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ELECTROKINETIC REMEDIATION STUDY FOR CADMIUM CONTAMINATED SOIL

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ABSTRACT

This paper presents the results of an experimental research undertaken to evaluate different purging solutions to enhance the removal of cadmium from spiked contaminated field soil by electrokinetic remediation. Three experiments were conducted when soil was saturated with deionised water and subsequently deionised water, ammonium citrate and sodium citrate were used as purging solutions at anode end. One experiment was conducted when the soil was saturated with ammonium citrate and itself was used as the purging solution. Results showed that 49% reduction of cadmium concentration was achieved in the case of soil saturated (washed) with ammonium citrate as well as purging solution also was ammonium citrate. The soil pH and washing solutions were the most important factors in controlling the removal of cadmium in electrokinetic remediation process.

Key words: Ammonium citrate, cadmium, electrokinetic remediation, sodium citrate

INTRODUCTION

Cadmium is a non-essential heavy metal pollutant of the environment resulting from various agricultural, mining and industrial activities and also from the exhaust gases of automobiles (Foy *et al.*, 1978). Due to its high toxicity and greater solubility in water and its wide distributions in aquatic ecosystem, it has been considered as extremely significant pollutant (Lockwood, 1976). Great efforts have been made on the studies for removal of contaminants from soil in recent past. There were few remedial technologies like soil flushing, phytoremediation, bioremediation etc. but all these technologies are not satisfactory in low permeable soils where electrokinetics has proved its own ability in such soils (Stichnothe *et al.*, 1996). Electrokinetic (EK) phenomena are the result of the coupling between hydraulic and electrical potential gradients in fine grained soils (Acar and Alshawabkeh, 1993). The phenomenon occurs due to the presence of the diffuse double layer around the fine-grained soil particles and fluids (Mitchell, 1993). The main mechanisms of contaminants movement in the electrical field involved in electrokinetic technology are electromigration of ionic species and elctroosmosis.

Soils with very low permeability, high cation exchange capacity and expansive nature due to presence of clay minerals of illite or montmorillonite groups are extremely difficult to remediate if they are contaminated by heavy metals. Electrokinetics has emerged as a viable option for field remediation of such a contaminated soil. A laboratory study has been carried out in the present work in which a soil from field has been spiked by cadmium under laboratory controlled conditions. Then, the cadmium has been removed under various situations to study the efficiencies of removal process and thus its possible application in field conditions.

Use of chelating agents is unavoidable for enhancement of electrokinetic extraction sometimes due to increase in pH (Puppala *et al.*, 1997). A number of studies on metal extraction using HNO_3 and HCl (Tampouris *et al.*, 2001) and the most commonly used chelater like ethylenediaminetetraacetic acid (EDTA) (Chaiyaraksa and Sriwiriyanuphap, 2004) have been reported. EDTA forms very stable soluble complexes that are highly effective in remediating

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heavy-metal-contaminated soils (Kedziorek and Bourg, 2000; Kim *et al.*, 2003). Despite satisfactory removal ratios by these extractants, many studies have observed that metal removal is associated with a number of disturbing physical, chemical and biological impacts (Bassi *et al*., 2000; Papassiopi *et al*., 1999). Also, use of EDTA increases the overall cost of the process.

Electrodialytic studies on the mobilization and electrochemical extraction of Cu, Cr and As using AC has been shown to be successful **(**Ottosen *et al*., 2004**)**. Ottosen *et al*., (2001) reported that AC has been a good enhancement solution for polluted calcareous soils at slightly alkaline environment. Sodium citrate (SC) displays high extracting capabilities similar to EDTA within certain limits of the pH values. It has been reported that SC can also be a more convenient ligand than ammonia (Lopez *et al*., 2003). The results discussed by López *et al*., (2004) indicate that the cadmium–sodium citrate system is very convenient to chemically deposit cadmium sulphide (CdS) films.

