Exchange electrode-electrokinetic remediation of Cr-contaminated soil using solar energy

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ABSTRACT

The present work focused on analyzing the effects of solar energy on the electrokinetic remediation (EKR) of Cr-contaminated soil, compared to direct current (DC) power supply. Meanwhile, to control the remedied soil pH and focusing phenomena, the exchange electrode-EKR (EE-EKR) has also been employed. Four runs of tests were conducted using DC power supply with the conventional EKR (run A, run D), DC power supply with EE-EKR (run B) and solar energy with EE-EKR (run C) respectively. Important electrokinetic parameters such as electrical voltage and current, electroosmotic flow, soil pH, the remediation efficiency of total Cr, Cr(VI), Cr(III) and cost analysis were investigated to evaluate EE-EKR using solar energy. The results show that run B had the highest removal efficiency of total Cr (43.65%), Cr(VI) (91.88%), and Cr(III) (19.32%), and run C, run A, run D follow in turn. It was proved that EE-EKR could increase the removal efficiency of Cr, especially Cr(III) from contaminated soil, because it could reduce focusing phenomena and enhance electrical current. Meanwhile, the experimental results also indicated that the combination of electrokinetics and solar energy was feasible and effective to some extent for the remediation of Cr-contaminated soil.

1. Introduction

Soil pollution in China, caused by rapid urbanization and economic development, had become an increasingly serious threat to public health and the environment. In 2014, the Ministry of Land and Resources and the Ministry of Environmental Protection of the People's Republic of China jointly issued the first-ever results of a nationwide soil pollution survey that took place from April 2005 to December 2013 [1]. The report admits that the situation of overall national soil environment in China is not optimistic. The 16.1% of soil in the Chinese mainland is contaminated, and more seriously, 19.4% of farming soil is contaminated. Inorganic soil pollutants are the major pollutants in China's soil, including cadmium, mercury, arsenic, copper, lead, chromium, zinc and nickel from high to low. Among these heavy metal pollutants, chromium (Cr) has been recognized as one of the most hazardous pollutants, unfortunately the standard-exceeding rate of Cr is 1.1% in soil based on the soil pollution bulletin. The toxic Cr in contaminated soil is a serious pollution problem affecting soil and underground water qualities, therefore presenting a direct hazard to human health. The release of Cr will can cause chronic alterations in the nervous system and gastrointestinal tract as well as renal dysfunction [2–4]. So decontamination of the Cr-contaminated soil is one of the most important challenges.

Nowadays, electrokinetic remediation (EKR) had been proved as the relatively cheap, effective and environmentally friendly technology for simultaneous removal multi-heavy metals in polluted soil [5]. During the EKR process, under the driving force of direct current (DC) electric field, heavy metals and organic pollutants can be migrated from soil towards electrode wells by electroosmosis, electromigration and other processes (such as electrophoresis). Electroosmosis (Electroosmotic flow) is the movement of liquid in the porous soil under an electric field, which mobilizes the organics and neutral molecules along with pore fluid. And electromigration is the transport of charged ions towards opposite charge of the electrode due to the applied electric field. Electrophoresis is the motion of dispersed particles relative to a fluid under the influence of a spatially uniform electric field. Advantages of this technology are: in-situ/ex-situ remediation, the applicability to a wide range of pollutants, and so on [6–9]. Because of these advantages, EKR has been successfully applied, alone or in combination, to remove a wide range of pollutants, such as a variety of heavy meals, organic pollutants from the contaminated soil, sewage sludge and dredged sediments [10–18].

However, compared to other soil remediation technologies, there are still many difficulties to carry out the soil remediation by EKR. Some of which are electrical energy consumption of EKR, focusing phenomena in the remediation process and adverse effects of EKR on

soil properties (such as soil pH) [19–21]. So, in this study, instead of DC power, we tried using solar cell to resolve the energy supply and study its possibility [22–24]. The focusing phenomena is occasionally observed only in the soil near electrodes during the EKR of heavy metal contaminated soil, due to chemical precipitation near cathode [25,26], which has become a limitation for the extraction or removal of heavy metal pollutants. In order to decrease the focusing effect of the EKR and improve the efficiency of Cr removal, we tried to use EKR with the exchange electrode method (EE-EKR). M. Pazos et al. reported the "polarity exchange" method that the technique can avoid the negative effect of OH^- on metal transportation and improve the metal removal from contaminated soil by EKR [27]. EE-EKR can neutralize the hydroxide ion in the cathode region and reduce the precipitation of chromic hydroxide by exchanging the anion and cathode in the electric field. However, there are few literatures on EE-EKR of Cr-contaminated soil, especially with regard to solar energy being used as the power supply [28,29]. So the objective of this study was to investigate the possible use EE-EKR with solar energy for removal of Cr from contaminated soil and explored the major factors influencing the remediation process.

2. Materials and methods

2.1. Sample preparation and its characterization

The experimental soils are primarily silty loam, collected at the chromium slag piled field located in Sanmenxia City, China's Henan province, at depth between 0 and 20 cm. The total Cr and Cr(VI) average concentration, organic matter content, pH, cation exchange capacity, redox potential of soil samples were 1858 mg/kg, 623 mg/kg, 4.12%, 8.13, 21.3 cmol/kg, 332.6 mv respectively. The soil samples were air dried, homogenized and sieved to remove the coarse particles by the 2 mm nylon sieve prior to experiments.

