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# STEP TOWARDS IN-SITU ELECTROKINETIC REMEDIATION OF CONTAMINATED SOILS IN PAKISTAN

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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 soil and water environment. Many developing countries are now employing this technology with great success for on-site decontamination of waste soils. Nevertheless, in Pakistan, such a technology has never been developed for *in-situ* remediation of toxic species in waste soils. This paper presents a brief account of our initial efforts made at PINSTECH, Islamabad regarding development and operation of electrokinetic cell for lab-scale remediation of toxic metals (also organic pollutants and radio-metals) and EKR related specific analysis of soil samples collected from three target sites (Korangi Industrial Zone-Karachi, Kala Shah Kaku-G.T. Road, and near Village Nilore, Islamabad).

**Keywords:** Waste soils, Electrokinetic remediation, Electrokinetic cell, Physiochemical analysis

## 1. Introduction

With the recent advancements in science and technology, and its wide use in industry, agriculture, health, energy production and defense, it is estimated that millions of tones of hazardous wastes are also being produced annually in the world. In developed countries, due to effectiveness of environmental protection agencies (EPAs) and related regulations, such wastes are properly sorted and treated before disposal onto land, into pits and water courses. Nevertheless, in many developing countries and especially, in the underdeveloped world, such wastes are mostly disposed untreated. Accordingly, in these countries, the disposal of hazardous materials has become a big challenge not only for the municipalities but also for the scientists and the community.

Pakistan is a rapidly developing sixth populous country of the world mainly depending on agriculture and partly on industries. In-spite of presence of Pak-EPA and Pakistan Environmental Protection Law, the repeated incidences of disposal of untreated industrial and domestic wastes directly onto land and into pits and water courses is severely polluting the soil and water environment in this country. Therefore, there is an urgent need to address this menace in terms of identification of contaminated waste sites and related pollutants and application of site specific waste remediation technique(s) to clean the affected soil and water environment.

To-date, many waste remediation techniques like soil washing, thermal enhancement, bioventing, phytoremediation, air sparging, permeable reactive barriers, electrokinetics, vitrification and stabilization have been developed for laboratory and field scale applications [1, 2]. Among these, the electrokinetic remediation has proved to be an excellent, trustworthy and cost effective technique for remediation of pollutants specially, in soils polluted with non-radioactive and radioactive metal species, as well as inorganic or organic chemical species [3 - 6]. In the recent past, this technique has received high priority for soil & water remediation. The electrokinetic phenomena was first observed at the beginning of the 19th century [7]. Later, similar but rather advanced electrokinetic studies were performed by a few researchers [8, 9]. To date, a lot of work on EKR has been done by various researchers [10-19]. In

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Pakistan, such an attempt has not been made in the past. Nevertheless, under the Higher Education Commission (HEC) Indigenous Doctoral Program, laboratory scale studies on electrokinetic remediation of artificially contaminated soils have been initiated at Geochemistry Laboratory of the Isotope Application Division-PINSTECH, Islamabad. The main objective of this study is to develop and apply electrokinetic remediation (EKR) technology for site specific *in-situ* remediation of soils such as around tannery industry, electroplating industry, petrochemical industry, textile industry etc. in Pakistan. The following sections present an account of the first ever field and laboratory work accomplished by PINSTECH for laboratory scale electrokinetic remediation of waste soils.

## 2. Experimental Investigations and Discussions

### *2.1. Design and fabrication of experimental apparatus*

To conduct viable electrokinetic remediation experiments, a typical electrokinetic soil cell (EK soil cell) of rectangular geometry was designed and fabricated from a 1 cm thick acrylic sheet (Fig. 1a & 1b). As such, the experimental apparatus consists of five essential components: (a) the soil cell compartment (inner dimensions: 10x10x10 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) DC power supply (40 V and 2 Amps.) locally fabricated by the Equipment and Maintenance Division, PINSTECH; (d) peristaltic pumps (fabricated locally using a car wiper motor) to re-circulate electrolyte in both electrode compartments; and (e) a multi-meter arrangement to measure the electrode potential and current distribution across the cell. Milli-ampere meters (ranging 0-999.9 mA) were locally designed and fabricated at electronics workshop-IAD, PINSTECH. 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, 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. Five tungsten wires (length= 15 cm, dia= 1 mm) were inserted as inter-spacing electrodes placed at equal spacing into the soil container to measure the voltage gradient in the soil cell. The electrode compartments can hold upto 350 mL of electrolyte solution to ensure presence of sufficient volume of electrolyte in order to avoid sudden variations of the electrolyte solution. These compartments also have exits for safely rejection of gases produced by electrolysis at the electrode. 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

