Effects of electrolyte characteristics on soil conductivity and current in electrokinetic remediation of lead-contaminated soil

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ABSTRACT

Characteristics of electrolytes as boundary conditions of soil affect the soil ionic composition and conductivity during electrokinetic remediation (EKR), which directly affect the effectiveness, energy efficiency and duration of EKR. This experiment studied how the characteristics of catholytes and anolytes affect the soil conductivity. The results showed that H^+ ions of higher ionic conductivity induced the increase in soil conductivity; by contrast, Fe^{2+} ions of lower ionic conductivity induced the decrease in soil conductivity. This experiment also found that when H^+ ions from anolyte met Ac^- ions from catholyte in soil, they associated into neutral HAc molecules resulting in the decrease in the soil conductivity, which reached the lowest at $pH \approx 3.7$. This proton-transfer reaction induced a potential gradient peak which caused a lead-focusing in the soil. The pH value for lead desorption from soil is no more than 4.0, and therefore HAc is not an optimal candidate for catholytes in the electrokinetic remediation of lead-contaminated soil. Results also showed that Fe^{2+} ions did not enhance desorption of lead from soil. This study provided a methodology to explain the change pattern of soil conductivity and current, and guide the selection of electrolytes.

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1. Introduction

Electrokinetic remediation (EKR) as a promising technology to remediate contaminated fine-grained soils has been studied extensively since the 1980s [1]. Many enhanced EKR technologies coupling with other remediation technologies were developed [2]. Nevertheless, the significant achievements in bench-scale were seldom repeated in field tests. One of the reasons is that some basic aspects of EKR are not studied very well up to now. One basic issue is how the characteristics of electrolytes influence the results of EKR experiments. Various electrolytes were used in EKR for different considerations. They include: (1) providing baseline electrolyte, e.g. KNO_3 [3], $NaNO_3$ [4]; (2) providing high buffering capacity to facilitate the electrolyte pH control, e.g. Na_2CO_3[5], K_2HPO_4, KH_2PO_4 [6], sodium acetate acid (NaAc) [7] and acetate acid (HAc) [8]; (3) enhancing desorption of metal ions, e.g. H^+ [5], EDTA[9]; (4) environmental friendship, e.g. Na/HAc, citric acid [10]; (5) oxidation/reduction, e.g. H_2O_2, H_2SO_4 [11], HCl, SDS [12]; and (6) supplying nutrients in EKR-bioremediation, e.g. Tris–acetate-buffer [13,14], starch [15], ammonium, nitrate [16], lithium lactate [17], $MgSO_4$, NH_4NO_3 [18]. The type and concentration of

electrolytes are the boundary conditions of the soil in migration tube. During EKR, the soil ions are gradually replaced by the ions from electrolytes, and the soil conductivity changes correspondingly. Therefore, the composition of soil ions and the current are the function of time, and it is necessary to investigate how the characteristics of electrolytes influence the soil conductivity and current.

In this study, H^+ ions and Fe^{2+} ions in anolytes were used to compare how ions of different conductivity influence the soil conductivity in the EKR of Pb -contaminated soil. The limiting equivalent conductivity of H^+ ions in aqueous solution is $350.1 \times 10^{-4} \, m^2 \, S \, equiv^{-1}$ (at 25 °C) much higher than that of Fe^{2+} ions ($53.5 \, m^2 \, S \, equiv^{-1}$) [19]. In addition, Fe^{2+} ions are necessary element in the EKR-Fenton-oxidation of organic pollutants in soils [21]. Therefore, this experiment also investigated if Fe^{2+} ions could enhance desorption of Pb^{2+} ions which mean much as EKR-Fenton-oxidation technology is used to remediate multi-contaminated soils by lead and organic pollutants. Na/HAc solution was used to control the pH of catholytes as in many experiments due to its excellent buffering capacity, environmental friendship and low cost.

In the experiments, it was found that a potential gradient peak (PGP) appeared regularly (in Test 1), so a Supplementary test (Test 3) and conductometric titration were performed to study

the mechanism of PGP and explain the changes of current and soil conductivity.

2. Materials and methods

2.1. Soil

The Pb-contaminated soil came from a lead-acid battery factory. The soil was air-dried, ball-milled, and sieved (40 meshes). The dried soil was mixed with super pure water (16.5 MΩ) to generate a soil sample of 35% moisture content. The characteristics are presented in Table 1.

2.2. Setups

Two setups were used. Setup A that was used in Test 1 and Test 2 had four parallel polymethyl methacrylate (PMMA) migration tubes (Φ3.8 cm × 20 cm). The top of the tubes (2.6 cm in width) were cut away in the demand of Pb measurement with X-ray fluorescence analyzer (XRF) and pH test with pH paper (Fig. 1a and Fig. S1). 1A and 1B were duplicate tests of Test 1 and shared the same PVC cathode compartment (Table 2). In order to decrease the frequency of adding HAc to hold the catholyte's pH = 4 during the EKR, a big-volume cathode compartment (31.2 cm × 19.9 cm × 19.9 cm = 12.4 L) was adopted. By contrast, in order to increase the concentration of H+ ions in the anode compartments soon and monitor the currents of 1A and 1B separately, small-volume anode compartments (9.6 cm × 4.9 cm × 9.4 cm = 442 mL) were adopted. 2A and 2B were duplicate tests of Test 2 and had the same structure as 1A and 1B.

