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LABORATORY SCALE ELECTROKINETIC REMEDIATION OF HEXAVALENT CHROMIUM FROM CONTAMINATED SOIL

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Pakistan hosts a variety of waste soils around industrial sites located in and around large population centers. Clean up of these waste soils is essential to save potable groundwater reserves beneath these waste soils. Among several waste remediation approaches, the electrokinetic remediation (EKR) technology has fast emerged as a reliable, powerful and highly prominent candidate for effective in situ removal of soluble and leachable toxic species of metals, radionuclides, organics from contaminated soils and water environment. This paper presents results of the first laboratory trial experiment performed at PINSTECH, Islamabad, Pakistan to demonstrate applicability of EKR approach for removal of aqueous phase chromium from silty clay soil around Islamabad. The electroosmotic flow rate was 3.13 ml/hour while the mass balance calculations revealed that the removal efficiency of Cr(VI) was 44.58% for the experimental soil.

Keywords: Waste soils, Electrokinetic soil cell, Chromium remediation, Electrokinetic remediation

1. Introduction

Pakistan hosts a variety of waste soils around industrial sites located in and around large population centers. Some of these waste soils contain chromium both in aqueous form and adsorbed form (depending upon type of soil). Such a contamination is caused by industries like leather tanneries, electroplating industries, dyes and pigments manufacturing industries, textile industries, power generation industries, etc., that discharge untreated industrial sewage containing chromium and many other toxic metals into unlined drains and ponds around these industrial sites. Chromium compounds, in either the Cr (III) or Cr (VI) states are used in manufacturing of dyes and pigments, power generation, leather and wood preservation, electroplating, petroleum refining and petrochemicals, plastic materials and synthetic organic chemicals, etc. [10]. Cr (VI) is used in many industrial processes like ore refining, cement production, leather tanneries, catalytic converters, making of steel and other alloys, etc.

Cr(VI) was selected for the present investigation as it is more toxic and carcinogenic and that a limited work has been reported on in-situ electrokinetic remediation of Cr(VI) in waste soils. Cr(VI) also causes ulcers, skin rashes, respiratory problems, kidneys and liver damages. As such, presence of chromium in waste soils poses serious threat to both soil and groundwater environment. Accordingly, clean up of these waste soils is essential to save potable groundwater reserves beneath these waste soils.

Among several waste remediation approaches, the electrokinetic remediation (EKR) technology has fast emerged as a reliable, powerful and highly prominent candidate for effective in situ removal of soluble and leachable toxic species of metals, radionuclides, organics from contaminated soils and water environment [1-13]. This paper presents results of the first laboratory trial experiment performed at the Ecological Research Laboratories of the Pakistan Institute of Nuclear Science and Technology (PINSTECH), Islamabad to demonstrate applicability of the EKR approach for removal of aqueous/adsorbed phase chromium from silty clay soils susceptible to contamination with this element. The main objectives of the study are to: (a) streamline operational procedures on use of e*lectrokinetic soil cell* for cost effective removal of Cr(VI) from site specific soil samples in

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laboratory scale experiments; (b) examine electrical response of the soil cell during the course of electrokinetic remediation of Cr(VI) under the influence of applied voltage from selected soils; (c) and determine remedial efficiency of Cr(VI).

2. Field and Laboratory Methods

Various field and laboratory experimental procedures used in the present study include the following:

a. Field collection of bulk soil sample;

b. Mineralogical, geotechnical (plastic/liquid limit), physico-chemical analysis of site specific soil sample;

c. Design and fabrication of electrokinetic soil cell, peristaltic pumps for purging of electrolytes, electrolyte storage reservoirs, DC Power supply;

d. Conduct of electrokinetic remediation experiments involving: (i) measurement of voltage/current across main electrodes (i.e. anode and cathode), interspacing electrodes in the soil compartment, and platinum reference electrodes placed at the junction of membrane and soil; (ii) electroosmotic flow rate;

e. Analysis of Chromium in the soil sample and anolyte solution.

