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Electrokinetic (EK) removal of soil co-contaminated with petroleum oils and heavy metals in three-dimensional (3D) small-scale reactor

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ABSTRACT

Electrokinetic (EK) soil remediation is a known powerful technology for decontamination of organic and inorganic pollutants or their combination. Classically, one- and two-dimensional (1D and 2D) EK cells have been utilized for remediation of a variety of co-contaminated soils. Preparatory to scale up or practical EK applications, in the present study, three-dimensional small-scale (3D) EK cells on the batch scale were tested for remediation of petroleum-oil- and heavy-metals co-contaminated soil. In the results, with 0.10 M KH_2PO_4 as the anolyte for 21 days, removal efficiencies of better than 95% of TPH, more than 50% of As species and ~20% of Cu species were achieved, though the removal of the Pb and Zn species was relatively inefficient, at less than 20%. Currently, new electrolyte designs and a scaled-up EK cell operation are being planned for obtainment of data on real-soil-remediation feasibility.

1. Introduction

Real-soil remediation of co-contamination (*i.e.*, organic pollutants mixed with inorganic metal contaminants) is currently a highlighted topic of academic research and environmental engineering (Alcántara et al., 2012; Annamalai et al., 2014; Ammami et al., 2015), especially as such treatment is both challenging and difficult (Cang et al., 2013). As a widely applied and cost-effective *in-situ* means of soil remediation, the electrokinetic (EK) technique, by which various electrolytes such as surfactant, complex agents, acid/base solution, or combinations thereof are supplied to the anode reservoir for flow into the cathode reservoir, has been reported (Kim et al., 2011a,b). According to established principles of pollutants removal (Kornilovich et al., 2005; Kim et al., 2005), due to generation of acid front, electro-osmotic flow (EOF) is moved from the anode to the cathode, after which produced H_3O^+ ions are moved from the anode region to the cathode region; then,

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by the process of electro-migration, anionic materials and species are moved to the anode electrode while the cationic ones are moved to the cathode electrode.

Recently, research has moved beyond one-dimensional (1D) and two-dimensional (2D) EK reactors on the batch or bench scale for many organic or inorganic pollutants and their combinations. Specifically, pilot and field scales have been applied and successfully trialed for practical soil remediation (Kim et al., 2011a; Rosestolato et al., 2015; Villen-Guzman et al., 2015; Lee et al., 2013) with plots of 3D mapping results of uranium (Kim et al., 2011b), plutonium (Agnew et al., 2011), phenanthrene (López-Vizcaíno et al., 2014), 2,4-D (Risco et al., 2015), and arsenic (As) (Jeon et al., 2015), etc. Designed and configured EK reactors on pilot scales, for example, have proved to be an innovative ground water/soil remediation technology for practical applications. Park et al. (2005) evaluated the EK-Fenton process as a cost-effective process for removal of hydrophobic-phenanthrene-contaminated sand soil in a 2D system consisting of two connected EK cells. In another 2D EK configuration approach, Kim et al. (2012a,b) restored saline agricultural lands contaminated with Mg^{2+}, Ca^{2+}, K^+, NO_3^-, SO_4^{2-}, and Cl^- in hexagonal 2D EK cells with a larger active area of electrical field and less energy consumption or from paddy soil.

With respect to EK field applications, the research trend has been from 1D to 2D to 3D EK reactors. However, whereas intensive 2D EK applications have been reported on in recent years, 3D EK results have been rarely reported in batch scales (Gent et al., 2004; Zhou et al., 2006). In the present study, anticipatory to potential pilot- or field-scale application, a 3D EK reactor on the small-scale was applied for constant-current remediation of real petroleum-oil- and heavy-metals co-contaminated soils obtained near a Korean rail road.