The aim of the present study is to develop an effective electrokinetic remediation system for the removal of cadmium from the spiked field soil obtained from agricultural field. Flushing solutions that are chelating agents (AC and SC) were examined for their potential use in the removal of cadmium from the field soil. A series of lab-scale electrokinetic experiments were conducted using these different flushing solutions to assess the extent of contaminant migration and removal.

MATERIALS AND METHODS

In the present work, field soil has been collected from unpolluted site Meja village, Allahabad district (Uttar Pradesh, India) at a shallow depth of 1-2m. After collection, the soil sample was air first dried and washed through 0.425mm sieve to obtain fine grained soil. Various physico-chemical tests were carried out. The important physico-chemical properties of the soil are presented in Table 1. X-ray fluorescence spectroscopy (XRF), qualitative X-ray diffraction (XRD) and scanning electron microscopy (SEM) characterization tests were performed for thorough understanding of soil mineral structure (Fig. 1 and Fig. 2).

Particle size distribution analysis indicated that the soil contained approximately 14.8% clay-size particles. Quartz, feldspar, calcite, dolomite, hematite and the predominant clay minerals Illite and Kaolinite constituted the bulk mineralogy. The XRF analysis revealed that the bulk soil chemistry is dominated by Si ((SiO_2)=59.27%), followed by Al ((Al_2O_3)=14.28%), Fe ((Fe_2O_3)=5.07%), Mg ((MgO)=3.55%) and CaO ((3.40%)). The phosphorus content was also uncommonly elevated ((P_2O_5)=0.105%), in comparison to its average value in soils (0.05%) (Sutton *et al*., 1999). The soil had unusually high organic content of 6.2%. The higher amount of organic content and phosphorus probably resulted from long-term cultivation activity. The background cadmium concentration was nil. The silica–sesquioxide ratio (SSR) was found to be 5.74. As a result, the soil was characterized to have very high adsorption capacity and very low conductive nature.

Table 1: Physico-chemical properties of soil used

Property Particle Size Distribution	Value
Gravel (%)	6.6
Sand (%)	18.4
Silt (%)	60.0
Clay (%)	15.0
Atterberg Limits	
Liquid limit (%)	45
Plastic limit (%)	17
Shrinkage limit (%)	13
Plasticity index (%)	28
Activity	1.87
Specific gravity	2.62
Cation exchange capacity (USEPA) (meq/100 g)	22
pH	8.36
Organic content (%)	6.25
Loss on ignition (LOI) (%)	9.93
$CaCO_3$ (%)	2.5
Soil classification (USCS)	CL
Cd	Nil

