

Chelate Agents Enhanced Electrokinetic Remediation for Removal of Lead and Zinc from a Calcareous Soil

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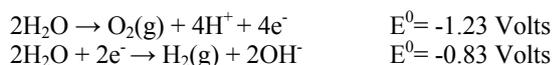
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Abstract—The electrokinetic remediation technique is a very effective method to remove metals from fine-grained soils having low adsorption and buffering capacity. However, remediation of soil having a high alkaline and adsorption capacity via the electrokinetic method is a very difficult process. Therefore, enhancement techniques are required for use in these soil types. In this study, we use enhanced electrokinetic to remove lead and zinc from an alkaline (pH=7.69) and natural polluted soil. We applied constant voltage of 25 volt and different chemical agents such as EDTA and ammonium citrate to enhance removal pollutants from soil. Experimental results have shown that ammonium citrate (pH=9) was more effective than EDTA in alkaline soil. Removal of lead in EDTA treatment was more than zinc and removal of zinc in ammonium citrate treatment was more than lead as a result of having high constant stability. pH Adjustment of anode solution is an important factor in electrokinetic remediation.

Keywords- Electrokinetic remediation; Lead; Zinc; EDTA; Ammonium citrate; Alkaline soil

I. INTRODUCTION

In recent years, there has been considerable interest in the application of new and innovative ways for removal of pollutants from soil and groundwater, but most methods have high cost, and they are unsuitable in low permeability soils. Electrokinetic is a relatively new way to remove environmental pollution from these soils [2]. Electrokinetic is a developing technology that is intended to separate and extract heavy metals, radionuclide and organic contaminants from saturated or unsaturated soils, sludges, sediments and groundwater [15]. Numerous studies dealing with the electrokinetic remediation of soils contaminated with cationic metallic contaminants such as lead, copper and cadmium have been reported [1,2,3,4]. The goal of Electrokinetic remediation is to effect the migration of contaminants in an imposed electric field. Under induced electrical potential, electrolysis reactions generate H⁺ ions and oxygen gas at the anode and OH⁻ ions and hydrogen gas at the cathode [1].



The H⁺ ions create an acidic environment, pH 2–3, at the anode and the OH⁻ ions create an alkaline environment, pH 10–12, at the cathode [2]. The migration of H⁺ ions from the anode towards the cathode produce an acid front which flushes across the soil. The contaminants in the soil are then transported towards either the cathode or the anode depending on their charge. This contaminant transport occurs primarily because of the following three mechanisms: electro-osmosis, electromigration and electrophoresis (Fig.1).

Electroosmosis is the movement of the pore fluid which contains dissolved ionic and non-ionic species, relative to the stationary soil mass, toward the cathode due to the application of a low direct current or voltage gradient to the electrodes [11]. Electromigration is the movement of the dissolved ionic species which are present in the pore fluid, including H⁺ and OH⁻ ions, which are produced by water electrolysis, toward the opposite electrode. Electrophoresis is a transport of charged particles or colloids under the influence of an electric field. Contaminants bound to mobile particulate matter can be transported in this manner. After transport of pollutants, they can be removed from anode and cathode reservoirs [2].

The precipitation and dissolution of the contaminant species during the Electrokinetic process can significantly influence the removal efficiency of the process [2]. The soil decontamination process is affected by the hydrogen ions generated at the anode migrating across the contaminated soil and neutralizing the hydroxyl ions at the cathode. However, in some types of soils, the migration of the hydrogen ions will be hindered due to the relatively high buffering capacity of the soil. The presence of the hydroxyl ions at the cathode will increase the pH value (pH 10–12).

