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Estimation of Optimum Conditions for Cadmium Removal from Contaminated Soil using Electro-Kinetic Remediation

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Abstract

The aim of this laboratory study is to estimate the best initial pH of purging solution for cadmium clean-up from an artificially contaminated soil using electro-kinetic cell. An efficiency enhancement scheme was employed involving pH control and injection wells as a part of the investigative program. Seven tests were performed at different pH controlled in the anode, cathode and injection wells start from 2 to 8. Sandy loam soil was contaminated with cadmium concentration equal to 2000 mg/kg and an initial moisture content equal to 30%. The duration of remediation was seven days with a potential gradient of 1.2 V/cm. The experimental results showed that the best removal efficiency was 62.8% at pH=3.

Keywords: Soil pollution, Cadmium removal, Electro-kinetic, pH, Soil remediation

1. Introduction

Soils can be contaminated with heavy metals derived from various sources including abandoned mining wastes, improper treatment of industrial wastes, incomplete collection of used batteries, leakage of landfill leachate, accidental spills and military activities. The contamination often affects a large volume of soil underlying several acres of the surface area. There are also various types of contaminated lands such as paddy fields, farms, factory sites, mine fields and residential districts. Contaminants migrating from these sources threaten the human health in the local area and the ground-water supply [1]. Heavy metals ions are detected in the waste streams from different industrial activities such as mining operations, tanneries, electronics, electroplating, petroleum refineries, and petrochemical industries [2, 3]. Heavy metals in soil can be present as soluble compounds like ions and metal complexes or in exchangeable forms. These metals are generally rendered immobile by associating with different soil fractions and compartments such as carbonate, oxide, hydroxide, organic matter and residual materials [4]. The toxicity of heavy metals can be listed in order of decreasing toxicity as Hg > Cd > Cu > Zn > Ni > Pb > Cr >Al >Co, although this is the only approximate as the vulnerability of species to individual metals varies. Toxicity also varies according to the environmental conditions that control the chemical speciation of the metals [5]. Cadmium in soils comes from natural and anthropogenic sources. Cadmium is relatively mobile in surface water and ground-water systems and exists primarily as hydrated ions or as complexes with humic acids and other organic ligands [6]. One of the emerging technologies to clean up heavy metal contaminated soils is the electro-kinetic remediation technique, which has been proven to be a very effective tool to remediate contaminated low hydraulic permeability fine grained soils [7-13]. Electro-kinetic remediation applies an electric field across a volume of soil to transport contaminants to a localized area where they can be effectively extracted [14-19]. The electrolysis reactions generate H^+ ions and O2 gas at the anode and OH^- ions and H2 gas at the cathode. The gases may be allowed to escape into the atmosphere, while the H^+ ions migrate towards the cathode and OH^- ions migrate towards the anode. Depending on the extent of migration of H^+ and OH^- ions, pH changes occur across the soil. Generally, low pH (acidic) condition exist near the anode and high pH (basic) conditions exist near the cathode. The pH changes in the soil will affect the geochemical processes, namely adsorption and desorption, precipitation and dissolution, and oxidation and reduction [20].

The object of this laboratory study is to investigation of the best initial pH value of purging solution for cadmium clean-up from artificially contaminated soil using electro-kinetic remediation proses with enhancement condition.

2. Experimental details

2.1 Materials

Cadmium was chosen as the contaminant which representative the heavy metal contaminants. Cadmium was used in the form of $Cd(NO_3)_2.2H_2O$ (manufactured by E. MERCK, Denmark). To prepare a soil sample with cadmium concentration equal to 2000 mg/kg and initial moisture content equal to 30% by weight, 16.156 g of $Cd(NO_3)_2.2H_2O$ was dissolve in one liter of distilled water and 300 ml of this solution was added to 1 kg of dry soil. Table 1 shows a summary of the composition and properties of the soil, the soil was cleaned and sieved to achieve satisfactory uniformity.

Table 1: Composition and properties of the soil sample.

