Journal of Hydrology 380 (2010) 4–13

Contents lists available at ScienceDirect

Journal of Hydrology

journal homepage: www.elsevier.com/locate/jhydrol

Application of iron electrode corrosion enhanced electrokinetic-Fenton oxidation to remediate diesel contaminated soils: A laboratory feasibility study

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ARTICLE INFO

Article history:
Received 7 April 2009
Accepted 4 September 2009

This manuscript was handled by L. Charlet, Editor-in-Chief, with the assistance of Ewen Silvester, Associate Editor

Keywords:
Soil contamination
Diesel
Electrokinetic (EK)
Electrokinetic-Fenton
Fenton oxidation

SUMMARY

Diesel soil contamination on gas stations or refinery plants is a worldwide environmental problem. The main objectives of this study were to (1) evaluate the efficiency of electrokinetic (EK) by using different electrode materials (graphite and iron rods) and electrolytes (tap water, 0.01 M NaCl, and 0.1 M NaCl) on the remediation of diesel contaminated soils, and (2) evaluate the feasibility of total petroleum hydrocarbon-diesel (TPH-D) reducing in soils via EK-Fenton oxidation enhanced by corroded iron electrode. The EK and EK-Fenton experiments were conducted in batch and sand box experiments, respectively. Batch experiments reveal that the most appropriate electrolyte was 0.1 M NaCl when iron electrode was used in the EK system. Sand box experiments indicate that the TPH-D concentration dropped from 10,000 to 300 mg kg^{-1} when amorphous iron/total iron (Fe_o/Fe_t) ratio increased from 0.1 to 0.33, with the addition of 8% of H_2O_2 and 0.1 M NaCl after 60 days of EK-Fenton operation. Electrokinetically enhanced oxidation with the presence of both H_2O_2 and Fe_3O_4 (iron electrode corrosion) resulted in higher TPH-D removal efficiency (97%) compared to the efficiencies observed from EK (55%) or Fenton oxidation (27%) alone. This demonstrates that EK-Fenton oxidation catalyzed by iron electrode corrosion is a valuable direction to efficiently and effectively remediate diesel contaminated soils.

Introduction

Petroleum hydrocarbons pollution is a tough environmental problem, not only by the quantities released but also because of their toxicity (Cunningham et al., 2004; Sarkar et al., 2005). Among petroleum hydrocarbon pollutants, diesel is one of the most widely used fuels today. It contains more recalcitrant and less biodegradable petroleum hydrocarbons. Diesel soils remediation has been considered as an environmental challenger.

Insitu remediation technologies including soil flushing, chemical oxidation, microbiological, and physicochemical procedures have been proposed for the clean up of diesel contaminated soil (Molina-Barahona et al., 2004; ITRC, 2005; Lee et al., 2005; Biache et al., 2008). Electrokinetic (EK) remediation has also been proposed as an innovative technology for remediation of saturated or unsaturated soils (e.g., low-permeability soils), sludges, and sediments. Briefly apply electric field to the contaminated site, pollutants will be migrated towards cathode or anode by electromigration, electroosmosis and electrophoresis (Acar et al., 1995; Kim et al., 2009). The removal efficiency of contaminants by EK reaction is influenced by parameters such as types of contaminants, soils, pH, electrodes, electrolyte and its concentration (Yang and Liu, 2001; Tsuchida et al., 2005; Schmidt et al., 2007; Wang et al., 2007). Several studies have also been assessed the effect of electrolytes such as NaCl, KCl, NH_4Cl, CH_3COONa, Na_2SO_4, Na_3PO_4, $CaCl_2$ and $AlCl_3$ on the electrokinetic and rheological behaviors of Na-bentonite suspensions (Duman and Tunc, 2009; Kim and Darve, 2009). It has been demonstrated to be successful and cost-effective in removing wide variety of inorganic such as heavy metals (Yuan and Chiang, 2008) and organic contaminants in many bench- and field-scale studies (Virkutyte et al., 2002). However, EK research that focused on petroleum hydrocarbons removal (e.g., diesel) is rare.