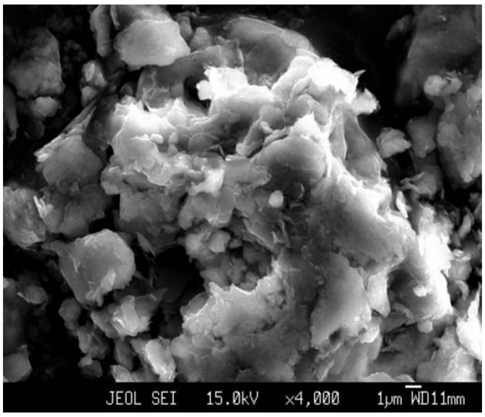
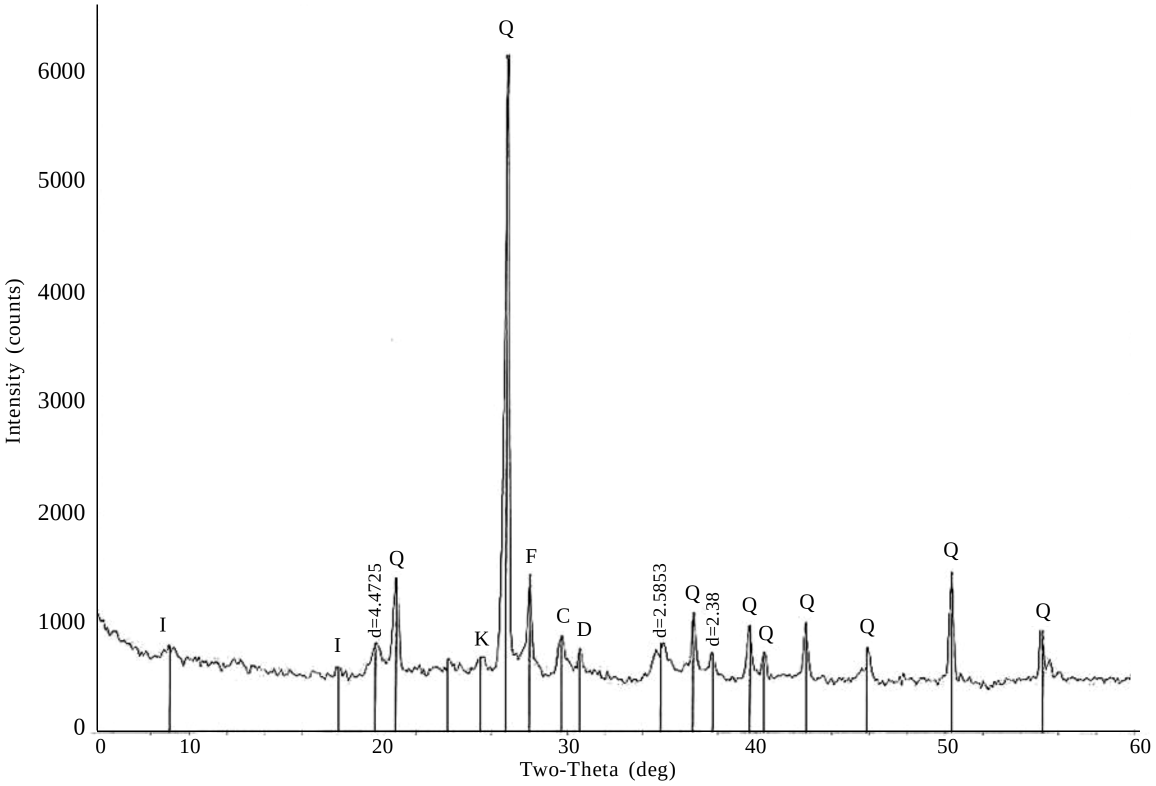


Fig. 1: Scanning electron image of virgin soil



Q-Quartz; F-Feldspar; C-Calcite; D-Dolamite; I-Illite; K-Kaolinite

Fig. 2: XRD pattern of virgin soil

Apparatus

pH meter (Orion model 920 A^{+}), atomic absorption spectrometry (PerkinElmer, AAnalyst 200), digital multi meters, dc power supply, inverter and graphite electrodes were used for the present study. The voltage, current and various incremental voltages of the unit were monitored and logged manually using digital multimeters. Schematic diagram of electrokinetic setup is shown in Fig. 3.