Property	*Sandy loam*

Particle size distribution (ASTM D 422)	
Sand (%)	57
Silt (%)	30
Clay (%)	13
Hydraulic conductivity (cm s^{-1})	2.7 x 10^{-4}
Cation exchange capacity (meq /100 g)	6.25
pH	7.5
Organic content (%) (ASTM D 2974)	0.17
Electrical conductivity EC (µS/cm)	1380
Porosity (n) (ASTM D7263)	0.42

2.2 Electro-kinetic Test Setup

Fig. 1 shows the schematic diagram of the electro-kinetic test setup used for this study. The system consists of an electro-kinetic cell, two electrode compartments, four injection wells, power supply, and a multi-meter. The glass electro-kinetic cell has an inner dimension of 350 mm x 60 mm x l00 mm high. The actual length of the soil specimen in this cell equal to 200 mm, each electrode compartment consisted of a valve to control the flow in the cell. Perforated plastic plates and filter paper were used to separate the soil at two ends of soil. Anode and cathode electrode were graphite rods of 20 mm diameter; DC power source (LODESTAR LP3005D (Taiwan)) was used to apply a constant voltage to the electrodes to removal cadmium from artificially contaminated soil. Multi-meter was used to monitor the voltage and measure the current flow through the soil sample during the test.

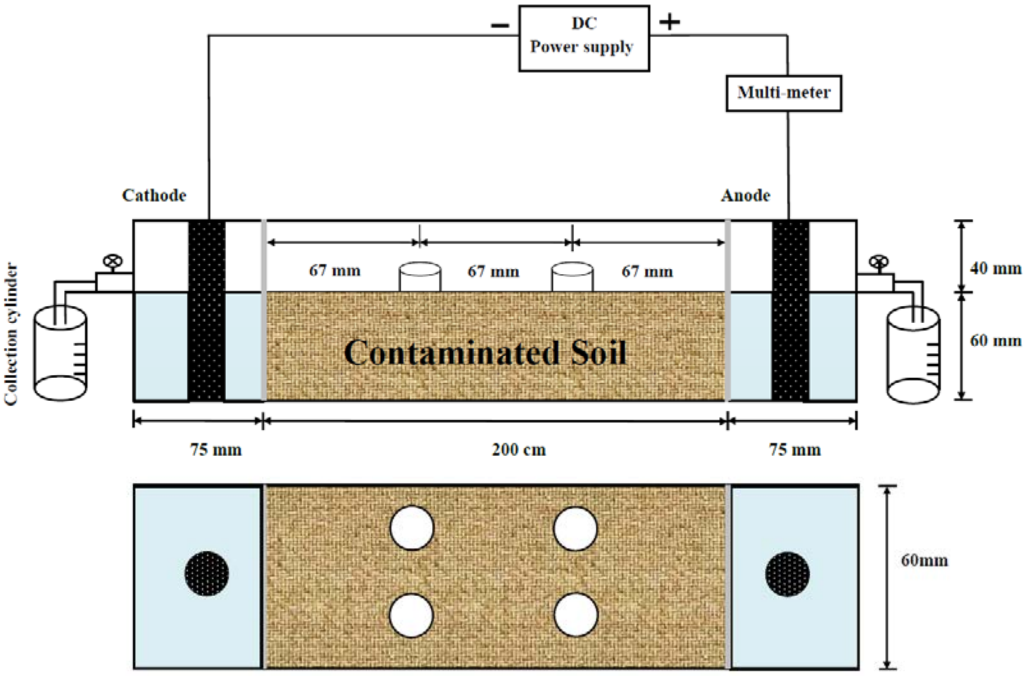

Figure 1: Schematic representation of electro-kinetic cell.

2.3 Experimental Design

Seven tests were performed to investigate the effect of pH; nitric acid (HNO_3) mixed with distilled water at different pH value 2, 3, 4, 5, 6, 7, and 8 was used as a purging solution in anode, cathode and injection wells with continuous adjustment of pH value. This was achieved by adding nitric acid HNO_3 and sodium hydroxide NaOH. Table 2 summaries the test conditions. 24 V potential was applied in the electro-kinetic cell from DC power supply, the duration of remediation was seven days.

