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A combination of reducing and chelating agents for electrolyte conditioning in electrokinetic remediation of As-contaminated soil

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ABSTRACT

Arsenic (As)-mobility in soils is dependent on redox chemistry. Generally, As(III) is more mobile than As(V), and reductive dissolution of Fe hydroxides promotes the release of As in soil. In this study, electro-kinetic remediation (EKR) coupled with a redox reaction was investigated for remediation of As-contaminated soil. To reduce As(V) and Fe hydroxides, reducing agents such as ascorbic acid, oxalic acid, and dithionite were used. In addition, chelating agents including oxalate, EDTA, and citrate were used to prevent the formation of Fe precipitates, well-known sinks for As(III) and As(V). After application of reducing and chelating agents, NaOH was used to enhance the electroosmotic flow (EOF) because As(III) is non-charged over a broad pH range (under pH 9.2). The reducing agents enhanced release of As in the form of As(III) or As(V). Additionally, NaOH application increased the removal of As(III) and As(V) by increasing the current and EOF. Ascorbic and oxalic acids removed only a small amount of As due to their mild reducing potential. Even dithionite, a powerful reducing agent, was not effective for the reduction of As(V) and Fe in the EKR because it was unstable under acidic conditions. Chelating agents did not prevent the formation of secondary Fe minerals in this system because of the low stability of complexes under acidic conditions. The overall removal efficiency of As was not exceeded 25%, therefore, precise pH control is required to apply the combination of dithionite and chelating agent to EKR.

1. Introduction

Arsenic (As) is a naturally occurring element that is abundant in the earth's crust. However, As contamination of soil has been aggravated by industrial activities such as mining, smelting, and combustion of fossil fuels. As is toxic to organisms, reduces soil fertility, and influences plant growth, moreover, it causes human diseases such as hyperpigmentation, keratosis, anemia, neuropathy, burning sensation of eyes, solid swelling of legs, chronic lung diseases, liver fibrosis and skin cancer [1–4]. Therefore, various technologies including soil washing, pyro-metallurgical extraction, soil flushing, and electrokinetic remediation (EKR) have been applied to treat As-contaminated soils [1,5,6]. Among these methods, EKR is effective even in fine-grained soils because the primary removal mechanisms are independent of soil pore size [7,8]. In EKR, removal of contaminants is basically achieved by electro-migration and electro-osmotic flow (EOF) of charged and uncharged pollutants, respectively. Additionally, phenomena such as adsorption/desorption, precipitation/dissolution, and complexation reactions could also influence contaminant transport [9], and various enhancements including electrolyte conditioning have been used to enhance contaminant transport [8].

Acid conditioning has been effective in the removal of cationic heavy metals; however, it was not effective for the removal of oxyanionic As [8]. Although acidic conditioning can enhance the release of As by dissolution of Fe-hydroxides associated with As, oxyanionic As is easily re-adsorbed onto the positively charged acidified soil surface [1,9]. The fate and transport of As is highly dependent on the speciation of As, *i.e.* As(III) or As(V). Under oxidizing conditions, As(V) is the predominant species existing as $H_2AsO_4^-$ (pH 2.2–6.9) and $HAsO_4^{2-}$ (pH 6.9–11.5) [7]. In a reducing environment, As(III) is the predominant species existing as H_3AsO_3 (below pH 9.2) and $H_2AsO_3^-$ (pH 9.2–12) [1]. A positively charged soil surface has high affinity for oxyanionic As, and the particular speciation influences adsorption. In the natural environment, As(III) has weaker binding affinity and more mobility than As(V) because of its neutral charge; therefore, the reduction of As(V) to As(III) could prevent re-adsorption of extracted As. Therefore, reducing condition is required to enhance reductive dissolution of Fe to facilitate As extraction from soil to soil pore. Oxalate,

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ascorbate, and dithionite have been used to achieve the reductive dissolution and/or reduce As(V) to As(III). Dithionite is a relative strong reducing agent compared to others, and the chemical has stand reduction potential (E^o) of −1.13 V or −1.12 V even in alkaline conditions, therefore, it was expected to work in EKR [2,10]. However, As mobility in soils is highly dependent on Fe minerals such as ferrihydrite, lepidocrocite, and goethite as well as their speciation [9,11]. Fe minerals are crucial adsorption sites for As due to their abundance and high affinity [12]. Fe minerals predominantly retain oxyanionic As under oxidizing conditions; however, As bound to such minerals is released under reducing conditions via reductive dissolution of Fe [11,13].

