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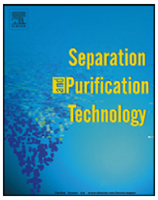

Effect of ammonia as a complexing agent on electrokinetic remediation of copper-contaminated soil

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ABSTRACT

Ammonium acetate was used as anolytes in the electrokinetic removal of copper from soil. The electrokinetic experiments were conducted using a rectangular reactor 7.5 cm in width, 10 cm in height, and 11 cm in length. Granular graphite was used as the electrode material. All experiments were conducted under constant current conditions (10 mA). The results show that a high concentration of ammonium acetate (>0.1 M) was needed to sustain electroosmotic flow. The apparent electrical conductivity of the system was dominated by a thin layer of soil (1 cm) close to the cathode. When the ammonium acetate concentration was less than 0.1 M, the apparent electrical conductivity of this soil layer decreased to less than 0.001 S/m and caused large voltage loss. The electroosmotic conductivity of the soil was increased and sustained at 1×10^{-4} cm^2/V-s by a high concentration of ammonium acetate, whereas it decreased to less than 1×10^{-6} cm^2/V-s when the concentration of ammonium acetate was low. The efficiency of copper removal increased with the concentration of ammonium acetate, reaching 36% after 1 wk of treatment. Most of the un-removed copper was concentrated in the soil close to the cathode. For the 0.5 M ammonium acetate experiment, the volume of copper containing soil was less than 10% of the original soil after treatment. Therefore, a remediation strategy can be developed to first treat the contaminated soil by electrokinetics and then, focus on removing copper from the soil close to the cathode.

1. Introduction

Heavy metal contamination is a severe issue in Taiwan. According to a comprehensive study conducted in 2002, most heavy metal contamination occurring in farm land can be attributed to the fact that the channels for irrigation and industrial effluents are interconnected in Taiwan [1]. The results of the study showed that the areas exceeding the copper standard were the highest, followed by chromium, nickel, zinc, lead, cadmium, and mercury.

Electrokinetic (EK) technique is one of the methods that have been shown to be capable of removing heavy metals from soil. EK remediation of soil usually involves the use of electroosmosis (EO) and electromigration. EO describes the phenomenon of water flow induced by application of an electrical field on porous media [2], whereas, electromigration describes the transport of ions under the influence of an electrical field [3]. The electroosmotic flux, q_{eo}, can be written as

$$q_{eo} = v_{eo}\tau n_e \qquad (1)$$

where v_{eo} is the electroosmotic velocity, τ is the tortuosity, and n_e is the effective porosity.

The electroosmotic velocity can be described by the Helmholtz–Smoluchowski equation [2].

$$v_{eo} = -\frac{\varepsilon\zeta}{\mu}\nabla V = -K_{eo}\nabla V \qquad (2)$$

where ε is the permittivity of the pore fluid, ζ is the zeta potential, μ is the viscosity of the pore fluid, ∇V is the electrical gradient, and K_{eo} is the electroosmotic conductivity.

According to Eq. (2), the electroosmotic velocity is directly proportional to the zeta potential and the electrical gradient, and inversely proportional to the pore fluid viscosity. It also indicates that unlike hydraulic flow, electroosmotic flow is independent of pore size [4]. Accordingly, the electroosmotic flow is unaffected by the presence of soil with low permeability and small pore size. As clay minerals that possess high zeta potential and electrical conductivity are preferentially found in low permeability regions, where removal of contaminants by hydraulic flow is time and cost prohibitive, electroosmotic flow has advantages over conventional methods, such as pump-and-treat, in mobilizing and removing contaminants from low permeability regions. The EK technique has been applied to remove inorganic and organic contaminants from low permeability soils [5–8]. It should be pointed out that the major mechanisms in removing inorganic contaminants (ionic) are

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EO and electromigration, whereas EO is the main mechanism for removing organic contaminants (non-ionic).

One of the major problems encountered in the EK removal of heavy metals from soil is the precipitation of metal oxide/hydroxide near the cathode, where soil pH significantly increases due to the production of hydroxide ion at the cathode [5,9]. The hydroxide ions are the product of the electrolysis of water at the cathode during the EK operations. Once they are generated, they migrate toward the anode under the influence of the electrical gradient. At the same time, hydrogen ions generated at the anode move toward the cathode and react with the hydroxide ions, creating a region called the pH front, where the pH changes significantly within a very short distance. Generally, this pH front is close to the cathode because the migration velocity of the hydrogen ions is higher than that of the hydroxide ions [10,11]. The pH front acts as a barrier for the removal of heavy metals, such as copper, lead, and zinc, from the soil during EK because the solubilities of most heavy metals are relatively low when the soil pH is high.

As copper is one of the most pervasive heavy metals found in contaminated soils, much research has been devoted to increase the efficiency of copper removal by addressing the problem caused by the pH front during EK. The research methods include neutralizing the hydroxide ions by flushing an acid solution through the cathode [12–18], flushing solutions containing surfactants, chelating or complexing agents through the cathode [19–24], modifying the configurations and placements of the electrodes [25–29], and switching the electrode polarities during electroosmotic operations [27,30]. However, these techniques showed limited success in removing the copper from soil. Therefore, maintaining a low pH at the cathode is unable to address the problems caused by the pH front during EK. The major reason for this is that, despite the flushing and neutralization of hydroxide ions produced at the cathode, significant amount of hydroxide ions were still transported into the soil and formed pH fronts in the vicinity of the cathode.