Table 2: Electro-kinetic remediation experiments.

Test NO.	*Initial water content%*	*Processing duration (days)*	*Applied voltage (V)*	*pH*
EK-1	30%	7	24	2
EK-2	30%	7	24	3
EK-3	30%	7	24	4
EK-4	30%	7	24	5
EK-5	30%	7	24	6
EK-6	30%	7	24	7
EK-7	30%	7	24	8

2.4 Testing Procedure

The soil samples were artificially contaminated with cadmium ions in all electro-kinetic tests. The required amount of the $Cd(NO_3)_2.2H_2O$ that would yield the desired concentration was weighed and then dissolved individually in distilled water. The contaminant solution was then added to 1kg of the dry soil and mixed thoroughly with a plastic spatula in polyethylene container. A total of 300 ml of distilled water (30% moisture content) was used to represent typical field moisture conditions. The contaminated soil was then placed in the electro-kinetic cell in layers and compacted uniformly using wooden rod. The exact weight of the soil used in the cell was determined and the soil was equilibrated for 24 hrs. Filter papers were inserted at the ends of the soil sample. The electrode compartments were filled with purging solutions. The elevation of water level in the electrode compartment was kept constant to prevent a hydraulic gradient from occurring across the specimen. The electro-kinetic cell was then connected to the power supply and a constant DC voltage gradient was applied to the system. The pH in anode, cathode and injection wells was adjustment to the desired value throughout the duration of the experiment. The electric current across the soil sample and the water flow were measured at different time periods throughout the duration of the experiment. At the end of each test, the soil specimen was extruded from the cell. The soil specimen was sectioned into five parts and each part was weighed and subsequently preserved in a glass container.

From each soil section, 5 g of dry soil was taken and mixed with 12.5 ml distilled water. The mixture was shaken thoroughly by hand for several minutes and the solids were then allowed to settle for one hour after that pH of the soil was measured [21].

2.5 Chemical Analysis

Cadmium in different soil sections were extracted by performed acid digestion in accordance with the Danish Standard DS 259:2003 (30 min at 200 kPa (120 °C)) by adding 20 ml 1:1 HNO3 to 1g dry matter and treating the sample in autoclave (JP SELECTA S.A. MICRO8(Spain)). The liquid was separated from the solid particles by vacuum through a 0.45 µm filter and diluted to 100 ml. The cadmium concentration was determined by atomic absorption spectrophotometer (novAA 300(Germany)) [21].

3. Results and discussion

Fig. 2 shows the pH of soil vs. normal distance from the anode after the end of each test. The initial pH of sandy loam soil before the test was 7.5. The change of pH in soil because the migrated of H+ ions from the anode towards the cathode compartment during the electrolysis of water in the electro-kinetic cell [7]. The continuous adjustment of pH in the anode, cathode and injection wells at EK-1 to EK-6 prevent the precipitation of hydroxides near the cathode due to generation of hydroxides ions by water electrolysis in the cathode compartment. The high pH (EK-7) indicated that some OH− ions were reaching the soil and possibly interfering with the mobility of cadmium ions. The high pH environment was favorable to make $Cd(OH)_2$ which precipitate near the cathode sections and decrease the soil conductivity. According to this fact, the higher Cd concentrations were found near the cathode sections [22].

Fig. 3 shows the Cd concentration vs. normal distance from the anode after the end of each test. As shown, the Cd migrated from the anode and accumulated toward the cathode. The initial concentration of cadmium throughout the soil was 2000 mg/kg. Final concentration of cadmium was lower and varied from 530-1900 mg/kg near the anode to 930-2100 mg/kg near the cathode. The concentration profiles in Fig. 3 indicate removal of cadmium from the soil system in the experiments EK-1 to EK-6 as all of them are below the initial concentration profile. Increased cadmium concentrations were observed near the cathode.

