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Electrokinetic Remediation of Copper and Zinc Contaminated Soil Using Carbon Nanotube

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Abstract. Soil and groundwater contamination have become a major environmental issue worldwide. Different contaminants, such as heavy metals, petroleum hydrocarbons, pesticides and other persistent organic pollutants is complex in nature due to the non-biodegradable and toxic properties and there is an urgent need to develop cost effective and sustainable remediation technologies. Electrokinetic remediation is one of the most promising soil decontamination processes that have high removal efficiencies for metal ions [2]. It is an effective and innovative method to remediate different kinds of soils, especially low permeable fine grain soils such as silty and clayey soils. In this method, by applying a direct-current electric field into a contaminated soil result in different transport phenomena such as electroosmosis, electromigration and electrophoresis. The present experimental study is aimed to examine the copper and zinc removal efficiency under various experimental conditions and to investigate the enhancement in removal of Copper and Zinc from contaminated soil by electrokinetic remediation using CNT. Laboratory tests were performed on clayey soil under the influence of direct current (DC) electric field. The use of CNT enhanced the electrokinetic remediation. The removal of copper was increased from 28.5 % to 94.6 % respectively. The removal of zinc was increased from 20.0% to 92.5 % respectively. The increase in removal efficiency indicates that CNT can be successfully utilized for electrokinetic remediation of copper and zinc contaminated soils.

Keywords: Electrokinetic remediation, Copper, Zinc, Carbon Nanotube.

1 Introduction

1.1. General

Soils gets contaminated by the accumulation of heavy metals and metalloids through emissions from the rapidly expanding industrial areas, mine tailings, disposal of high metal wastes, leaded gasoline and paints, land application of fertilizers, animal manures, sewage sludge, pesticides, wastewater irrigation, coal combustion residues, spillage of petrochemicals, and atmospheric deposition[4].Soil contamination is a major environmental issue worldwide. Heavy metals are released into the soils by both natural and anthropogenic sources and human activities. The current worldwide mine production of heavy metals is considerably huge. Heavy metals commonly present in soils include nickel (Ni), lead (Pb), cadmium (Cd), arsenic (As), chromium (Cr), copper (Cu), cobalt (Co), zinc (Zn), manganese (Mn), aluminum (Al) and mercury (Hg)[7]. Among these heavy metals, As, Pb, Cd and Hg are included in the top 20 Hazardous Substances of the Agency for Toxic Substances and Disease Registry (ATSDR) and the United States Environmental Protection Agency (US EPA).

Electrokinetic remediation is an effective emerging technology for the decontamination of heavy metal contaminated soil. It can be used as an in situ or ex situ remediation for fine grained soils [3]. In this process a low voltage DC is applied across the electrodes which are inserted into the soil. This causes the generation of H+ and OH- ions at anode and cathode due to the process of electrolysis. The potential difference between the electrodes causes the migration of contaminants to respective electrode chambers. The main contaminant transport mechanisms are electromigration, electroosmosis and electrophoresis. Electrokinetic process has been successfully applied in treating both heavy metals and organic compounds contaminated soil[5].For removal of soil contamination whether it is in situ or ex situ, electrokinetic remediation is one of the most effective methods, as it has high removal competence and time usefulness in soil with low permeability. Soil electrokinetic remediation is a new and cost effective physical method for the remediation of heavy metals.

2. Experimental Procedure

2.1. Materials

Cochin Marine Clay. Marine clay collected from a site at Vallarpadam, Kochi, India. For uniformity soil samples were collected and pooled together and thoroughly mixed into a uniform mass and preserved in polythene bags to maintain the water content. The properties of marine clay used in the study are given in Table 1.

Table 1. Properties of Marine Clay used in the study

Property	Value
Water content (%)	112
Specific Gravity	2.6
Liquid limit (%)	138
Plastic limit (%)	48
Plasticity Index (%)	90
Shrinkage limit (%)	20
Grain size distribution	
Clay (<0.002 mm)	55
Silt (>0.002 mm< 0.075 mm)	35
Sand (>0.075 mm)	10

Zinc Powder. Zinc is a transition metal with the following characteristics, atomic number 30, atomic mass 65.4, density 7.14 g cm-3, melting point 419.5°C, and boiling point 906°C. The maximum allowable limit of Zn concentration in soil is 300mg/kg. The Zinc powder used in the study was procured from Alpha Chemicals, Kochi.