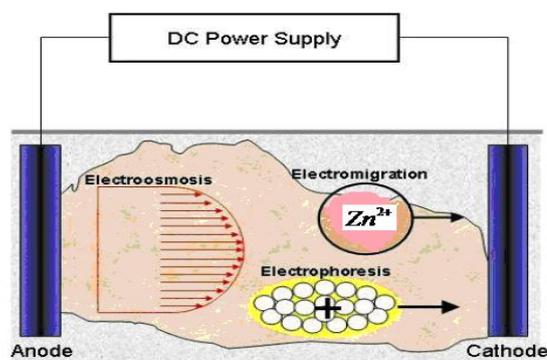


Figure 1. Sketch of the electro-mechanisms in an electrostatic cell [9]

In a high pH environment, heavy metals will precipitate, and the movement of the contaminants will be impeded, so it is needed to be added an enhancement solution. Enhancement solutions can be either used for changing the physicochemical conditions in the soil as pH and redox conditions, or the enhancement solutions can be used to form mobile complexes with the actual heavy metals. Popov et al. [12] found that the electroosmotic flow increased in the experimental soils after addition of different complexants as citric acid, ethylenediaminetetraethanoic acid (EDTA) or 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) compared to distilled water. EDTA was found to enhance the removal of Pb and Zn from spiked soils [16,17]. Even though EDTA is a good complexing agent, it may not be the best choice of enhancement solution due to the toxicity of EDTA itself. In this research, we used this technology to remove lead and zinc from an alkaline soil. To enhance the potential of this method in alkaline soils, we used chelating agent EDTA and Ammonium citrate. At the end we compare the role of these chelating with distilled water on removal of lead and zinc from an alkaline and natural polluted soil.

II. MATERIALS AND METHODS

The soil was taken from the site of alkaline mine, and several kilograms were mixed on the site. The soil had been polluted with zinc, lead, iron and contained several other heavy metals at elevated concentrations due to the mining activity on the site. The initial concentration of zinc and lead in the soil was respectively 530 and 450 mgkg⁻¹. At the laboratory, the soil was sieved and the fraction smaller than two mm was used for the experiments.

A. Electrokinetic Experiments

Electrokinetic experiments were conducted in a 40×10 ×10 cm plexiglas box (Fig. 2). Graphite plate electrodes were placed at the ends of the box in electrode compartments, separated from the soil by a porosity sheet. Six kg soil was placed in the middle compartment. The total length of the soil column was 40 cm. The solutions in the electrode compartments were stirred continuously, so we use Marriot bottle to enter enhancement solution to soil. An electric field of 25V was applied for 30 days. In experiment 1, we saturated soil by distilled water and the solution in the

TABLE I. CHARACTERISTICS OF THE ORIGINAL SOIL

Zn (mgkg ⁻¹)	530
Pb (mgkg ⁻¹)	450
CCE (%)	18.7
Organic carbon (%)	0.154
Clay (%)	43.2
Silt (%)	26
Sand (%)	30.8
CEC (cmolkg ⁻¹)	21.2
pH	7.69

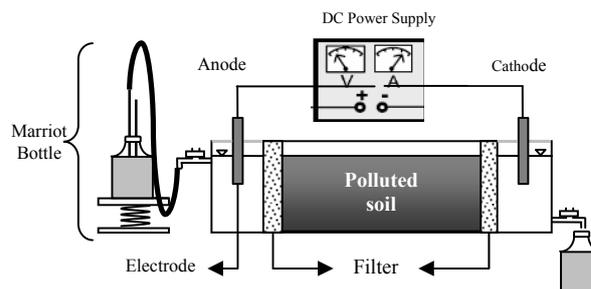


Figure 2. A schematic diagram showing the electrokinetic soil remediation system.

electrode compartments and in the Marriot bottle was distilled water. In experiment 2, the solution in the electrode compartments and in the Marriot bottle consisted of 0.02 M EDTA at the start. Solution was added regularly to prevent drying. In experiment 3, the solution in the electrode compartments and in the Marriot bottle was ammonium citrate that its pH was adjusted on 9.

III. ANALYSIS

The pH in the soil was measured in-situ at regular intervals during the experiments. Solution samples were taken every two days. After 30 days, soil samples were taken and the samples were dried and sieved and the fraction smaller than 2 mm was used for analysis. Zinc and lead were extracted by nitric acid 4 N and was filtered with Whatman No.42 filter paper. Concentrations of zinc and lead were determined using an atomic absorption spectrophotometer (Shimadzu AA-670).

