated HA increased with increasing volume of effluent. It is known that HA is a weak-acid polyelectrolyte and has large numbers of negative charges at pH 7 [16,17]. If the velocity of HA for EM is faster than that for EOF, HA can move in the direction of the anode. When the velocity of HA for EM is slower than that for EOF, HA may be transported into the cathodic chamber, even though HA is a polyvalent anion. Therefore, it can be concluded that EOF is the main driving force for the movement of HA from the soils to the cathodic chamber.
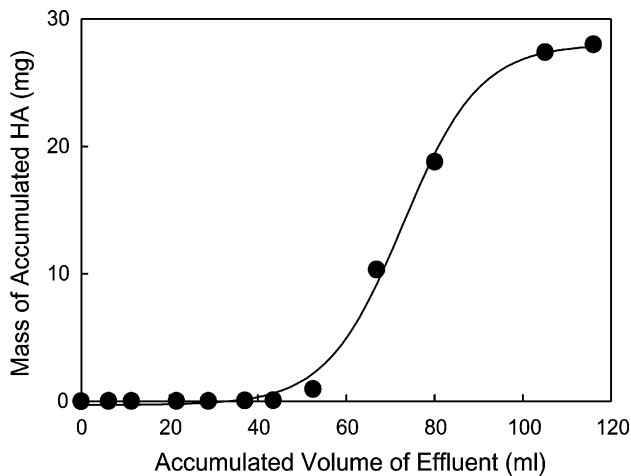

Fig. 4. Mass of accumulated HA as a function of volume of effluent.
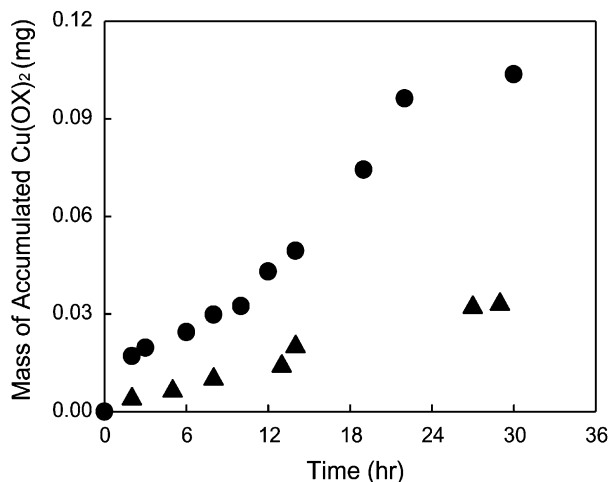
Fig. 5. Mass of accumulated $Cu(OX)_2$ as a function of time in the presence of or absence of HA. Symbols: ($\bullet$) amounts of $Cu(OX)_2$ in the presence of HA, ($\blacktriangle$) amounts of $Cu(OX)_2$ in the absence of HA.

In addition, HA (approximately 10 mg) could be observed in the anodic chamber after 30 h. In this case, HA migrated from the upper side of the migration chamber, where a void space existed. However, the majority of the HA in the soil was largely transported to the cathodic chamber by the EOF.

3.4. Effects of HA on the dissolution of $Cu(OX)_2$

Fig. 5 shows the mass of accumulated $Cu(OX)_2$ as a function of time. In the absence of HA, the accumulated $Cu(OX)_2$ increased slightly with time. The total volume of effluent transported by EOF was 116 ml, and the mass of accumulated $Cu(OX)_2$ in the effluent and cathodic chamber was 0.03 mg. Thus, the value of S_w in the total effluent could be calculated from the ratio of the mass of accumulated $Cu(OX)_2$ to the total volume of effluent, which was calculated to be 0.74 μM. This value was in good agreement with the solubility of $Cu(OX)_2$ in pure water (0.80 μM at 293 K) [26]. This shows that the mass of accumulated $Cu(OX)_2$ is related to its water solubility. In the presence of HA, the value of S_w in the total effluent was calculated to be 2.45 μM from the amount of accumulated $Cu(OX)_2$ at the end of run. This shows that the amount of $Cu(OX)_2$ removed in the presence of HA is three times larger than that in its absence. As described in Section 3.1, the water solubility of $Cu(OX)_2$ was clearly enhanced by the presence of HA. Therefore, increasing the removal of $Cu(OX)_2$ in the ER system is due to the solubilizing effect of HA.