Copper Powder. Copper is a transition metal which belongs to period 4 and group IB of the periodic table with atomic number 29, atomic weight 63.5, density 8.96 g cm^{-3}, melting point 1083°C and boiling point 2595°C. Copper is the third most used metal in the world. The maximum allowable limit of Cu concentration in soil is 100mg/kg. The Copper powder used in the study was procured from Alpha chemicals, Kochi.

Carbon Nanotubes (CNT). Carbon Nanotube (CNT) can now be considered as the “king” of nanomaterials. Carbon Nanotube is a tube-shaped material, made of carbon with a diameter measuring on the nanometer scale. As a group, Carbon Nanotubes typically have diameters ranging from < 1 nm upto 50 nm. Overall, Carbon Nanotubes show a unique combination of stiffness, strength, and tenacity compared to other fiber materials which usually lack one or more of these properties. Thermal and electrical conductivity are also very high, and comparable to other conductive materials. Carbon Nanotube (CNT) is selected for the study because of the exceptional sorptive ability which is driven by their characteristically large surface areas and highly hydrophobic nature. CNT exhibit many exceptional properties, including large surface area, can be easily modified chemical or physical, and they have ability of removing both organic and inorganic contaminants. The Carbon Nanotube used in the study was procured from Platonic Nanotech Pvt Ltd, Bangalore.

2.2. Experimental Setup

Figure below shows the schematic diagram of the experimental setup and the fig.0 shows the experimental fabricated in the lab. The EK tests were performed in clear glass rectangular tank. Glass being chemically and electrically neutral material, the tank was fabricated with glass. The experimental tank has to be large enough to hold reasonable quantities of soil so that samples can be obtained to conduct the planned physicochemical tests at the specified regions between the electrodes during and after the EK treatment. Considering these requirements, it was decided to fabricate the glass tank with dimensions: 45 cm in length, 35 cm in width and height of 25 cm. The glass tank was divided in to three compartments – two compartments for electrolyte, each having dimension 10cm length and 35cm width and one compartment for soil with dimensions 25 cm length and 35 cm width.

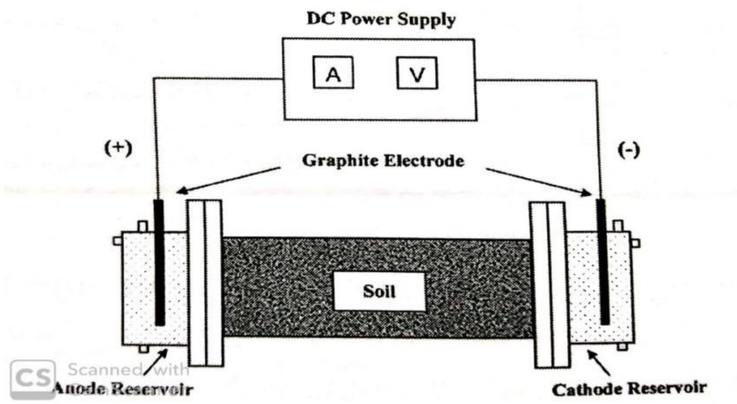

Figure 1. Schematic view of the experimental model (Yuan S et al ,2012)

The tank was divided into three compartments using permeable layer made up of nylon mesh of 2mm size and filter paper. The photograph of experimental set up made in the laboratory is as shown in Figure 3.6. The selection of electrodes is important in EK treatments. Cost and chemical reactions are the main considerations in the selection of electrodes. The use of gold and platinum is impractical because they are very expensive metals. Non-metallic conductors such as carbon and graphite have been found to give very poor performance. Stainless steel was chosen as the electrode. Material due to the following considerations: available at low cost, easy to fabricate, considerable strong, less likely to corrode, and also a common material that can be used in field situations. The electrodes used for the study were made in the shape of hollow tubes with 35 mm in diameter, 2 mm thickness and 25 cm in height and were perforated. A 30 V DC Supply is used for applying current to the soil. The DC supply is connected to the electrode via an electric probe.