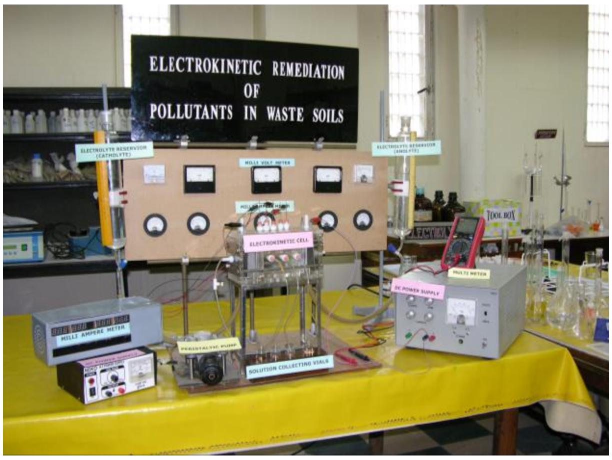

**Fig 1 (a)**

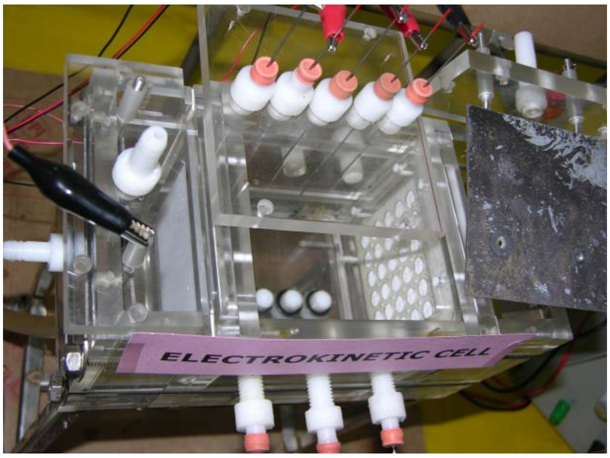

**Fig 1 (b)**

Figure 1(a). Electrokinetic soil cell setup at the Isotope Geochemistry Laboratory, IAD, PINSTECH, Islamabad.

1(b). A closer view of the inner soil compartment with GF/B filter paper attached to both ends, and side holes for collection of solution and top holes for installation of interspacing electrodes.

Table 1. XRD analysis of soil samples.

| Mineral Analysis by XRD | | |
|---|---|---|
| Karachi Soil | Islamabad Soil | Kala Shah Kaku Soil |
| Quartz (56%) | Quartz (53%) | Quartz (71%) |
| Muscovite (4%) | Muscovite (9%) | Muscovite (13%) |
| Albite (4%) | Albite (6%) | Albite (8%) |
| Calcite (29%) | Calcite (12%) | Thuringite (6%) |
| Thuringite (3%) | Kaolinite (4%) | |
| Cristobolite (2%) | Montmorilonite (14%) | |

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 and five holes (at 1.5 cm spacing) on the top plate to insert and hold interspacing electrodes.

### *2.2. Soil sampling and initial handling*

Possible virgin soil samples were collected in polythene bags from three different sites namely, Kala Shah Kaku [representing silty clay (muscovite) soils near Kala Shah Kaku Industrial Area facing both inorganic and organic pollutants], Karachi [representing sandy, calcite rich clayey (muscovite) soil located near Korangi Industrial Area-Karachi facing pollutants from tannery industry, electroplating industry, petrochemical industry, textile industry etc.], and Islamabad [representing silty clay (Montmorilonite) located off village Nilore, Islamabad facing mainly poultry wastes to some extent]. In the laboratory, bulk soils were air dried under cover and visible roots, shoots, shells, pebbles etc. were handpicked. Later, the soils were grinded, mixed, sieved (0.5mm mesh) and well homogenized, for subsequent physico-chemical, mineralogical and electrokinetic remediation experimentation.

