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Technical Note

Enhanced-electrokinetic remediation of copper–pyrene co-contaminated soil with different oxidants and pH control

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HIGHLIGHTS

- A new technology was developed to decontaminate a compound contaminated soil.
- The highest removal percent of soil pyrene and Cu was 52% and 94%, respectively.
- Acid catholyte (pH = 3.5) and application of $Na_2S_2O_8$ was the best operation condition.
- The reduction product of $KMnO_4$ prevented the migration of Cu.

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ABSTRACT

Electrokinetic (EK) remediation has potential to simultaneously remove heavy metals and organic compounds from soil, but the removal percent of these pollutants is very low in general if no enhancing treatment is applied. This study developed a new enhanced-EK remediation technology to decontaminate a heavy metal–organic compound co-contaminated soil by applying different oxidants and pH control. A red soil was used as a model clayed soil, and was spiked with pyrene and Cu at about 500 mg kg^{-1} for both to simulate real situation. Bench-scale EK experiments were performed using four oxidants (H_2O_2, NaClO, $KMnO_4$, and $Na_2S_2O_8$) and controlling electrolyte pH at 3.5 or 10. After the treatments with 1.0 V cm^{-1} of voltage gradient for 335 h, soil pH, electrical conductivity, and the concentrations and chemical fractionations of soil pyrene and Cu were analyzed. The results showed that there was significant migration of pyrene and Cu from the soil, and the removal percent of soil pyrene and Cu varied in the range of 30–52% and 8–94%, respectively. Low pH favoured the migration of soil Cu, while $KMnO_4$ was the best one for the degradation of pyrene among the tested oxidants, although it unfortunately prevented the migration of soil Cu by forming Cu oxide. Application of $Na_2S_2O_8$ and to control the catholyte pH at 3.5 were found to be the best operation conditions for decontaminating the Cu-pyrene co-contaminated soil.

1. Introduction

Thousands of sites are contaminated with both heavy metals and organic compounds, which brought the difficulties and challenges for soil remediation. According to the reports of USEPA, more than 67% of contaminated sites are found to contain heavy metals and organic pollutants simultaneously (USEPA, 2004). For such heavy metal–organic compound polluted soils, there has no appropriate technology to decontaminate them because of their enormous property difference. Heavy metals are usually water/acid-soluble, easily migrated and integrated with soil Fe–Mn oxides and organic matter. In contrast, most of organic pollutants are hydrophobic, easily integrated with soil organic matter and difficult to be removed. Therefore, the remediation of heavy metal–organic compound co-contaminated soil is difficult and challenging.

Electrokinetic (EK) remediation is a technology that was introduced for soil and groundwater remediation around 1980s. The technology applies DC electric field in soil to generate a voltage gradient driving soluble pollutants out of soil by electromigration, electroosmosis and/or electrophoresis (Acar and Alshawabkeh, 1993; Probstein and Hicks, 1993). Electromigration is the main migration mode for heavy metals, and electroosmosis is the main migration mode for organic pollutants.

Some previous studies showed that EK technology had potential to remove heavy metals and organic compounds from soil simultaneously (Maini et al., 2000). However, EK remediation itself cannot remove heavy metals and organic pollutants at the same time because of the accumulation of heavy metals near cathode for high

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soil pH over there and the weakly migration of organic pollutants for their hydrophobicity. Recently, some enhanced-EK remediation technologies are used to decontaminate the compound soil. The research group of Reddy at University of Illinois at Chicago had carried out lot of works about cosolvent-enhanced EK remediation (Maturi and Reddy, 2006, 2008; Reddy and Ala, 2006; Reddy et al., 2006; Maturi et al., 2009). In their studies, some cosolvents (Igepal CA-720, Tween 80, HP-β-CD, *n*-butylamine and so on) are used. However, a large amount of heavy metals were still accumulated in the soil near the cathode. The organic pollutants moved to the anolyte or catholyte according to the direction of electroosmosis, and the electrolyte containing organic pollutants needs to be further treated. The removal percent of pollutants was low, especially for heavy metals. Oxidant-enhanced EK remediation technology can oxidize the organic pollutants during the migration of organic pollutes. Reddy and Karri (2008) studied the oxidant-enhanced EK remediation technology to decontaminate the nickel and phenanthrene compound soil by adding H_2O_2 solution in electrolyte. About 28–57% phenanthrene were removed from soil. In the case of no pH control, few amount of nickel was removed for the high soil pH.

In this study, the main objective was to achieve the simultaneous removal of Cu and pyrene from soil. By applying different oxidants in electrolyte and controlling soil pH, we want to drive Cu to electrolyte and degrade pyrene during their migration process. Through this study, a new technology to decontaminate the co-contaminated soil was developed, and the remediation mechanism was disclosed. It will help us to develop the remediation technology for heavy metals–organic co-contaminated soil.

2. Materials and methods

2.1. Soil

A red soil (*Udic Ferrosols*) was sampled from barren surface soil (0–20 cm depth) in Yingtan County, Jiangxi Province, China. Soil samples were air-dried and sieved through a nylon sieve (0.84 mm). Its cation exchange capacity (CEC) was 24.8 cmol (+) kg^{-1}. The soil pH, electrical conductivity (EC, 1:2.5 soil to water), and organic carbon (SOC) were 4.80, 28 μS cm^{-1}, and 3.75 g kg^{-1}, respectively. The background values of soil Cu, Zn, Pb and Cd were 27, 25, 60, and 0.04 mg kg^{-1}, respectively. No PAHs were detected in the soil.