Setup B that was used in Test 3 consisted of one PMMA migration tubes (Φ1.5 cm × 10 cm) and two PVC electrode compartments of the same size (10.0 cm × 7.0 cm × 7.6 cm = 532 mL) (Fig. 1b). Nine tiny holes of 1.0 cm distance each other were drilled in the migration tube for the purpose of potential measurement. Table 2 presents the parameters of Test 1, Test 2, and Test 3.

2.3. Electrokinetic experiments

2.3.1. Test 1 and Test 2

These two tests were simultaneously conducted in Setup A. There were two differences between Test 1 and Test 2. The first difference was the anode. In Test 1, the anodes were Pt. H+ ions were generated at the Pt anodes and migrated into the soil during EKR. In Test 2, the anodes were Fe (four iron nails, about 12.6 g/nail) [22]. Fe^{2+} ions were generated at the anodes by Eq. (1) and migrated into the soil during EKR.

Fig. 1. Schematic of the setups. (a) Setup A. (b) Setup B.

$$Fe - 2e^- = Fe^{2+} \quad E_0 = -0.44\ V \tag{1}$$

Iron nail surface must be carefully and completely polished with abrasive paper and used immediately. Otherwise, iron surface could be passivated and the H+ ions were generated together with or instead of Fe^{2+} ions at the anodes [23]. The polarization curve of iron nail was measured by chemical working station (CS300, WuHan Corrtest Instrument Co., Ltd) and presented in Fig. 2. The ORP measurements of electrodes and electrolytes were provided in Supplementary Data (Table S1).

The second difference was that, from the 8th day of EKR, the pH of anolyte of Test 2 was decreased from 5.0 to 2.8 with dilute HNO$_3$ in order to enhance desorption of Pb from the soil (Table 2).

In Test 1 and Test 2, potential gradients, pH, concentrations of Pb and Fe were measured per day or at any desired time. The methods and equipments are provided in Table 1 and in our previous works [3].

Table 1
Characteristics of the soil sample.

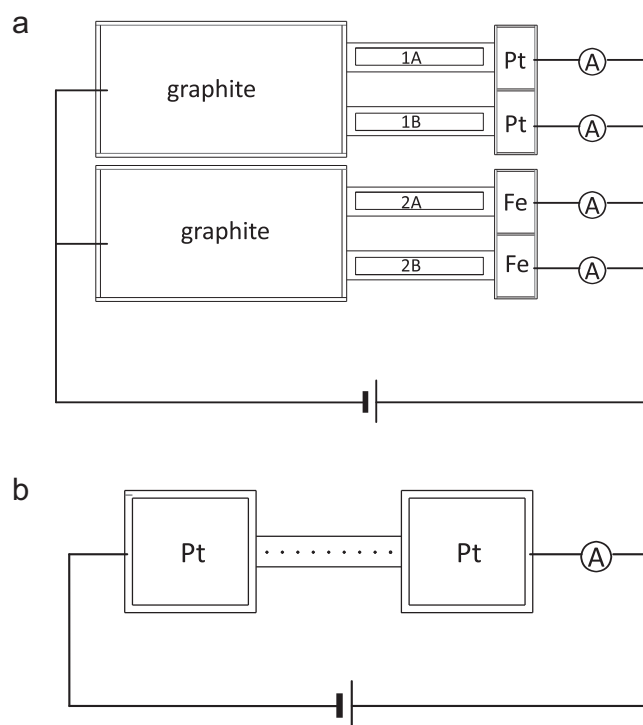| Soil properties	Parameters	Methods and equipments
Liquid limit	0.282	Standard for soil test method (GB/T 50123-1999). SYS liquid plastic limit apparatus, Nanjing TongRen photoelectric instrument research institute, China
Plastic limit	0.206	
Moisture content	35%	Standard for soil test method (GB/T 50123-1999)
Specific gravity	2.57	
Porosity	0.445	
Permeability coefficient	1.30×10^{-5} cm/s	
Pb	875 ± 24 mg/kg	XRF Inno-X Alpha4000. Innov-X System Inc., Woburn, MA, USA)
Fe	47.5 ± 1.4 g/kg	
Carbonate	137.6 g/kg	Method for determination of soil carbonate NY/T 86-1988 (GB 9835-1988)
pH	6.0	pH paper
Soil particle size	Rang: 0.817–591.9 μm Mean: 56.93 μm	Microtrac S3500 laser particle size analyzer, Microtrac Company, USA
Organic	3.97%	Methods for the determination of total organic carbon (TOC) in soils and sediments. NCEA-C-1282 EMASC-001