IV. RESULTS AND DISCUSSIONS

A. Characteristics of the original soil

Table (1) shows characterization results of soil was sieved and the fraction smaller than 2 mm. This soil is categorized as clay according to U.S. Department of Agriculture Classification system. The soil pH was determined to be 7.6 and carbonate content was 18.7% [14]. This original soil can be considered as a polluted soil according to the soil quality standards.

B. Changes of pH in the soil column

Fig. 1 Show the variation of pH profile with distance from anode. For all tests, the initial pH was about 7.69. As the test proceeded and finished, we supplied five samples with distance 5 cm each other from the anode. As it has been shown pH graph for experiment No 1 and 3 was elevative, but at the experiment No 2 was different. At the beginning, it was elevative and then at distance about 12-22 cm came down.

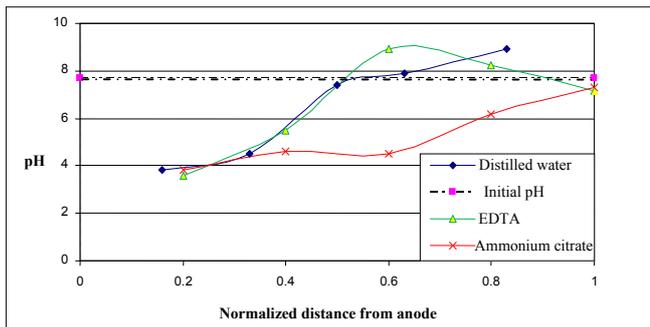


Figure 3. Changes of pH in the soil column

C. Residual lead concentration distribution in soil column

To performance of usual electrokinetic remediation (without using enhancement solution), we use distilled water to remove lead and zinc from a natural polluted soil with these two heavy metals. As it has shown (Fig. 4) removal of lead at the distance between 3-12 cm from anode was increased (41.5% of initial soil lead) and at the distance between 12-22 cm was decreased (4.2% of initial soil lead). As a result of water electrolysis at the cathode, OH was produced, so pH of catholite was read about 12.5. Hydroxyl ions cause precipitation of lead near the cathode [3,13].

Under certain circumstances, such as soils with high buffering capacity, the use of enhancement agents to solubilize the contaminants is necessary for cost-effective implementation. Chelating or complexing agents, such as ammonium citrate and EDTA, have been demonstrated to be feasible for the extraction of different types of metal contaminants from soils. The enhancement agents should form charged soluble complexes with the metal contaminants [8]. With regard to high pH of soil, we use EDTA and ammonium citrate to increase capability of electrokinetic.

As it has shown (Fig. 4) when we use EDTA as an enhancement solution, precipitation of lead was occurred between cathode and anode [5]. When EDTA-lead complexes flowed through the soil column and entered the cathode reservoir, a pH of greater than 10 further dissociated EDTA to a species EDTA^{4-} . Consequently, the EDTA-lead complexes became negatively charged and began to migrate back toward the anode. As a result of this conflict, lead was accumulated in the middle part of the soil column, this area probably is contact of two acidic and basic front [4] and also soil pH was increased between anode and cathode while it became more than initial soil pH (Fig. 3). At experiment No 3, we use Ammonium citrate as an enhancement solution. As it has shown (Fig. 4) with distance from anode amount of lead was decreased, because as a result of water electrolysis

H^+ and OH^- are induced respectively at the anode and cathode,

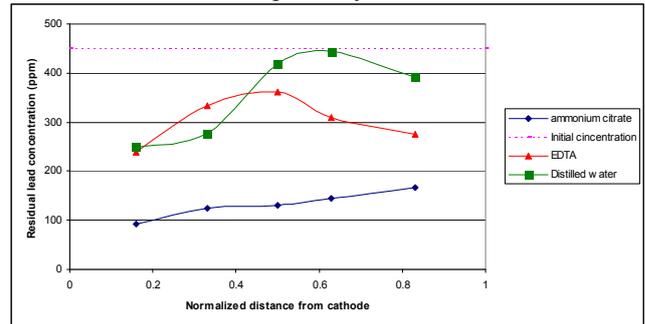


Figure 4. Residual lead concentration distribution in soil column

when H^+ was migrating in soil column, it replace with positive ion such as lead and then lead releases to soil solution, but OH^- causes precipitation of lead.