2.3. Preparation Of Test Bed In The Tank

Marine clay collected was mixed uniformly and stored in airtight bags. Before filling the tank it is again uniformly mixed. The slurry sample was prepared by mixing the clay soil with deionised water to achieve a water content of 135%, which is equal to the LL of sample. Firstly a dissolved solution of Zn/Cu was prepared. For which 10% of zinc/copper is taken and dissolved in deionised water using mechanical stirrer. This Zn/Cu solution is mixed with 5kg soil sample in the mechanical mixer, achieving a uniform Zn/Cu spiked soil mix of water content of 135% for the test sample. The soil sample is poured into the soil compartment of tank and properly tamped to remove the trapped air inside the soil and the top is leveled .Filter paper and nylon mesh is attached at each end of soil column to avoid leakage of soil particles. The electrolyte compartment is filled with deionized

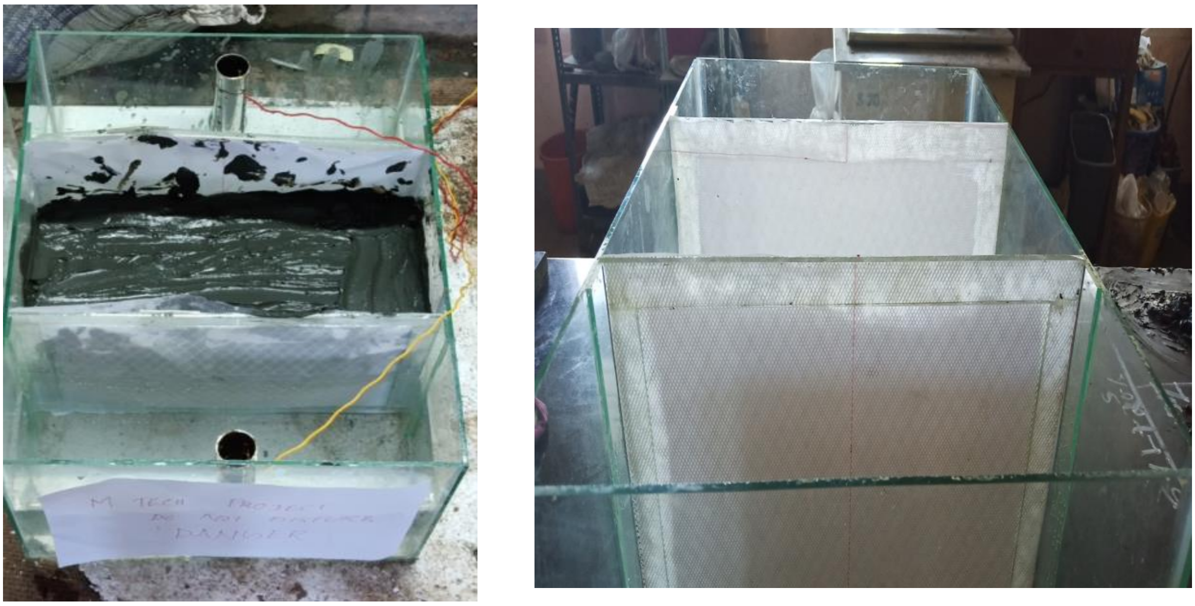

Figure 2. Photograph of experimental setup made in the laboratory

water till level of soil. Then, two hollow perforated stainless steel tubes were placed apart in the electrolyte compartments. The electric probes are connected to the anode and cathode which in turn connected to the DC power supply, providing total voltage 30V. During the main experimental programm, the electric current and the voltage were maintained continuously throughout the test period. A voltage of 30V was maintained throughout the test. Soil sample at different normalized distances from anode such as 0.15, 0.5 and 0.85 were collected on 5, 10 and 15 days and were tested. Inorder to study the effect of CNT on enhancement of removal efficiency of contaminant the electrolyte used were deionized water mixed with 0.05% of CNT.
In the present study we determine the effect of electrokinetic remediation on different regions between the electrodes; therefore the soil between the electrodes in the soil compartment is divided into 3 regions with average normalized distance of 0.15, 0.5 and .85 cm respectively within the soil column. Normalised distance is the distance from the anode to the sample position divided by the distance between the electrodes .The soil at these sections was tested for variations in moisture content, index properties and concentration of contaminant as a result of EK process for various periods 5,10 and 15 days. For testing the change in concentration of contaminant soil where collected from the vicinity of anode and cathode. The soil samples collected were tested to find the final concentration of contaminant.

2.4. EK Treatment on Zinc and Copper Contaminated Soil