The pyrene-Cu co-contaminated soil represents typical contaminates found at some contaminated sites. It was prepared by spiking $CuCl_2$ and pyrene (each at about 500 mg kg^{-1} as Cu and pyrene) according to the following method. First, the red soil (300 g, 10% total quantity of soil to be spiked) was spiked with a highly pure pyrene (1.500 g, Sigma 98%) in acetone. The spiked soil was transferred in a wide rectangular pan and then left under the fume hood for 1 d to evaporate any traces of acetone. Second, the spiked soil with pyrene were further spiked with 30 mL $CuCl_2$ solution (containing 4.027 g $CuCl_2{\cdot}2H_2O$) and put in the fume hood for 1 d. Third, the spiked soil (300 g) was thoroughly mixed with uncontaminated soil (2700 g), and then the total contaminated soil was passed through a 0.84 mm nylon sieve again to ensure homogeneity of treatment. The final concentrations for pyrene and Cu in the treated soil were analysed, and their values were 486 and 524 mg kg^{-1}, respectively.

2.2. Experimental design

The set-up used for EK experiments and pH control system is similar with that in our previous studies (Zhou et al., 2004; Cang et al., 2007). As shown in Table 1, there were five treatments in this trial. Different oxidants (6% H_2O_2, 0.1% NaClO, 9 g L^{-1} $KMnO_4$ and 0.5 M $Na_2S_2O_8$) and pH control were used. The concentrations of different oxidants were confirmed according to some references (Thepsithar and Roberts, 2006; Cang et al., 2007; Reddy and Karri, 2008). 1.0 M NaOH and 1.0 M HCl were applied to control the pH in the anolyte and catholyte, respectively. The applied voltage gradient was 1.0 V cm^{-1}. During the experiments, electric currents, electroosmotic flow (EOF), electrolyte pH, and EC were monitored. After the treatments, each soil column was divided into five equal sections, labelled as S1–S5 from the anode to the cathode. The soil pH, EC, and the contents and chemical fractionations of pyrene and Cu in soil subsamples were determined. According to the soil weight and the contents of pyrene and Cu in S1–S5, the total removal percents of pyrene and Cu were calculated.

2.3. Chemical analysis

All chemicals used in the experiments were of analytical grade, and deionized water was used to prepare all solutions. Soil pH, EC, CEC, and SOC were analyzed using conventional analytical methods (Lu, 2000). The soil pH and EC were determined by a pH meter (Shanghai REX Instrument, model pHS-3B, China) and an EC meter (Shanghai REX Instrument, model DDS-11A, China), respectively, with a ratio of 1:2.5 soil to water. SOC and CEC were analyzed by dichromate oxidation method and ammonium acetate extraction method, respectively.

Soil samples were air-dried, and part of the samples were ground to pass through a 100-mesh nylon sieve (0.149 mm), and then digested with HF–HNO_3–$HClO_4$ for determination of total soil Cu concentration by a Hitachi Z-2000 Atomic Absorbance Spectrometer. Two Chinese national standard soil samples (GBW07406 and GBW07407) were used for checking. The chemical fractionations of Cu in soil subsamples were performed according to BCR (European Community Bureau of Reference) method (Ure et al., 1993) with four fractions: F1 acid soluble form; F2 Fe–Mn oxide bound form; F3 organically bound form; F4 residual form.

The procedure utilized to extract soil total pyrene was modified from USEPA 3550B (Sun et al., 2010). The soils were air-dried, homogenized, and passed through a 20 mesh stainless steel sieve (0.84 mm). The soil extracts were analyzed using a HPLC (Agilent 1100, USA) fitted with a reverse phase C18 column (LC-PAH 250 mm × 4.6 mm, 5 μm, Supelo, USA). Acetonitrile (Sigma, USA) was used as the mobile phase at a flow rate of 1.5 mL min^{-1}. Chromatography was performed at 30 °C and pyrene was detected at 254 nm with ultraviolet detection, and their detection limitation was 0.36 ng L^{-1}. The average recovery efficiency was 112% (n = 4, relative standard deviation less than 1.3%) for pyrene. The bioavailable pyrene content in soil was performed as described by Paton et al. (2009). 2 g of soil sample was shaken in 20 mL of 10% HPCD (hydroxypropyl-beta-cyclodextrin) solution for 24 h at 25 °C followed by 4000 rpm centrifugation. Then, 10 mL of the solvent fractions were mixed with 10 mL n-hexane by vortex for 1 min followed by 4000 rpm centrifugation. 5 mL of organic phase from the solvent fractions was evaporated by nitrogen gas and exchanged by acetonitrile with a final volume of 2.0 mL. After filtration through 0.22 μm filter, the treated soil extracts were analyzed using a HPLC according to the similar method as for the total soil pyrene.

3. Results and discussion

3.1. Change of electric current and EOF

Fig. 1 shows the change of electric current and EOF across the soil column with time for different treatments. From Fig. 1a, the