### *2.3. Soil analysis*

### *2.3.1. Soil mineralogical analysis*

Soil mineralogical XRD analysis was performed in the X-Ray Diffraction Laboratory of Materials Research Group, Material Division, PINSTECH. The results for all the three soils are given in Table 1.

### *2.3.2. Soil physiochemical analysis*

Soil samples were subjected to a variety of standard physiochemical analysis of importance in electrokinetic remediation experimentation. Results are shown in Table 2.

***Moisture content:*** In electrokinetic remediation experiments, saturation of soil can alter the electroosmotic flow rate [20, 21], which in turn may influence the removal efficiency of heavy metals in the contaminated soil. Uneven moisture distributions and regions of consolidation may lead to negative pore pressures [4, 22] during electrokinetic remediation experiments (EKR). Heating effects of electric current can cause drying of soils during the EKR process [23]. This effect is likely to be more severe in unsaturated soils but occurs even in soils which are initially saturated. In the present study, moisture content of the soil samples was measured using standard procedures [24]. The measured values of moisture content are 15.66% (Korangi Karachi soil), 2.83% (Nilore, Islamabad soil), and 7.52% (Kala Shah Kaku soil) (Table 2).

***Liquid limit*:** Liquid limit (LL) of soil represents moisture content at which soil begins to behave as a liquid material and starts to flow. As electrolytes flow through the soil cell during electrokinetic process, it is important to know the values of liquid limit of the experimental soil for effective control during the process of electrokinetic remediation in order to avoid rupture of porous media and induction of hydraulic heterogeneity. Further, the value of liquid limit is required to calculate the plastic index. The liquid limit of the soil samples was measured with a locally fabricated *Casagrande Apparatus* (Figure 2a) using ASTM D-4318 Standard Method. The liquid limit thus calculated for the selected soils is 15% (for Karachi), 31% (for Islamabad) and 26% (for Kala Shah Kaku).

***Plastic limit and plastic index:*** The plastic limit (PL) is the water content at which a soil can no longer be deformed by rolling into 3.2 mm (1/8 in.) diameter threads without crumbling. Plastic limit was measured with a Plastic Limit Device

Table 2. Physiochemical characteristics of the soil samples.

| Parameter | Location | | |
|---|---|---|---|
| | Karachi | Islamabad | Kala Shah Kaku |
| Moisture Content (%) | 15.66 | 2.83 | 7.52 |
| Atterberg Limits | | | |
| *Liquid Limit (%)* | *15.0* | *31.0* | *26.0* |
| *Plastic Limit (%)* | --- | *15.35* | *16.12* |
| *Plastic Index* | --- | *15.65* | *9.88* |
| pH | 7.98 | 7.91 | 6.61 |
| Buffering capacity (mM/g) | 0.08 | 0.09 | 0.08 |
| Electrical Conductivity (µS/cm) | 66.7 | 56.8 | 54.5 |
| Organic Content (%) | 0.17 | 0.22 | 0.99 |
| Density (g/cm$^3$) | 1.44 | 1.14 | 1.41 |
| Percent Porosity (%) | 40.6 | 54.1 | 49.4 |
| Specific Gravity | 2.46 | 2.52 | 2.11 |