Electrokinetic remediation treatment was carried out on copper and zinc contaminated soil with and without CNT. This study was carried out to evaluate enhancement of the treatment efficiency of a heavy metal contaminated soil by combined process of the injection of carbon nanotube (CNT) and electro kinetic remediation. The Cu/Zn contaminated soil sample prepared is placed into the soil compartment of tank in three layers at and properly tamped to remove the trapped air inside the soil and the top is leveled .The electrolyte compartment is filled with deionised water. The electrodes are placed in electrolyte compartment and are connected to DC supply of capacity 30V.During the experimental programme, the electric current and the voltage were maintained continuously throughout the test period. A voltage of 30V was maintained throughout the test. Soil sample at different normalized distances from anode such as 0.15, 0.5 and 0.85 were collected on 5, 10 and 15 days and were tested.

3. Result And Discussion

3.1. Results Of Physicochemical And Engineering Properties Of Soil After EK Treatment

Metal Concentration. Variation of metal concentration in the soil sample from anode to cathode is shown below in Table.4.2. The samples collected were digested in HNO_3,and made into a 100ml solution, then filtered and analyzed with ICP-MS system to obtain the concentration on Zn and Cu. For all test periods, experimental values show a similar trend from anode to cathode. A decrease in the concentration of Zn from anode to cathode was observed from the average values of the corresponding heavy metal concentrations in the soil at different treatment periods. The initial zinc concentration in the soil is 10.208 % of soil. Total Zn removed from soil after 15 days treatment is 2.043 % of soil, Hence the removal efficiency is 20.0 %.The initial copper concentration in the soil is 9.866 % of soil. Total Cu removed from soil after 15 days treatment is 2.821 % of soil, Hence the removal efficiency is 28.6 %.

Table 2. Variation in Zn concentration after EK treatment on Zn contaminated soil

Treatment duration (days) / Normalized distance	Zn concentration (%)	
	0.15	0.85
0	9.981	10.436
5	9.484	8.301
10	9.303	7.518
15	8.432	7.898

Table 3. Variation in Cu concentration after EK treatment on Cu contaminated soil

Treatment duration (days) / Normalized distance	Cu concentration (%)	
	0.15	0.85
0	10.121	9.610
5	8.98	8.509
10	8.015	7.958
15	7.981	6.109

3.2. Results of Physicochemical and Engineering Properties of Soil after EK Treatment with CNT

Metal concentration. Variation of metal concentration in the soil sample from anode to cathode is shown below in Table 4.13.The samples collected were digested in HNO_3, and made into a 100ml solution, then filtered and analyzed with ICP-MS system to obtain the concentration on Zn and Cu. Experimental values show a similar trend from anode to cathode for all test periods. A decrease in the concentration of Zn from anode to cathode was observed from the average values of the corresponding heavy metal concentrations in the soil at different treatment periods. The initial zinc concentration in the soil is 9.9505 % of soil. Total Zn removed from soil after 15 days treatment is 9.206 % of soil, Hence the removal efficiency is 92.517%.The initial copper concentration in the soil is 9.664 % of soil. Total Cu removed from soil after 15 days treatment is 9.147 % of soil, Hence the removal efficiency is 94.650 %.