A few enhanced suggestions with the EK soil remediation technologies obtained acceptance that may be beneficial or even necessary to effectively treat contaminants. Among various insitu chemical oxidation methods, the Fenton process has received much interest in destruction of various organic pollutants in different media. Normally, the Fenton reaction involves two steps (Watts and Dilly, 1996; Yang and Liu, 2001): firstly, decomposition of hydrogen peroxide (H_2O_2) catalyzed by ferrous iron (Fe^{2+}) or other transition elements resulting in generation of hydroxyl radicals and secondly, degradation of organic pollutants by hydroxyl radicals via oxidation. There are two categories of

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doi:10.1016/j.jhydrol.2009.09.010

Fenton processes. One is the standard Fenton reaction which utilizes soluble Fe^{2+} as catalyst, and the other is so-called modified Fenton or Fenton-like process, which includes the use of ferric iron (Fe^{3+}), iron oxides such as magnetite (Fe_3O_4), goethite (α-FeOOH), hematite (α-Fe_2O_3) and iron chelates (Watts and Dilly, 1996; Yeh et al., 2008). These make Fenton oxidation become an effective mechanism for the decomposition of toxic organic compounds. However, when applied alone, Fenton's process fails to treat low permeable soil. Also, hydroxyl radicals generated in Fenton's reaction have limited capability to oxidize the contaminants sorbed in soil. This drawback can be overcome by integrating enhanced EK with Fenton's process (Virkutyte et al., 2002; Kim et al., 2007).

In EK-Fenton process, H_2O_2 passes through low permeable soil from anode to cathode by electro-osmosis and produces hydroxyl radicals in the presence of iron in soil. Finally hydroxyl radicals oxidize or decompose organic contaminants. Some researchers have successfully integrated EK with Fenton's process to treat various organic contaminants (Yang and Long, 1999; Kim et al., 2005, 2006; Park et al., 2005). Nevertheless, there is a lack of information about EK-Fenton process enhanced by iron electrode corrosion lose, which generates Fe^{2+} ions and react with H_2O_2 to produce hydroxyl radicals in the diesel contaminated soils system. Kim and Kim (2008) showed that corrosion of iron was composed of two electrode reactions: (1) anodic reaction-dissolution of iron to Fe^{2+} ions; and (2) cathodic reaction-reduction of oxygen to hydrogen ions.

The main objectives of this study were to (1) evaluate the efficiency of EK by using different electrode materials (graphite and iron rods) and electrolytes (tap water, 0.01 M NaCl, and 0.1 M NaCl) on the remediation of diesel contaminated soils, and (2) evaluate the feasibility of reducing total petroleum hydrocarbon-diesel (TPH-D) in soils via EK-Fenton oxidation enhanced by corroded iron electrode. The EK and EK-Fenton experiments were conducted in batch and sand box experiments, respectively.

Materials and methods

Chemicals and tested soil

The diesel used in this study was purchased from Chinese Petroleum Corp. (Taiwan) and used as received. The H_2O_2 (30%) was purchased from Merck KGaA Chemicals (German) and used as received. The tested soils were collected from the subsurface layer (15 to 30 cm below surface) in Pingtung, Taiwan. The collected soils were air-dried, passed through a 2 mm sieve, and kept refrigerated at 4 °C until used. Soil samples were analyzed to determine the characteristics including particle size, soil pH, soil organic matter, total iron (Fe_t), amorphous iron (Fe_o) and free iron. Particle size distribution was detected by the pipette methods (Gee and Bauder, 1986). Soil pH was measured with glass electrode. The Walkley–Black wet oxidation method was used to analyze soil organic matter (Nelson and Sommers, 1982). Total iron concentration was tested by AA (Atomic Adsorption, Hitachi Z6100) with a Fe hollow cathode lamp. Amorphous iron concentration was quantified by ammonium oxalate extraction (Mckeague and Day, 1966). Free iron was extracted by the dithionite–citrate–bicarbonate method (Mehra and Jackson, 1960). Table 1 shows the physical–chemical characteristics of tested soil. The soil was classified as Typic Hapludox based on the U.S. soil classification system (Soil Survey Staff, 2003). Particle tests reveal the texture of tested soil is clay. It has 19% of sand, 34% of silt, 47% of clay, and 4.6 g kg^{-1} of amorphous iron (e.g., Fe^{2+}, Fe^{3+}).