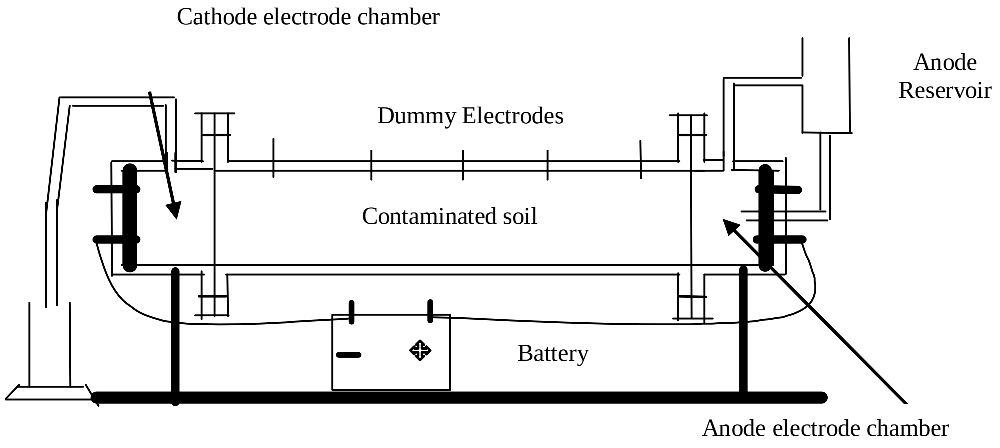


Fig. 3: Schematic diagram of electrokinetic test set-up

Experimental Programme

A total of four different experiments were conducted to evaluate the removal efficiency of desorbing agents. Three experiments were conducted when soil was saturated with deionised water and deionised water, AC and SC as desorbing agents, used as purging solutions in the anode compartment. One experiment was conducted when the soil was saturated (washed) with AC and as the purging solution also AC was used. The deionized water was used in all tests as catholyte. The experimental program and parameters used in each test are summarized in Table 2. For each electrokinetic test, approximately 1800g of dry soil were saturated (washed) with 720mL of water or AC solution and mixed thoroughly by hand in order to achieve homogeneity. Afterwards, the soil sample was tamped into the cell so that the amount of void space was minimized and desired density was achieved. A constant DC electric potential was then applied across the specimen in all the experiments for a treatment time of 5days. The loss of liquid due to evaporation or the electrolysis reactions was compensated by addition of desorbing agent in the anode compartment by creating constant external hydraulic gradient of 0.3 across the cell.

Table 2: Basic information of experiments

Test	Amount of Cd^{++} (mg/kg)	Soil Saturation	Anolyte
EKCdD	10,044	DI water	DI water
EKCdSC	10,044	DI water	SC(1M) (8.6 pH)
EKCdAC	10,044	DI water	AC (1M) (10 pH)
EKCdAA	10,044	A.C. (1M) (5 pH)	AC (1M) (10 pH)

EKCdD: Electrokinetic remediation of cadmium contaminated soil using Deionized water
EKCdSC: Electrokinetic remediation of cadmium contaminated soil using sodium citrate
EKCdAC: Electrokinetic remediation of cadmium contaminated soil using AC
EKCdAA: Electrokinetic remediation of cadmium contaminated soil saturated with AC and it used as flushing agent

A number of physicochemical parameters like overall current along the soil cell and electrode compartments, pH variations of catholyte and anolyte solutions, soil pH variations and electroosmotic flow were measured at regular time intervals during the experiment. At the end of the experiments the soil was sectioned into 6 slices from anode to cathode and the length of slices at anode to section 1 and cathode to section 5 was 15mm thick. The middle slices lengths were 80mm thick. Each slice was mixed thoroughly then dried and crushed by hand before post EK analysis.

RESULTS

Fig. 4 and Fig. 5 show the electric current and electroosmotic flow across the soil column with time in different experiments. The distribution of moisture is shown in Fig. 6. Fig. 7 and 8 present the cadmium concentration variations along the normalized distance from anode and soluble form of cadmium after EK process. pH variations are presented in Fig. 9. Fig. 10 and Fig. 11 show the observations of XRD data related to various EK experiments. Scanning Electron Microscope (SEM) images of EK treated soil are presented in Figs. 12-17.