Details of these procedures are as following:

2.1. Soil sampling

The electrokinetic remediation technique is a site specific remediation technique. In the present investigations, soil sample was collected from a small village located in the North of federal capital, Islamabad at the periphery of village Nilore adjacent to Pakistan's largest nuclear research facilities namely Pakistan Institute of Nuclear Science & Technology (PINSTECH). The area represents silty clay soils. Virgin topsoil sample was taken by removing the soil A, B, C horizons.

2.2. Soil mineralogical, geotechnical and physicochemical analysis

Soil mineralogical XRD analysis was done in the X-Ray Diffraction Laboratory of Materials Research Group, Material Division, PINSTECH. Site specific soil samples were cleaned, crushed and pulverized in an inert atmosphere to avoid oxidation. X-ray diffraction patterns were recorded using the computer controlled powder diffractometer, model DMAX IIIC of M/S Rigaku Corporation, Japan. Cuka radiation (λ = 1.5418), monochromatized by a graphite crystal placed in the diffracted beam, was used. Intensities were recorded at 0.02^0 using NaI (sodium iodide) detector. Indexing and refinement of unit cell parameters were accomplished using the computer program ITO (1967) and PDP 11 (1990). Identification of mineral phases was done using the JCPDS files. Standard geotechnical parameters of importance in electrokinetic remediation experimentation were determined. These included measurements of Atterberg Limits (*Liquid Limit, Plastic Limit*, *Plastic Index)*, and standard physico-chemical parameters such as pH, moisture content , buffering capacity , density , porosity, specific gravity, organic content , electrical conductivity and toxic metal analysis. Details of these procedures are given elsewhere [14]. Metal analysis of soil was performed using ICP-EOS (ICP Lab/ Central Analytical Facility Division-PINSTECH) and UV-VIS Spectrophotometer (Model SPECORD® PC 205).

2.3 Fabrication of electrokinetic soil cell

To conduct viable electrokinetic remediation experiment, a typical electrokinetic soil cell (EK soil cell) of rectangular geometry was designed and fabricated from a 1 cm thick acrylic sheet (Fig. 1). As such, the experimental apparatus consisted of five essential components: (a) the soil cell compartment (inner dimensions: 10 x 10 x 10 cm^3) sandwiched between two electrode/electrolyte compartments (each with inner dimensions: 3.5 x 10 x 10 cm^3); (b) two Pyrex glass electrolyte solution reservoirs (700 mL) to measure the water volume transported; (c) the DC power supply (100 V and 2 Amps.); (d) peristaltic pumps (fabricated locally by using a car wiper motor) to re-circulate electrolyte in both electrode compartments; and (e) a multimeter arrangement to measure the electrode potential and current distribution. Milliampere meters (ranging 0-999.9 mA) were designed and fabricated locally. Each end of the soil compartment was blocked with a 1mm thick acrylic plate containing 36 holes (each with dia=1cm) to enhance uniform electroosmotic flow. Platinum wire (dia=0.1 mm) was plated like a net (mesh size: 1 cm^2) around this plate to catalyze the electrokinetic process and to measure the overall voltage drop of the soil cell and electrode/

electrolyte compartments (volume ~ 350 mL each). Behind this thin acrylic plate, two sheets of Glass Fiber Filter Paper (GF/B type) were inserted to prevent soil particles from flowing into the electrode compartments. Titanium plates (size: 9.2 x 9.4 cm^2 and thickness 2mm) were used as anode and cathode in electrolyte compartments.

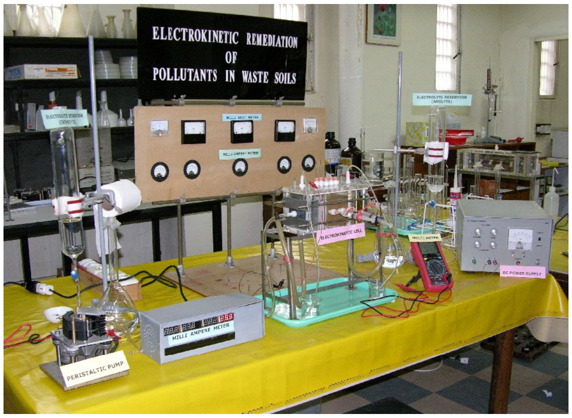

Figure 1. Laboratory setup for electrokinetic remediation of Cr in waste soils.