$$H_2AsO_4^- + 3H^+ + 2e^- \leftrightarrow HAsO_2 + 2H_2O \qquad (13)$$

$$Fe(OH)_{3(s)} + 3H^+ + e^- \leftrightarrow Fe^{2+} + 3H_2O \qquad (11)$$

Reduction of As and/or Fe could increase the mobility of As which is complex with Fe minerals. However, reductively dissolved Fe^{2+} and Fe^{3+} could form secondary Fe minerals such as goethite, magnetite, green rust, siderite, and ferric arsenate, which act as new adsorption sites for extracted As [2,6,14,15]. Thus, it is necessary to prevent the formation of secondary Fe minerals to enhance As removal from soil. Chelating agents forming complexes with dissolved Fe^{2+} and Fe^{3+} could reduce or prevent the formation of secondary Fe minerals when the reductive dissolution of Fe mineral occurs [2,15]. Kim et al. (2015) applied various combination of reducing and chelating agents including oxalate, ascorbate, dithionate, EDTA and citrate to extract As, and reported that the combination of reducing and chelating agents could extract more than 90% of As from soil and mine tailing, but sole application of reducing agent was not effective due to the re-adsorption of As onto the secondary Fe mineral formed in the solution [15]. Although As contamination of soil is highly related to redox reactions, few studies applying redox chemistry to EKR have been reported for As-contaminated soil, and those have been mainly the combination of biotic reduction and EKR [8]. However, the combination of chemical reduction and chelating agents is worthy of application to EKR because such a method could release As without re-adsorption [2,15]. In this study, we investigated the applicability of the combination of reducing and chelating agents in EKR to remediate As-contaminated soil. To evaluate the combination of reducing and chelating agents in EKR, ascorbate, oxalate, and dithionite, were used for reducing agents and oxalate, citrate, and EDTA were used for chelating agents. The agents were used for electrolytes to improve mobility and extractability of As. The mass balance of As was prepared to verifying the mobility of As.

2. Materials and methods

2.1. Soil sampling and characterization

Soil samples were collected from rice fields nearby a former smelter located in Janghang-eup, Chungcheongnam-do, Republic of Korea As (193.5 mg/kg), Cu (284.3 mg/kg), and Pb (591.1 mg/kg) concentration of soil samples exceeded the Korean regulation level (As: 25 mg/kg, Cu: 150 mg/kg, Pb: 200 mg/kg). Among the metals, we focused on As because of the relatively high concentration and widespread contamination in the site. The soil texture was clay loam consisting of 27% clay, 41% sand, and 32% silt. Samples were air-dried and passed through a No. 10 sieve (2.0 mm) before experiments. Other soil characteristics are summarized in Table 1.

Table 1
Initial soil properties.

Chemical Properties		
Soil pH	5.5	
Soil EC (μS/cm)	88.6	
Soil texture (wt%)		
Sand (50 μm–2 mm)	41	
Silt (2 μm–50 μm)	32	
Clay (<2 μm)	27	
Concentration of heavy metals (mg/kg)		
As	193.5	25[a]
Cu	284.3	150
Pb	591.1	200
Cd	3.9	4
Zn	210.3	300
Ni	12.7	100
Fe	30,270.7	–

[a] Soil Environment Conservation Act Standards for Arsenic in Republic of Korea.

2.2. Experimental setup

A schematic diagram of the experimental setup is shown in Fig. 1. The apparatus consisted of one soil chamber (20 × 4 × 4 cm^3), two electrolyte chambers (5 × 4 × 4 cm^3), two electrolyte reservoirs (1 L), two peristaltic pumps, two electrodes (3.5 × 5.5 × 0.1 cm^3) and a power supply. After adjusting the water content to 30%, the soil sample was placed in the soil chamber. One liter of electrolyte, circulated in the electrolyte chamber and reservoir by a peristaltic pump, was replaced every two days. Mesh type iridium-coated titanium oxide electrodes (3.5 × 5.5 × 0.1 cm^3) were placed in each electrolyte chamber. Direct current was supplied with a voltage gradient of 1 V/cm. Reducing agents (such as ascorbic, oxalic acids and dithionite) and chelating agents (such as EDTA, citrate and oxalate) were used for electrolyte conditioning. After application of reducing or chelating agents for 22 days (EKR1) or 16 days (EKR 2-6), the electrolyte was changed to NaOH to enhance the electroosmotic transport of neutral As(III). Detailed conditions are listed in Table 2.

2.3. Analytical method

The pH, electrical conductivity (EC), oxidation-reduction potential (ORP), and As concentration of the electrolytes were regularly measured with a pH/EC meter (Istek, Republic of Korea), ORP meter (Istek, Republic of Korea), and inductively coupled plasma optical emission spectroscopy (ICP-OES, Agilent, USA), respectively. After the experiments, the soil compartments were divided into 5 equal sections from the anode to cathode and dried. Each section was crushed and sieved with a No. 100 sieve (0.125 mm) before analysis. The pH and EC of soils were measured with a pH/EC meter (Istek, Republic of Korea) after extraction with deionized water using a ratio of 1: 5 (soil: water). Heavy metals in the soils were extracted with aqua regia as follows: hydrochloride: nitric acid = 21: 7 at 80 °C for 1 h, and then ICP-OES (Agilent, USA) was used to analyze the metal concentration in the extract. As fractionation in soil was analyzed by the modified Wenzel's method [3], and As fractionations were classified as non-specifically bound (F1), specifically bound (F2), amorphous and poorly crystalline hydrous oxides (F3), well-crystallized hydrous oxides (F4), and residual phase (F5). We modified the extraction of residual phase (F5) using *aqua regia* instead of HNO_3/H_2O_2.

3. Results and discussion

3.1. Electrical current

The change of current during operation is presented in Fig. 2. The initial current of EKR 1–5 was higher than 10 mA because the pre-treatment process provided ionic matter to the system (Table 2). The current of EKR 1–5 decreased gradually with operation time because ionic matter was removed from the system