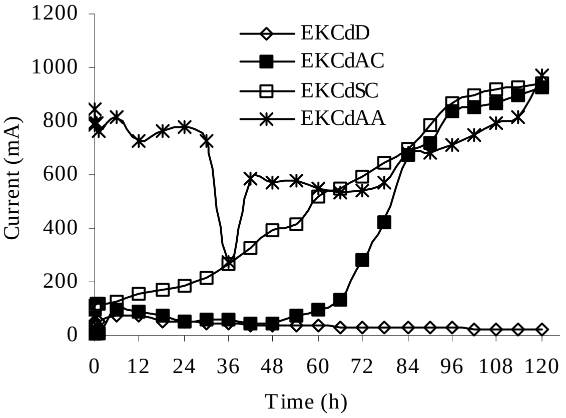


Fig. 4: Current flow with time during EK process

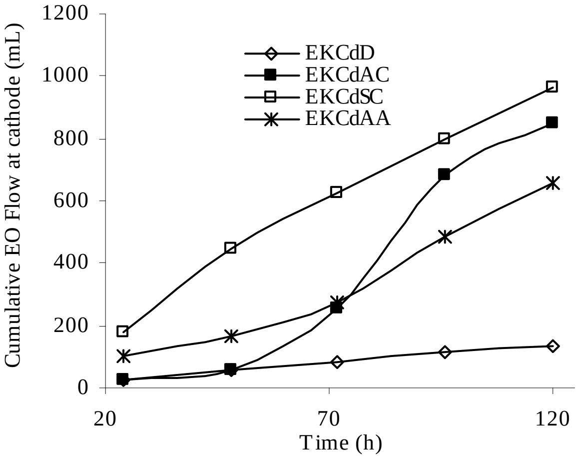


Fig. 5: Cumulative Electroosmotic flow measured during electrokinetic remediation