The electrode compartments were designed to hold upto 350 mL of electrolyte solution to ensure presence of sufficient volume of electrolyte. Holes were drilled in the cover plates of the reservoirs compartments to safely reject H_2 (g) and/or O_2 (g) produced as a result of electrolysis at the electrodes. A stainless steel sampler (dia=1.2 cm) was fabricated locally to extract soil core samples from the bottom holes (located at ~1.5 cm interval) at the end of the experiment to analyze the concentrations of contaminants and soil pH. Similarly, provision of 3 - 5 holes was kept (at 3.5 cm spacing) on both sides of the soil cell to drain experimental solution. Five holes (at 1.5 cm spacing) were drilled in the top plate to insert and hold interspacing electrodes made of tungsten wires (length=15cm, dia=1mm) into the soil bed to measure the voltage gradient in the soil cell.

2.4 Electrokinetic waste remediation steps

2.4.1. Spiking of test soil with chromium

Before electrokinetic remediation experiment, test soil sample was artificially contaminated with Cr by dissolving 0.75g Cr(VI) as $K_2Cr_2O_7$ in 750 ml deionized water and then adding it to 1.5 kg soil contained in a plastic tub. The solution and soil was thoroughly mixed by constant stirring with a glass rod to get a soil/liquid homogenized mixture. The soil thus contained 176.7505 µg/g of Cr in addition to 28.15 µg/g parent Cr in the soil (ref. Table 2).

2.4.2. Loading of chromium contaminated soil in the soil compartment

About 1.2 kg of Chromium spiked homogenized soil/liquid mixture was loaded into the test cell gradually. The cell was vibrated on the shaking table to remove the trapped air. Upon filling, a vacuum was drawn on the cell with a vacuum pump for ~ 5-min interval to degas the mixture. After the vacuum was released, the cell was tapped on the floor to further consolidate the soil. The process of drawing a vacuum and tapping the test cell was repeated until nearly all of the air bubbles in the soil bed got removed.

2.4.3. Electro-remediation procedure

After the soil compartment of the electrokinetic soil cell was loaded with Cr(VI) contaminated soil, suitable electrolytes were added into both electrolyte compartments. In the present trial experiment, 0.05 M H_2SO_4 was added into the anolyte compartment, while 0.5 M H_2SO_4 was added into the catholyte compartment. In order to ensure, ionic transport solely due to electrokinetic mechanism, a zero hydraulic head was maintained across the soil cell. This was facilitated by an overflow mechanism arrangement made in the anolyte and catholyte compartments and attachments of auxiliary electrolyte reservoirs with these compartments. The electrolyte reservoirs were attached with the respective compartments with Tygon tubing to maintain solution level in both reservoirs. Throughout the course of electrokinetic experiment, reservoir electrolytes were recirculated to maintain homogeneity of electrolytes in the compartments. A constant voltage of 15 V DC (equivalent to1.5 V cm^{-1}) was applied across the Cr contaminated soil bed. The experiment was conducted for a period of 24 hours. At the end of the electrokinetic treatment, one sample each of electrolyte solutions from anolyte and catholyte reservoirs and three samples of test soil were obtained from the soil bed for measurement of residual concentrations of Cr(VI) in the soil.

2.4.4. Analysis of hexavalent chromium

The test soil samples were subjected to Cr(VI) analysis before and after the trial experiment to evaluate efficiency of the electrokinetic treatment

Table 1. Mineralogical, geotechnical and physiochemical characteristics of experimental soil.