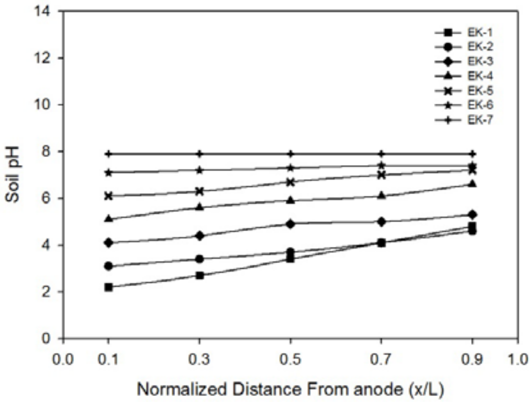

Figure 2: pH in soil.

Fig. 4 shows the profile of electric current during the tests, the current initially varied from 19-43 mA and finally 20-340 mA. As shown, in EK-1 to EK-4 the current was increases continuously and this indicate that the time is important to increase the removal efficiency. In other words, the removal efficiency increases when time of remediation increase. While in EK-5 the current was increases to 188 mA after 102 hour, current was decreased and finally stabilized to 157 mA. These indicate that the removal efficiency was decreased with time; we can observe the same behavior in EK-6 and EK-7 and these results agree with [4, 13, and 25].

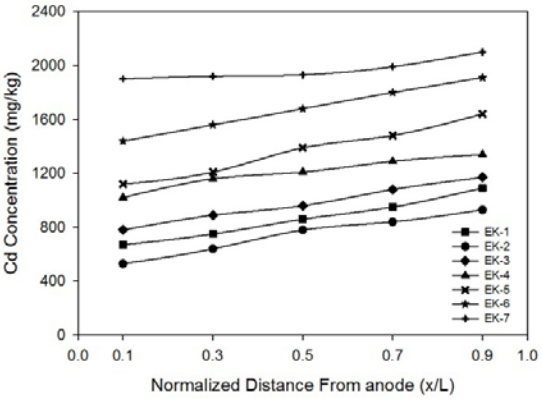

Figure 3: Cadmium concentration in soil

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Direction of fluid flow was from the anode to the cathode reservoirs (zeta potential ζ <0). Fig. 5 shows the plot for cumulative volume of effluent versus time. The effluent flow increased with time in EK-1 to EK-6, while in EK-7 increased slightly with time and finally stabilized at 16 ml because clogging of pores that happen from deposition in the soil of compounds such as metal hydroxides which may be formed by reaction between hydroxyl ions near the cathode and heavy metal contaminants and eventual cessation of flow [22]. Furthermore, the calcium precipitation close to the cathode clogged the soil pores; restraining further transport of heavy metal ions for removal [23].

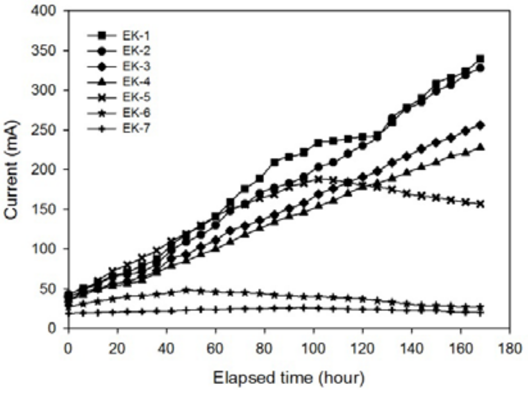

Figure 4: Electric current variation versus the time.

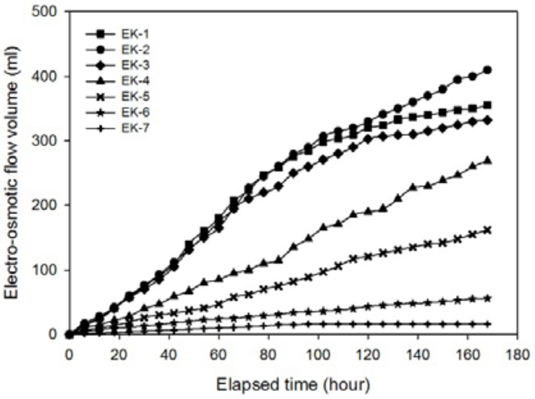

Figure 5: Electro-osmotic flow variation versus the time.