Another reason might be due to the small surface area of the electrodes. In most electroosmotic experiments, rod- or plate-like electrodes are used to transfer the current between the power supply and the soil. As the applied voltages are usually significantly higher than those of the water electrolysis reactions and the contact area between the electrodes and the electrolyte solution is small, large amounts of hydroxide ions are produced and migrate toward the anode. Thus, for copper, increasing its solubility in the pH front zone and minimizing the generation of hydroxide ions at the cathode is necessary to enhance the efficiency of copper removal by EK.

Ammonium (0.01 M) was used as the anolyte in a study by Vereda-Alonso et al. [21] and was found to remove about 40% of the copper from a test cell. The copper removal rate increased to 85% when acetic acid was used as the catholyte. This suggests that the hydroxide ions produced at the cathode migrated into the soil, forming a pH front and preventing the copper from being removed. According to the reactions between copper and ammonium, as described in Eqs. (3)–(8), the high pH condition close to the cathode should favor copper–ammonia complex reactions, thus increasing the solubility and removal rate of copper during EK.

$$NH_4^+ \Leftrightarrow NH_3 + H^+ \quad pK_a = 9.25 \tag{3}$$

$$Cu^{2+} + NH_3 \Leftrightarrow CuNH_3^{2+} \quad pK_1 = -4.31 \tag{4}$$

$$Cu^{2+} + 2NH_3 \Leftrightarrow Cu(NH_3)_2^{2+} \quad pK_2 = -7.98 \tag{5}$$

$$Cu^{2+} + 3NH_3 \Leftrightarrow Cu(NH_3)_3^{2+} \quad pK_3 = -11.02 \tag{6}$$

$$Cu^{2+} + 4NH_3 \Leftrightarrow Cu(NH_3)_4^{2+} \quad pK_4 = -13.32 \tag{7}$$

$$Cu(OH)_{2(s)} \Leftrightarrow Cu^{2+} + 2OH^- \quad pK_{sp} = 19.66 \tag{8}$$

Therefore, the limited removal rate of copper when using ammonium as the anolyte can be due to an insufficient amount of ammonia ions that are available to complex with the copper ions and the excessive amount of hydroxide ions produced at the cathode. This study focused on evaluating copper removal efficiency by EK using ammonium as a complexing agent for copper. The objectives of this research are to evaluate the efficiency of copper removal and sol properties related to the EK process, i.e., apparent soil electrical conductivity, electroosmotic conductivity, as a function of ammonium concentration.

2. Experimental

EK experiments were conducted using a reactor constructed from a rectangular acrylic tube. The inside dimensions of the reactor's cross section are 7.5 cm height by 10 cm width with a length of 11 cm. One electrode compartment with the same cross section as the reactor and a length of 5.5 cm was attached to each end of the reactor during the experiments (Fig. 1). The electrode compartment was filled with granular graphite and a stainless steel mesh (#20) was sandwiched between the electrode and the soil. Contact between the power supply and the electrodes was made by inserting a graphite rod into the granular graphite of each electrode. A reference electrode was installed inside the cathode compartment (Fig. 1). In situ voltage monitoring ports were installed within the reactor close to the anode and cathode compartments. These ports not only can be used to monitor the voltage distribution inside the soil column but also can be used to measure the redox potential with respect to the reference electrode.

The contaminated soil used in this study was prepared according to the following procedures. Oven-dried (105 °C, 24 h) kaolinite soil was mixed with a copper sulfate solution with a loading of approximately 200 mg copper to 1 kg of dry soil. It has been shown that at this level of contamination, most copper is retained by the soil mass [31]. After through mixing of the soil and copper sulfate solution, extra water was removed from the slurry in an oven (105 °C) until no free-standing water was observed on top of the soil, at which point this soil slurry was assumed to be saturated and was further mixed and packed into the reactor. The anode and cathode reservoirs were packed with granular graphite (<2 mm), which had been treated with 1.0 N HNO_3 and rinsed with de-ionized (DI) water to remove impurities from the surface. During the EK experiments, the anode compartment was filled with an ammonium acetate solution, of which the concentrations were predetermined as the following: blank (DI water), 0.01, 0.1, and 0.5 M. The cathode compartment was filled with DI water. The solution levels at the anode and cathode compartments were kept constant during experiments so that no hydraulic gradient/flow was induced.

The duration of each EK experiment was about 1 wk under a constant current of 10 mA, which was equivalent to a current density of 7.125 mA/cm^2. The EO flow was collected with a beaker placed at the outlet of the cathode compartment. The copper concentration and pH of the EO effluent were measured every 2 h during daytime and every 8 h during nighttime. Current and voltage measurements were also conducted at the same frequency. After EK experiments, the soil in the reactor was evenly cut into 4 sections; each section was analyzed for pH and electrical conductivity using soil extracts with a DI water to soil mixing ratio of 5 to 1. The copper in the soil after EK experiments was extracted by 1 N nitric acid. The mixture of soil and nitric acid was equilibrated for 12 h and the copper concentration in the extract was measured by a flame atomic absorption spectrometry (Varian, model AA-240). The recovery rate of copper extracted with 1 N nitric acid is more than 95% in preliminary recovery tests.