---* Not determined

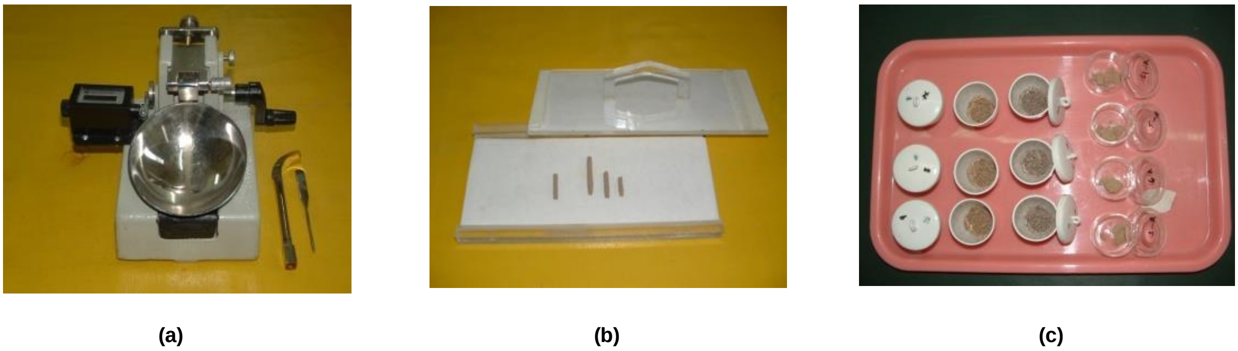

Figure 2:. Typical devices used in soil analysis

(Figure 2b) fabricated locally at PINSTECH Technical Workshop, following the test procedure used at Geotechnical Engineering Laboratory, University of Texas at Arlington. The soil gathered after rolling onto the device was kept in crucibles and weighed before and after drying in oven at 105ºC (Figure 2c). Plastic index (PI) = LL – PL, is the moisture content range at which the soil remains plastic. The values for plastic index of soil from Islamabad and Kala Shah Kaku is 15.65% and 9.88% respectively (Table 2). Plastic index (PI) value of Glacial Till soil is reported as 10% (close to the PI of Kala Shah Kaku soil sample) [16, 25, 26]. It was not possible to calculate the plastic index for Karachi soil as it was difficult to knead the soil due to its sandy nature as the soil crumbled at stage of rolling.

***Soil pH:*** In an electrokinetic soil cell, the change of pH of the pore fluid serves as an indicator to track the leading edge of the acid front during its migration from the anode to the cathode. During this migration, the pH of the soil cell tends to decrease, thereby showing an acid movement through the soil medium [24]. In the present study, soil solution was made in order to measure the pH of the soil with a portable pH Meter (Model 3070 ELE and Model PP – 201 K). Table 2 shows the measured pH values for the three test soils. As such, the measured pH is 7.98 (Karachi soil), 7.91 (Nilore-Islamabad soil) and 6.61 (Kala Shah Kaku soil). It appears that the soils collected from Korangi-Karachi area and Nilore, Islamabad area is mildly alkaline while the soil collected from Kala

Shah Kaku area is mildly acidic conditions. These factors may affect the initial rates of electromigration of target ions.

***Buffering capacity:*** The buffering capacity (BC) of a soil provides a measure of the resistance of the soil to a change in the pH due to a chemical reaction under the experimental condition. The generation of $H^+$ ions and their penetration through the soil matrix during the process of electrokinetic extraction of species is the first indication of ionic transport in an electrokinetic environment. This factor is quite important in electrokinetic remediation, as it provides a basis for the dissociation of metal ions from a specific soil. The higher the buffering capacity of test soil to acid treatment, the more difficult this dissociation becomes. In the present investigations, buffering capacity of the soil samples was measured using standard procedures [24]. The buffering capacity of the three target soil samples is ~0.08 mM/g (Table 2).

***Soil electrical conductivity*:** During an electrokinetic remediation process, the electrical conductivity (E.C.) of the pores water in soil bed within the electrokinetic cell gives an indication on how the current will pass through the soil. If the electrical conductivity is high, it means that there will be low resistance in the soil and the current will pass easily through the soil. In the present studies, electrical conductivity of the soil was measured in test soil slurry using a portable electrical conductivity meter. Table 2 shows the measured E.C. values for the three test soils. As such, the measured E.C. values are 66.7 µS/cm (Karachi soil), 56.8 µS/cm (Nilore-Islamabad soil) and 54.5 µS/cm (Kala Shah Kaku soil)

***Organic matter*:** The sorption distribution coefficient of soil depends upon the content of organic matter in the soil as the heavy metals tend to sorb onto the soil organic matter, which makes it difficult for the metal species to mobilize. In the present investigations, organic matter of the test soil samples was determined using the Walkeley Black procedures [2]. Table 2 shows the measured values of organic carbon in the three test soils, i.e., 0.165 % (Karachi soil), 0.22 % (Islamabad soil) and 0.99 % (Kala Shah Kaku). The value of Nilore, Islamabad soil is similar to that of the Paducah WKWMA clean soil (mixture of sandy clay loam), i.e., 0.2 % [27], however, value of organic content of near 0.00 % for Kaoline soil /loamy clay and 2.8 % for Glacial Till /silty clay have also been reported [28].