2.2. Laboratory-scale electrokinetic experiments

Four runs of tests were carried out using DC power supply with the conventional EKR, DC power supply with EE-EKR and solar cell with EE-EKR respectively. The details of experimental conditions are described in Table 1. The sketch map of the EKR experimental system is shown in Fig. 1. The EKR experimental system was divided into the following major parts: the soil cell (an inner length of 14 cm, a width of 8 cm, and a height of 6 cm), two electrode chambers (an inner length of 4 cm, a width of 8 cm, and a height of 6 cm), two electrolyte reservoirs, four channels dispensing peristaltic pump (DG-4/BT00-300T, Longerpump, China) and a digital DC power supply (GPC6030D, GW Instek, China) or solar cell. Graphite sheet electrodes were used as the working electrodes in the experimental system (an inner length of 1 cm, a width of 8 cm, and a height of 6 cm). To prevent soil leakage from the soil cell to the electrode chambers, two non-woven fabrics were used.

The solar cell panel was made of monocrystalline silicon with a length of 35.5 cm, a width of 25 cm, and a thickness of 2.5 cm. The nominal voltage, nominal peak power and photoelectric conversion

efficiency, are 22 V, 10 W and 18%, respectively. In this study, the solar cell panel was installed on the balcony (the sixth floor, about 18 m height) and the longitude and latitude of experimental site is E 112.4237 and N 34.6042, respectively. The side of monocrystalline silicon was faced to sunlight. Because in darkness, the output potential of solar cell is zero, so run C worked nine hours a day (8:00 am to 5:00 pm) (total 144 h in 16 days, in March 2016). In the 16-day EKR experiment, it included ten sunny days and six cloudy days, and daily air temperature fluctuated from 8 °C to 26 °C.

In every experiment, 675 g of soil sample mixed with 225 mL of distilled water were placed in the soil cell. At the flow rate of 15 mL/min, the four channels dispensing peristaltic pump was cycled to refresh anolyte and catholyte in electrode compartments. In run A, B and C, electrolyte was circulated as 0.1 mol/L KCl solution and the initial pH and conductivity of electrolyte is 6.95 and 1.074 s/m respectively. By using KCl solution as electrolyte, the electrical conductivity of the electrolyte has been improved and meanwhile KCl is the fertilizer to soil. For the comparison, in run D, electrolyte was circulated as distilled water, other conditions are consistent with run A. Each electrolyte solution was refreshed every 9 h and the cumulative amount of total Cr and Cr (VI) in each electrolyte during the processing was measured. After the EKR experiment, the soil sample was taken out from the soil cell and was sectioned into ten equal parts from left to right and each part was used to analyze for the total Cr, Cr(VI) concentration and pH respectively.

2.3. Analytical methods

The Cr(VI) concentration in the electrolyte was quantified based on the diphenylcarbazide colorimetric method using a UV–vis spectrophotometer at 540 nm (Metash UV-5200PC, China). The detection limit of Cr^{6+} is 0.2 μg and 0.004 mg/L by the method. The total Cr concentration in the electrolyte was determined on the diphenylcarbazide colorimetric method after oxidating Cr(III) into Cr(VI) with excess potassium permanganate. The Cr(VI) concentration in the soil was determined by selectively extracting Cr(VI) according to the EPA Method 3060A (alkaline digestion procedure by 0.28 mol/L Na_2CO_3 and 0.5 mol/L NaOH), and the Cr(VI) concentration was quantified in the digestion solution by the same method (diphenylcarbazide colorimetric). The total Cr concentration in the soil was determined by an atomic absorbance spectrometer (Varian AA240, USA) after digesting with aqua regia. The detection limit of total Cr in soil is 0.3 mg/kg by the method. The Cr(III) concentration need be obtained during the experiment. Its concentration can be calculated from the difference between the total Cr and Cr(VI) concentrations.

Soil pH was monitored using the pH meter (pHS3C, SPSIC, China) in the slurries with soil to distilled water ratio of 1:2.5. The soil organic matter content was measured by the PE-2400 elemental analyzer (Perkinelmer, USA). Redox potential of soil was determined by potential method. The CEC (cationic interchange capacity) of soil was measured by the ammonium acetate extraction method (EPA 9080). Electrical current and voltage through the soil cell was measured by the multimeter (F15B+, Fluke, USA) in the EKR process. To ensure data quality, all chemical analyses were performed in duplicate. The recovery experiments by adding standard Cr samples were carried out, the average recovery ratio was 98.29%.

3. Results and discussion

3.1. Electrical voltage and current during the experiment

Electrical voltage is one of the key factors in the EKR of contaminated soil. During the EKR, the variation trends of electrical voltage are given in Fig. 2. Fig. 2 shows that the variations of electrical voltage in run A, B, D were different from that in run C. In run A, B and D, electrical voltage fluctuated very slightly, and was maintained

Table 1
Electrokinetic experimental conditions.

Run	Electrolyte concentration (KCl mol/L)	Voltage (V)	Treatment time (h)	Energy	Exchange of electrode
A	0.1	22	144	DC power	0
B	0.1	22	144	DC power	At the 72th hour
C	0.1	–	144	Solar cell	At the 72th hour
D	Distilled water	22	144	DC power	0