2. Materials and methods

2.1. *Soil properties in 3D small-scale EK cell operation*

Table 1 lists the physical properties of the soil used in this study. As indicated, the soil was contaminated with diesel oil and heavy metals (As, Cu, Pb and Zn); its organic matter content was 15.57% by K_2CrO_4, its sand composition 86.25%, and its clay content, 6.25%, all contributing to a soil texture that could be characterized as loamy sand (Kang et al., 2014). The initial concentration of diesel oil was 16,560 mg/kg, while those of arsenic (As), copper (Cu), lead (Pb), and zinc (Zn) were 59.32, 96.82, 442.85, and 10,113.13 mg/kg, respectively. Preparatory to the present experimentation, the co-contaminated soils were mixed with double distilled water (DI water, electrical resistivity >18.2 MΩ cm, Milli-Q® water, USA) to a moisture content of approximately 18% and packed tightly into 3D small-scale EK cells.

2.2. *Preparation of 3D small-scale EK cells prior to operation*

As shown in Fig. 1, a three-dimensional (3D) acrylic reactor (10 cm × 10 cm × 10 cm, $L \times W \times H$) on the small-scale was supplied, respectively, with 0.05, 0.10, and 0.20 M KH_2PO_4 solution whose electrolyte was chosen because of EOF enhancement, to the anolyte reservoir by peristaltic pumping; meanwhile, within the cathode reservoir, 1.0 M HNO_3 solution was circulated to prevent pH rise and subsequent heavy-metal hydroxide precipitation therein (Fig. 1 left panel). The lid of 3D small-scale EK cell was capped tightly to prohibit the water evaporation. The sampling locations were distributed among top, middle, and bottom sites, each with five specific points (Fig. 1 right panel), in order to examine the gravity effect both in terms of electro-osmotic flow (EOF, mL) and heavy-metal-ions movement into each reservoir.

Table 1 – Physical properties of soil used in this study (Kang et al., 2014).

Parameters	Value (%)
Soil-particle distribution (American Standard Testing Method)	
Sand (%)	86.25
Silt (%)	7.50
Clay (%)	6.25
Initial soil pH (Korea Standard Testing Method)	5.89
Organic matter (%) (American Standard Testing Method)	15.57
Total Fe content (%) (American Standard Testing Method)	10.56
Contaminants	Initial concentration (mg/kg soil)
Diesel oils concentration (mg/kg) (Korea Standard Testing Method)	16,560
Heavy-metal concentration (mg/kg) (Korea Standard Testing Method)	
As	59.32
Cu	96.82
Pb	442.85
Zn	10,113.13

Both anode and cathode electrodes were utilized with the reactor design of 0.5 cm × 9 cm × 9 cm ($L \times W \times H$) dimensions incorporating acid-resistant Iridium (Ir)-coated dimensionally stable anodes (DSA) of the perforated mesh type (Suzuki et al., 2014). As a catholyte, 1.0 M HNO_3 solution was circulated at a 0.5 mL/min rate by a peristaltic pump connected using silicon tubes. For 3D small-scale EK cell operation, the electrical current was fixed at 0.5 A for 7 or 21 days.

2.3. *Analysis of TPH and heavy metals*

The total petroleum hydrocarbons (TPH) concentrations were measured in approximately 0.1 g samples obtained from the 15 sampling points (Fig. 1 right panel) and mixed in separate beakers with a proper amount of anhydrous Na_2SO_4 (Sigma Aldrich, USA) and 50 mL of dichloromethane (Sigma

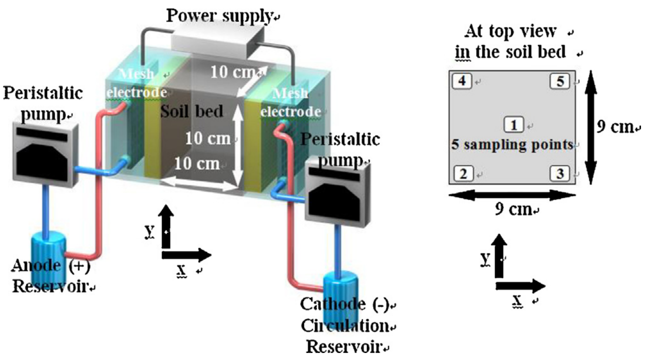

Fig. 1 – Schematic representation of three-dimensional (3D) electrokinetic (EK) reactor (left panel) and its sampling points (right panel).