3.5. Relationship between the cumulated mass of $Cu(OX)_2$ and HA

In the ER system, if $Cu(OX)_2$ is removed by only solubility enhancement in the presence of HA, it can be expected that the linear relationship between the masses of accumulated
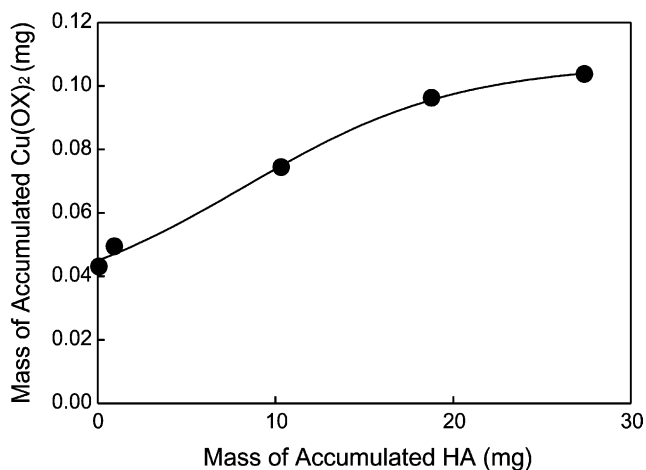
Fig. 6. Mass of accumulated $Cu(OX)_2$ as a function of mass of accumulated HA.

$Cu(OX)_2$ and HA may be observed. However, the mass of accumulated $Cu(OX)_2$ as a function of the mass of accumulated HA in Fig. 6 indicates a Langmuir-type curve rather than a linear line. The apparent K values in the ER system were estimated by the S_w values, which were calculated from the amounts of $Cu(OX)_2$ at some duration time in Fig. 5: 0.014 for 2.45 μM at 28.5 h, 0.011 for 3.37 μM at 21.5 h and 0.017 for 3.41 μM at 19.0 h. The values of K, estimated in the ER system, were much smaller than that in batch experiment of Section 3.1 (0.17). These results suggest that $Cu(OX)_2$ is remained in the soils by some interactions with the soil surfaces. Moreover, it was reported that Langmuir-type relationships between the concentrations of HA and hydrophobic chemicals can be obtained in an aqueous solution containing HA and an adsorbent such as activated carbon [29]. In this paper, the curvature can be attributed to the hydrophobic chemical being re-adsorbed to the adsorbent, which is coated with HA. Therefore, the reason for the curvature relationship in Fig. 6 can be attributed to the fact that HA adsorbs to the surface of soil particles and a small portion of $Cu(OX)_2$ may distribute to the HA adsorbing to the soils.

4. Conclusions

The results reported herein demonstrate that HA acts as a surfactant and that the functionality of HA can be utilized for removing $Cu(OX)_2$ from clayey soils by the driving force of EOF. HA can be manufactured in bulk from coal. The cost of HA (US$ 1.5–3.0/kg) is nearly equal to that of the artificial surfactant, such as US$ 2.6/kg for SDS. However, use of SDS may give rise to secondary contamination to soil environment, since SDS has been reported to be a toxic compound to biota [30]. This implies that use of HA has the advantages in terms of the clean processes for soil remediation. HA is widely distributed in soil environment and has been known to be non-toxic material. Therefore, the functionality of HA as a surfactant may be effective for the electrokinetic remediation of the soils that

are contaminated with hydrophobic pollutants and has an advantage on safety compared to the one of artificial surfactant.

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