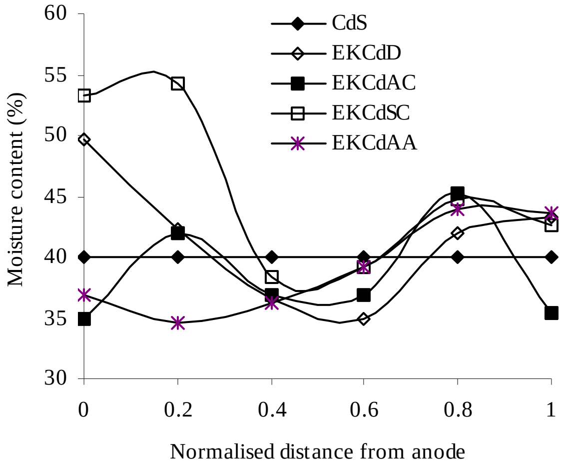


Fig. 6: Variation of moisture content after EK process

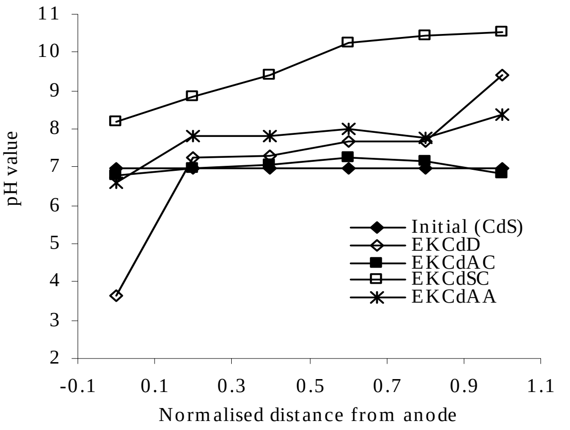


Fig. 9: Variation of Soil pH with distance after treatment

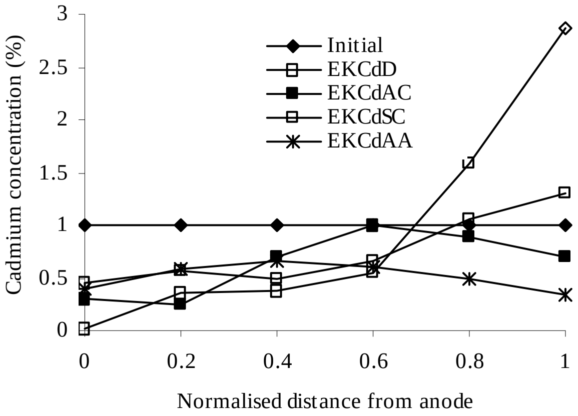


Fig. 7: Distribution of residual cadmium concentration in soil

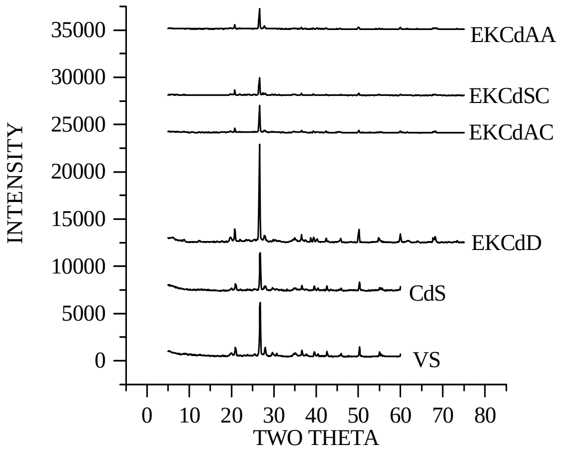


Fig. 10: XRD of the virgin, contaminated and treated soils from anode section

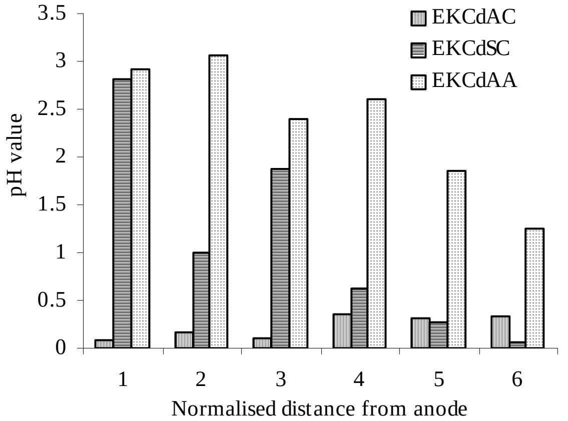


Fig. 8: Soluble concentration of cadmium after contacting with 7 pH deionised water