XRD Mineralogical Phase Analysis	Value (% in bulk soil sample)
Quartz	53%
Muscovite	9%
Albite	6%
Calcite	12%
Kaolinite	4%
Montmorilonite	14%
Atterberg Limits	Value
Liquid Limit	*31.0 (%)*
Plastic Limit	*15.35 (%)*
Plastic Index	*15.65*
Physiochemical Characteristics	Value
pH	7.91 (%)
Moisture Content	2.83 (%)
Buffering Capacity	0.09 (mM/g)
Density	1.14 (g/cm^3)
Porosity	54.1 (%)
Specific Gravity	2.52
Organic Content	0.22 (%)
Electrical Conductivity	56.8 (µS/cm)

Table 2: Metal analysis of experimental soil (Islamabad Soil). Concentration are in µg/g.

Na	K	Mn	Zn	V	Ni	Cr	Pb	Cu	Co	Fe	Cd
1178.94	3026.72	2033.91	26.73	22.70	8.21	28.15	3.15	1.30	0.76	170	ND*

ND* = Not Detected

process. About 15 gram of test soil samples were extracted before the conduct of trial experiment. Similarly, after the electrokinetic remediation experiment, ~15 gram soil sample was extruded from the soil cell each from anode side and the cathode side. Each soil sample was acid digested (U.S.EPA Method 3050) and analyzed for Cr(VI) by UV-VIS Spectrophotometry.

3. Results and Discussion

3.1. Soil analysis

Table 1 presents results of typical soil analysis (XRD based mineralogical phases analysis, Atterberg Limits, physiochemical parameters). The analysis clearly shows that the test soil represents silty clay soil. The clayey fraction mainly consists of Montmorilonite (14%) and Muscovite (9%) contents. Thus, the clay present in the test soil is partially swelling type clay. It also hosts significant proportions of calcite which acts as a buffer during the process of remediation. Atterberg limits of test soils bear great importance in electrokinetic remediation experimentation, because these parameters govern conditions of soil during the experimental phase such as development of fractures, ruptures and swelling etc. which in turn affect the electroosmotic flow rates, changes in applied voltage and current distribution and contaminant transport efficiency. In the present study, the measured Atterberg limits of test soil are: liquid limit (31.0 %) and plastic limit (15.35 %), which are very similar to those quoted in literature for silty clay soils [15].

The ICP-EOS analysis of test soil is shown in Table 2. It appears that Na (1179 µg/g) and K (3026 µg/g) are the major alkaline earth elements present in the collected soil sample. Significant concentrations of Mn (2033 µg/g) are also present. Similarly, Pb (3.15 µg/g), Ni (8.21 µg/g), Cr (28.15 µg/g), V (~22.70 µg/g), and Zn (26.73 µg/g), are the major trace metal constituents in the soil sample. Co is found at concentrations less than 1 µg/g while Cu is found at concentrations less than 1.3 µg/g. No Cd was detected in the soil sample.

The silty clay soil used in the present investigations hosts an indigenous Cr concentration of about 28.15 µg/g. However, the mineral phase in which chromium is present remains to be identified by XRD technique. Nevertheless, an effort was made to demonstrate the level of Cr absorbed in the test soil matrix. For this purpose, a well homogenized portion of the experimental soil sample artificially contaminated with $K_2Cr_2O_7$ solution in the plastic tub was extruded and given successive washings with de-ionized water followed by centrifugation. This cleaned soil sample was then shaken in acidified water to leach the adsorbed Cr. It was found that the adsorbed concentrations was of the order of 8 µg/g. There is also some concern about secondary reactions due to presence of significant amounts of Fe, Mn, Na and Mg. For example, Cr(VI) is readily reduced in the presence of Fe while Cr(III) is readily oxidized in the presence of Mn.