D. Residual zinc concentration distribution in soil column

Concentration variation of zinc in soil column in distilled water treatment has shown (Fig. 5) and it is similar to concentration variation of lead in soil column in this treatment. Residual zinc concentration in soil column decreased near the anode (amount of 59% initial zinc concentration of soil), while near the cathode it became 22.2% of initial zinc concentration of soil. Hydroxyl generation and thus increasing soil pH causes precipitation of zinc. In other words efficiency of distilled water to remove zinc near cathode and near the anode was respectively delicate and acceptable [10].

As it has shown (Fig. 5) in experiment No 2, at the middle of soil column zinc was accumulated, at accumulated point soil pH was increased so high soil pH causes precipitation and accumulation of zinc at this point. When EDTA-zinc complexes flowed through the soil column and entered the cathode reservoir, a pH of greater than 10 further dissociated EDTA to a species EDTA^{4-} . Consequently, the EDTA-zinc complexes became negatively charged and began to migrate back toward the anode.

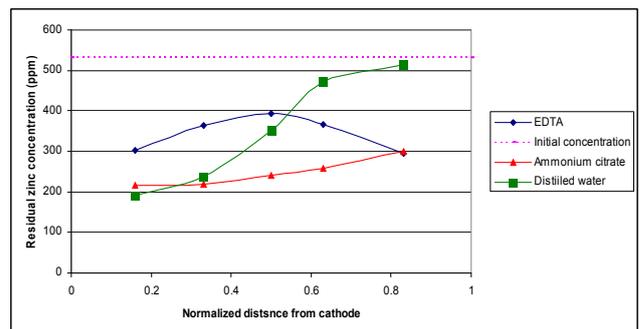


Figure 5. Residual zinc concentration distribution in soil column

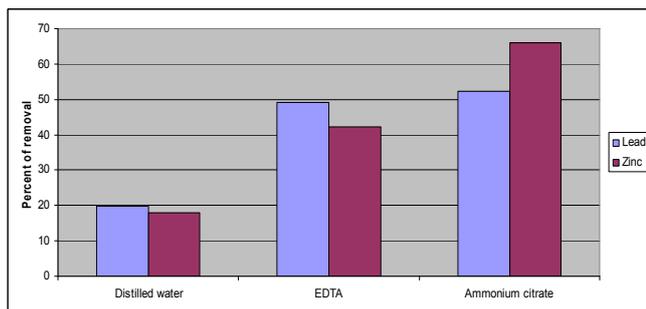


Figure 6. Percent of removal of lead and zinc

In experiment No 3, concentration variation of zinc with distance from anode was regular unlike experiment No 2. In other words with distance from anode, removal of lead was decreased because OH⁻ that was generated by water electrolysis results precipitation of zinc.

E. Percent of removal of lead and zinc

As it has shown (Fig. 6), removal percent of lead and zinc at ammonium citrate treatment was more of other treatments and also amount of removal of lead and zinc at each treatment depended on kind of elements, for example removal of lead in experiment 2 (EDTA treatment) was more than removal of zinc at this experiment.

V. CONCLUSION

Enhanced electrokinetic was more effective than electrokinetic. Chelating agents defend heavy metal (lead and zinc) to complex with hydroxyl ions and so precipitation of heavy metal decreases.

In spite of have high constant stability of EDTA, ammonium citrate was more effective than EDTA, because adjustment of pH is an important factor to remove heavy metal from soils. For example, with increasing pH, percent of EDTA⁴⁻ was increased, so it results increasing of percent of EDTA-heavy metals. Order of removal of lead and zinc at catholite reservoir in three treatments is:

Ammonium citrate (pH=9) > EDTA > Distilled water
 Removal of lead in experiment No 2 was more than removal of zinc at this experiment, because stability constant of complexes of lead with EDTA (log k=17.88) is more than complexes of zinc with EDTA (log k=16.44). As we know if a complex has high stability constant it became more than stable and percent of this complex became more than the other complex with lower constant stability. With regard to high constant stability of complex ammonium citrate with zinc (log k=6.1) in comparing with ammonium citrate with lead (log k= 5.7), removal of zinc was more than lead in this experiment.

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