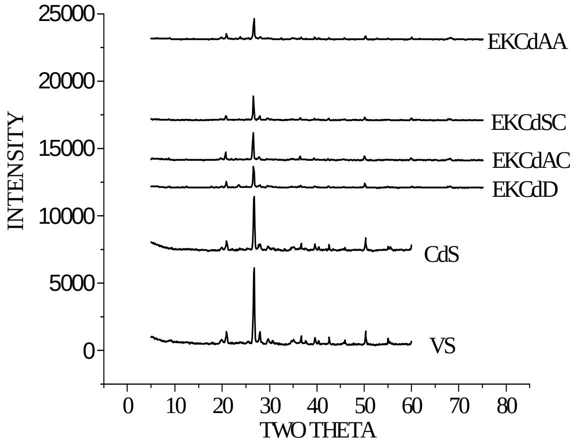


Fig. 11: XRD of the virgin, contaminated and treated soils from cathode section

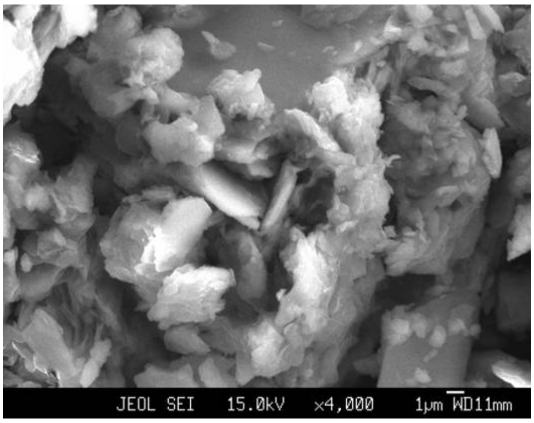


Fig. 12: SEM image of near anode soil of EKCdSC

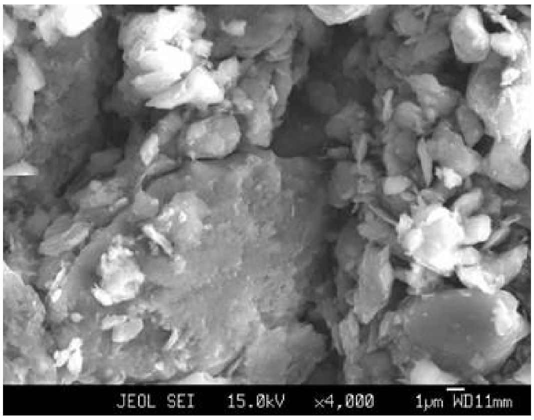


Fig. 13: SEM image of near cathode soil of EKCdSC

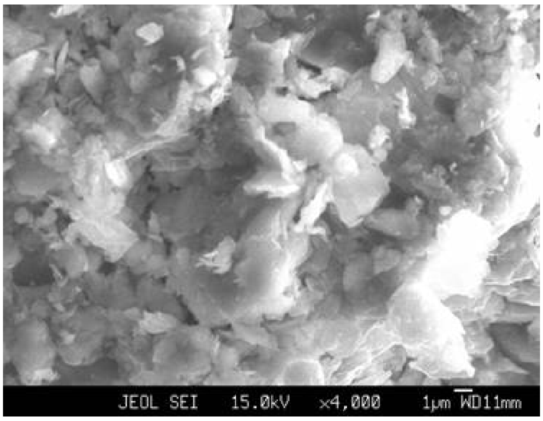


Fig. 14: SEM image of near anode soil of EKCdAC

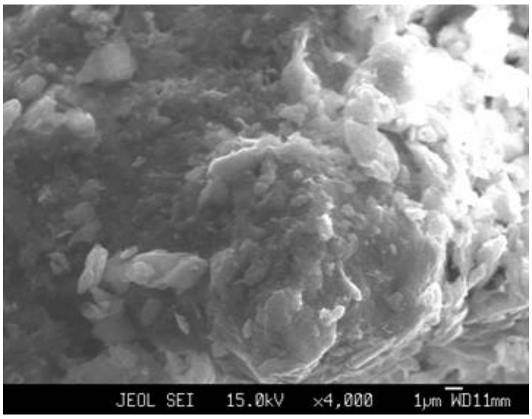


Fig. 15: SEM image of near cathode soil of EKCdAC

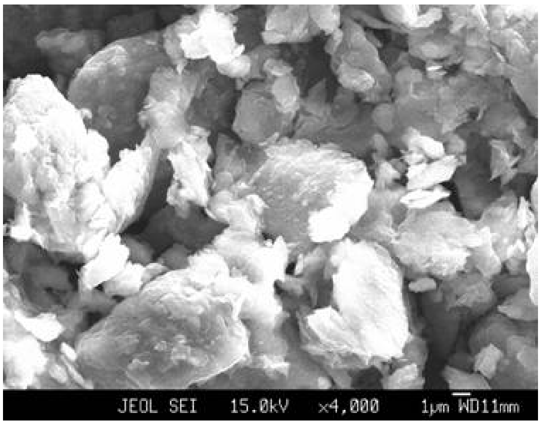


Fig. 16: SEM image of near anode soil of EKCdAA

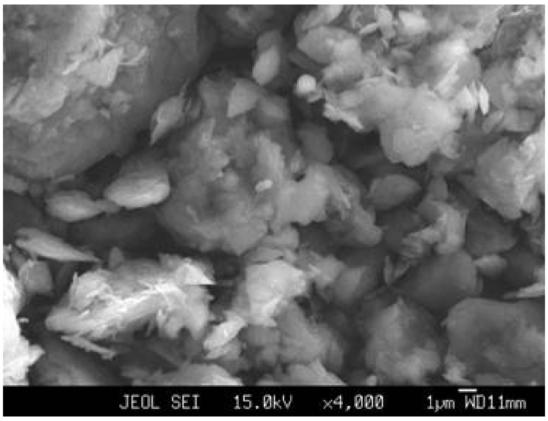


Fig. 17: SEM image of near anode soil of EKCdAA

DISCUSSION

According to Fig. 4 the electric current in EKCdD (no pH control) was relatively low. When AC was used as purging solution (EKCdAC), the current flow initially increased and remained constant up to 60-70 and hours afterwards it increased to a high value with treatment time. In EKCdAA, initial current flow started with high value and after 36 h of test run, it suddenly dropped down due to crack formation at the section 2 and after few hours it rose again. The initial high current value is largely a reflection of the amount of sorbed or associated ions in the soil, or of the amount of mineral dissolution that occurred in the experiment EKCdAA. However, the current in EKCdSC increased to a high value with treatment time, the reason might be the high percentage of Na^+ throughout the soil which is observed by XRF analysis. As a result the cumulative electroosmotic flow observed is highest among all other test runs. From the Fig. 5, the Electro osmotic (EO) permeability, k_e (cm^2/V-s) was calculated using the equation (1).

$$K_e = Q_e/(i_e.A)., \qquad (1)$$

Where:
Q_e=EO flow (mL/d);
i_e=Electric gradient (V/cm);
A=Cross-sectional area of soil cell (cm^2).

The EO permeability values of EKCdD, EKCdSC, EKCdAC and EKCdAA are 1.039×10^{-5}, 7.99×10^{-5}, 6.73×10^{-5}, $5.17\times10^{-5} cm^2$/V-sec. respectively. The sequence of the EO flow in all tests was EKCdSC>EKCdAC>EKCdAA>EKCdD.

From Fig. 6 it is observed that the low moisture regions are seen in the normalized section between 0.2 to 0.6 (middle of the soil column). The reason might be the drag of fluid in the region to both anode and cathode. In all experiments the moisture content was observed higher than the initial moisture content towards cathode region. The reason could be that due to high pH, cadmium ions sorbed or formed precipitates, such as hydroxides which block the soil pores.