Table 1
The main characteristics of tested soil.

Parameter	Value
US soil classification	Typic Hapludox
Sand content (%)	19
Silt content (%)	34
Clay content (%)	47
Texture	Clay
Soil pH (1:5 H_2O)	4.4 ± 0.1
Soil organic matter (%)	3.4 ± 0.1
ORP (V)	0.247 ± 0.003
Total iron (g/kg)	45.8 ± 0.2
Amorphous iron (g/kg)	4.6 ± 0.1
Free iron (g/kg)	17.1 ± 0.3
Fe_o/Fe_t	0.1

Average ± standard deviation of three replicates.

Batch experiment of EK

A multiple-anode system was assembled in the batch experiments. Tested soils were mechanically homogenized in a stainless steel container. The soil was spiked with diesel dispersed in 1.5 L of a 1:1 (v/v) *n*-hexane/acetone and then further homogenized. The solvents were allowed to evaporate from the soil by placing the spiked soil container in a fume hood, thus leaving behind the diesel in the soil at a theoretical initial TPH-D concentration of approximately 10,000 mg kg^{-1} of soil. The initial TPH-D concentration was confirmed by triplicate analyses. Less than 1% of variation was observed from the triplicate (data not shown).

A glass circle module is composed of one main compartment 20 cm in diameter (∅), and 3 cm in depth (shown in Fig. 1a). In all EK-related experiments, graphite and iron electrodes (0.4 cm in diameter, 5 cm in length) were used for both anode and cathode. One electrode (graphite or iron rods) put in the middle as cathode and four sets of electrodes were put at four corners of circle modules as anode. A DC power generator supply 40V electric strength. To avert corrosion between the electric wire and electrode, the junctions were covered with water-resistant glue. Solid samples such as iron rod, magnetite, hematite, and goethite were analyzed by X-ray powder diffraction (XRD) to verify the crystal structure of minerals. They were collected with a Rigaku Rint-2000 (Japan) diffractometer using Ni-filtered Cu Kα radiation generated at 30 kV and 10 mA. The XRD patterns were recorded over the range 0–40°2θ with a scanning speed of 1.0°2θ/min (Hseu et al., 2007). Results indicate that the only mineral species of iron identified by XRD is magnetite (Fe_3O_4).

The EK-related experiments was conducted in glass circle module with Teflon caps batch containing 700 g of diesel contaminated soils with the same initial TPH-D concentration as above, and 300 ± 20 mL of electrolyte (tap water, 0.01 M NaCl, or 0.1 M NaCl solution). Detailed experimental conditions are shown in Table 2. After each reaction period was expired (0, 0.2, 2, 4, 7, 13, 21, 30, and 45 days), 20 g of soil samples were collected from four sample location (Fig. 1b). Current density, soil pH, ORP, Fe_t, Fe_o, and TPH-D during the experiment were monitored by periodical measurement (APHA, 2001; Park et al., 2005). Samples were spun on a Hettich-Zentrifugen EBA 21 Centrifuge for 30 min at 10,000 rpm, and stored until analysis at 4 °C in dark. Removal of TPH-D was monitored by shake-extracting the vial contents for 24 h with mixture of *n*-hexane/acetone (v/v, 1:1). Analysis of TPH-D extract was performed using a Varian CP3800 gas chromatography (GC) equipped with a flame ionization detector and a DB-1 capillary column (0.53 mm × 30 m). The injector temperature was 250 °C and detector temperature was 300 °C. The oven temperature was programmed to increase from 45 °C (5 min) to 300 °C (20 min) at 12 °C min^{-1}.