3.2. *Electrokinetic removal of hexavalent chromium*

Table 3 shows the variations of pH and electrical conductivity of the fluid in cathode compartment (catholyte) and the anode compartment (anolyte) respectively during the EK treatment process. The catholyte pH decreased from 0.89 to 0.64, which may be due to huge migration of H^+ from anode. The electrical conductivity of the catholyte also decreased from 115 to 72.1 mS/cm with the course of experiment. The pH at the anolyte (0.05 M H_2SO_4) increased from 1.24 to 1.59 with a corresponding increase in the electrical conductivity of the anolyte from 11.9 to 30.6 mS/cm with the course of experiment.

Table 3: Changes in pH and electrical conductivity of anolyte and catholyte solutions before and after experiment

Parameters	Anolyte (0.05 M H_2SO_4)		Catholyte (0.5 M H_2SO_4)	
	Before Expt.	After Expt.	Before Expt.	After Expt.
pH	1.24	1.59	0.89	0.64
Electrical Conductivity (mS/cm)	11.9	30.6	115	72.1

3.3. *Relationship between applied voltage and cell current*

Fig. 2 shows changes in the applied voltage and cell current with the course of time of electroremediation. A drop of 0.06 V in applied voltage at about 2.5 hours after start of experiment was caused due to restart of the experiment on account of replacement of burnt fuse of DC power supply. The applied constant voltage did not vary by more than 0.12V DC and remained within the range of 15 -14.88 Volts throughout the course of experiment. This indicates a good control on the experimental performance conditions. However, current across the soil cell was very low (~ 11 mA) at the start of the experiment because of the low conductivity of the soil. However, it gradually increased to a relatively stable value of 24 mA within a period of 12 hours and remained consistent upto a value of 25 mA during the remaining 12 hours of the experiment. In general, the measured electric current should be proportional to the dissolved species in the porous medium (test soil). The measured current increased initially as the dissolved metal species (and other ions) and desorbed metal contaminants came into the solution phase and migrated/ transported through the soil in response to electroosmosis and electromigration. Thereby, the conductivity of the soil cell started increasing and the cell current also increased. The consistency of voltage and current shows that at low pH of the soil matrix, the migration of the contaminant species in the soil cell continued throughout the course of electroremediation experiment.

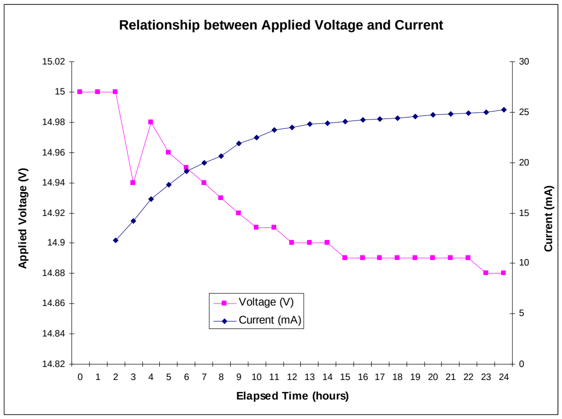

Figure 2 Distribution of applied voltage and cell current with time

Table 4. Mass Balance Calculations for Cr (VI) Remediation Experiment.

Mass Fractions of Soil and Electrolytes	Cr(VI) Concentration (µg/g)	Removal Efficiency (%)
(a) Cr removed from the soil	91.3433	44.58%
(b) Cr remained in the soil	73.6055	
(c) Total: (a) + (b)	164.9488	
(d) Initial total mass of Cr in experimental soil (parent Cr+ spiked Cr).	28.15+ 176.7505= 204.9005	

3.4. *Electrokinetic remediation efficiency*

The electrokinetic remediation efficiency was determined through mass balance calculation as shown in Table 4. The % removal efficiency was calculated as following:

% removal efficiency =

(Conc. of Cr in electrolyte / initial conc. of Cr in solid) X 100

= (91.3433/204.9005) X 100

= 44.58%

4. Conclusions

Experimental procedures for remediation of Cr(VI) in silty clay soils have been streamlined. A moderate electroosmotic flow rate of 3.13 ml/hour was measured at the exit of catholyte overflow port. A recovery of 44.58 % Cr(VI) was established through mass balance calculations during a period of 24 hours of electroremediation.

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