Distribution of cadmium concentrations in the soil with respect to their pH variation are shown in Fig. 7. In all tests, results show transport of cadmium to the cathode region. But in case of EKCdSC, EKCdAC and EKCdAA the transport of the cadmium as anionic complex is confirmed by the examination of residual cadmium concentration profiles towards anode region. It was also confirmed from the Fig. 8, representing the soluble form of cadmium after EK tests. The residual cadmium concentrations were increased significantly in EKCdD and it appeared much high than the initial concentration towards cathode. There is decrease of cadmium in the areas near the anode due to low pH values, but a significant increase at the section 5 and 6 of soil column due to increase in pH. Under these experimental conditions, removal efficiency for EKCdD, EKCdSC, EKCdAC and EKCdAA, 4.15%, 24.7%, 36.3% and 48.9% respectively.

The mineralogical changes occuring during EK process have been studied by XRD. It is understood that acidic and basic conditions destroyed the soil minerals moderately as shown in Fig. 10 and Fig. 11. The SEM images (Fig. 12-17) indicate that minor changes occur in soil morphological structures. Observations from Figs. 10, 11, 16 and 17 of XRD and SEM of EKCdAA indicate that there was slightly higher amount of major oxides were leached out during EK process and it caused the high removal of cadmium also. Ricart *et al*., (2001) studies on removal of multiple species from a sludge by electromigration have identified the large removal of major oxides Fe (23%), Ca (22%), Mg (31%), Na (3.5%), Mn (70%) and Zn (68%) from sludge sample. Ricart *et al*., (2004) reported that elements such as Al, Si, K, Ti, and Zr that are forming the crystalline structure of different minerals, showed no migration, since minerals did not suffer any alteration in the acidic environment of experiment when pH of the soil was adjusted below 2 but dissolution of Fe and Ca was observed which ultimately made much more removal of Mn. EDTA was shown to extract large amounts of soil minerals such as Ca, Mg, and Fe (Wasay *et al*., 1998). Cline and Reed (1995) noted that soil contaminated by heavy metals is effectively leached by EDTA or HCl but that these may destroy the soil structure. In the present study an effort has been made for remediation of soil contaminated with cadmium using electrokinetic process by chelating agents. Between AC (1M) and SC (1M) AC has emerged as best chelating agent to extract the cadmium.

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