Fig. 6 shows the overall contaminant removal efficiencies (calculated based on the residual contaminant masses in the soil) for all the tests conducted. The removal efficiencies was 56.8 % in EK-1, 62.9 % in EK-2, 51.2 % in EK-3, 39.8 % in EK-4, 32.5 % in EK-5, 16.1 % in EK-6, 1.6 % in EK-7. The results showed that the cadmium removal in EK-2 was the highest when pH equal to 3 and the lowest removal efficiency of cadmium was achieved in EK-7 when pH equal to 8. Reference (19) study the effect of the initial pH of sand in an electro-kinetic cell on the amount of copper that can be extracted from different regions of the cell and the results showed an optimum pH of ~2.6.

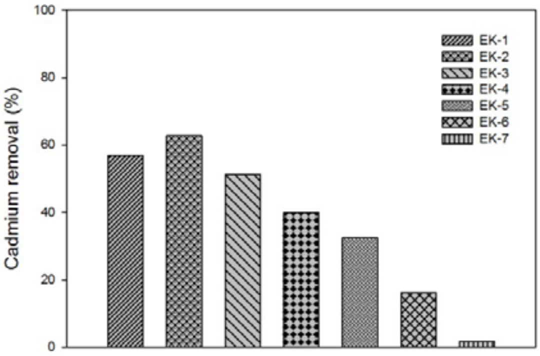

Figure 6: Removal of cadmium from soil.

4. Conclusions

According to results obtained from the experimental measurements, the following conclusions can be drawn:

1. The optimum pH value was 3.0 in the anode, cathode, and injection wells had a significant positive impact on the removal efficiency of cadmium during the remediation proses. Although these enhancement the mobility of cadmium towards the cathode.
2. Higher pH values lead for increase the concentration of OH^- ions causing the

precipitation of cadmium in the form of insoluble $Cd(OH)_2$, which decreased the amount of Cd that can be removed [19].

3. At low pH value, the greater concentration of H^+ causes electro-osmotic flow to decrease. In electro-osmosis, movement generally occurs toward the negatively charged cathode, causing the more mobile $[H^+]$ front to move towards and neutralize OH^- ions close to the cathode. While the addition of HNO_3 decreased the concentration of hydroxide, decreasing precipitation of cadmium, excessive H+ ion concentration decreased electro- osmosis, preventing the effective reclamation of Cd^{2+} at the cathode as shown in Fig. 5 [19, 24].

4. Electro-kinetics remediation friendly environmental procedure, it is less risky and this technology is applicable in low permeable soils. Enhancement with HNO_3 by using injection wells can be effective for the removal of cadmium ion from contaminated soil.

5. The enhanced cadmium mobility due to pH control could be further improved by introducing acid-injection wells in the treated soil, where the pH was also controlled to the same extent. However, other factors such as the concentration of the purging solutions, total chemical costs associated with the use of the purging solutions, and the energy expenditure of the process need to be optimized.

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تقدير الظروف المثلى لازالة الكادميوم من التربة الملوثة بأستخدام الطريقة الكهروحركية

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قسم هندسة البيئة
الجامعة المستنصرية

الخلاصة

تهدف هذه الدراسة المختبرية لتقدير افضل قيمة ابتدائية للدالة الحامضية المستخدمة في محلول غسل التربة الملوثة مختبريا بالكادميوم بأستخدام الطريقة الكهروحركية. تم استخدام ظروف تحسين للطريقة تمثلت بالسيطرة على قيمة الدالة الحامضية وابار حقن لمحلول الغسل. تم اجراء سبعة تجارب مع السيطرة على قيمة الدالة الحامضية في الانود والكاثود وابار الحقن بقيم مختلفة تبدأ من 2 الى 8. تم استخدام تربة ملوثة بالكادميوم بتركيز 2000 ملغم\كغم وبنسبة رطوبة ابتدائية 30 % وفترة معالجة 7 ايام بفرق جهد 1.2 فولت \سم. اظهرت النتائج المختبرية ان افضل كفائة ازالة كانت 62.8 % عندما تكون قيمة الدلة الحامضية مساوية الى 3.