Table 4. Variation in Zn concentration in Zn contaminated soil after EK treatment with CNT

Treatment duration (days) / Normalised distance	Zn concentration (%)	
	.15	.85
0	9.721	10.180

5	8.055	6.750
10	5.075	4.819
15	1.260	0.229

Table 5. Variation in Cu concentration in Cu contaminated soil after EK treatment with CNT

Treatment duration (days) / Normalised distance	Cu concentration (%)	
	.15	.85
0	9.809	9.519
5	6.591	4.230
10	3.984	3.019
15	0.907	0.127

3.3. Comparison of removal efficiency of Copper and Zinc through EK treatment with and without CNT

The following equation was used to calculate the removal efficiency of Copper and Zinc from contaminated soil after the EK treatment .

$$Removal\ efficiency\ (\%)\ R_e = \frac{C_o - C_f}{C_o}$$

Where:
C_o = the initial metal concentration
C_f = the final metal concentration
The removal efficiency of heavy metal from contaminated soil shown higher removal efficiency of Cu and Zn in EK treatment with CNT than EK treatment alone. The removal efficiency of Zinc from the contaminated soil increased from 20.01% to 92.51%.The removal efficiency of Copper from the contaminated soil increased from 28.56% to 94.65%. Figure 4.9 shows the removal efficiencies of EK treatment and EK treatment with CNT.

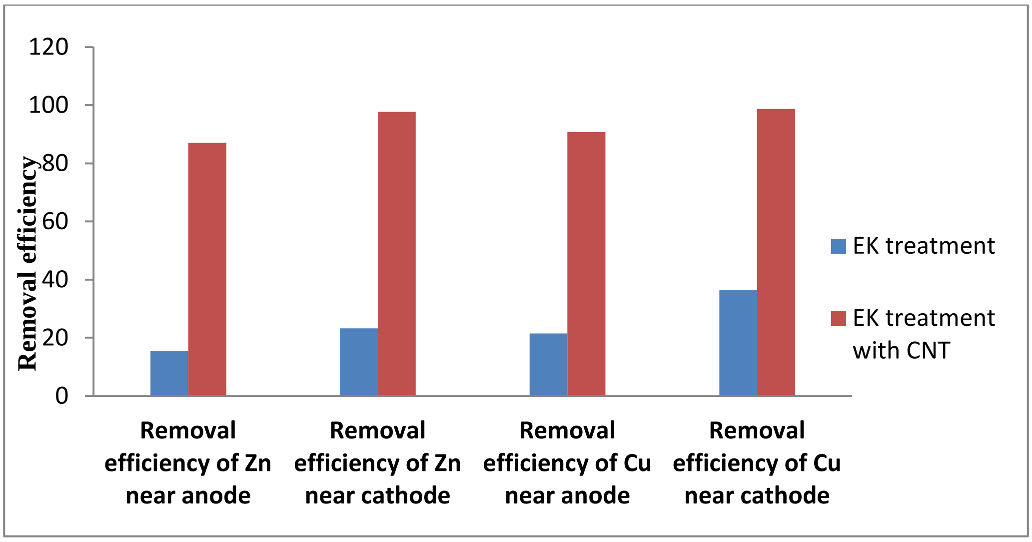

Figure 3. Bar chart showing the comparison between the removal efficiency of EK treatment and EK treatment with CNT

4. SUMMARY AND CONCLUSIONS

The present study enables a better understanding of physical and chemical changes of different properties of soil that occurs during the application of electrokinetics. The entire study carried out in the present work focused on the determination of enhancement rate in Zn and Cu removal from the contaminated soil using CNT. The important conclusions derived from the present work are as follows:

- From the study, it is concluded that eletrokinetic remediation is a feasible treatment method for the remediation of fine grained soil contaminated with zinc and copper.
- Use of CNT enhanced the contaminant removal efficiency of electrokinetic treatment.
- The electrokinetic treatment coupled with CNT, enhanced the removal efficiency of zinc from 20.0% to 92.5 %.
- The electrokinetic treatment coupled with CNT, enhanced the removal efficiency of copper from 28.5 % to 94.6 %.

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