***Density and porosity:*** Bulk Density is the weight of a given volume of soil, which includes the pore spaces and porosity is the capacity of soil or rock to hold water. Density (at room temperature ~ 22 $^oC$) and porosity of the soil samples were measured by heating (105 $^oC$) and drying procedures. Table 2 shows the density of the three soils determined as ~1.4 g/cm$^3$ for both Karachi and Kala Shah Kaku soils, and 1.14 g/cm$^3$ for Nilore, Islamabad soil. The porosity of three soils ranges between ~ 40 – 54 % thereby indicating capacity of soils to hold high water contents. The lowest porosity corresponds to Karachi soil as this soil bears relatively lower clay content as compared to soils from Nilore and Kala Shah Kaku sites.

***Specific gravity:*** Specific gravity $G_s$ is defined as the ratio of the unit weight (or density) of soil solids to unit weight (or density) of pore water. Specific gravity of target soils was measured using a 500 mL volumetric flask with a stopper and Tygon tube (for attachment to vacuum pump or aspirator). Specific weights were measured as following:

weight of flask + DI water ($W_1$),

weight of soil + water + flask ($W_2$),

weight of soil after drying at $105^oC \pm 5$, ($W_s$),

weight of equal volume of water as the soil solids [$W_w = (W_1 + W_s) – W_2$]

Finally, the specific gravity ($G_s$) results were obtained using the following formula

$G_s (T_1{}^oC) = W_s/W_w$

Table 2 shows typical values of specific gravity of test soil samples**.** The values obtained for Islamabad soil is 2.52 which is close to specific gravity value of 2.63 documented in literature for loamy clay [28].

### *2.3.2. Metal analysis*

Metal analysis of the three soil samples was carried out at ICP Lab / Central Analytical Facility Division, PINSTECH (Table 3). The metal analysis shows that Na (1179-4682 µg/g), K (1343-4848 µg/g), Mn (877–2034 µg/g) are the major elements in the soil samples collected from the three target sites. Similarly, Pb (1.6-3.8 µg/g), Ni (4.4-8.6 µg/g), Cr (27-38 µg/g); V (~22 µg/g) and Zn (16-32 µg/g) are the major trace metal constituents in the soil of three target sites. Co is found at

Table 3. Metal analysis of soil samples.

| Metals (µg/g) | *Location* | | |
|---|---|---|---|
| | *Karachi* | *Islamabad* | *Kala Shah Kaku* |
| Na | 4682.70 | 1178.94 | 1454.86 |
| K | 1343.20 | 3026.72 | 4847.82 |
| Mn | 876.60 | 2033.91 | 1440.00 |
| Cr | 38.26 | 28.15 | 27.45 |
| V | 21.60 | 22.70 | 21.78 |
| Zn | 16.10 | 26.73 | 32.01 |
| Ni | 4.37 | 8.21 | 8.64 |
| Pb | 1.57 | 3.15 | 3.75 |
| Cu | 0.43 | 1.30 | 1.28 |
| Co | 0.38 | 0.76 | 0.79 |
| Cd | ND* | ND* | ND* |

ND* = Not detected

concentrations less than 1 µg/g while Cu is found at concentrations less than 1.3 µg/g at the target sites. No Cd was detected in soil sample collected from any target site.

## 3. Conclusions

The scenario of unplanned disposal of untreated domestic and industrial wastes onto land, in soil pits and into water courses in/around large population centers and industrialized zones in Pakistan over the past many years is quite alarming in view of adverse impacts on soils and related potable water quality and community health. This calls for urgent development of cost effective *on-site* soil and groundwater reclamation techniques in this country. The indigenous fabrication of electrokinetic soil cell and related accessories as well as physiochemical, mineralogical and metal analysis of soil samples collected from three target areas (Karachi, Kala Shah Kaku and Islamabad) in Pakistan for laboratory scale electrokinetic remediation experiments at IAD, PINSTECH will pave the way for application of this technology for field scale remediation of polluted soils. At present, laboratory scale electrokinetic remediation of soil artificially contaminated with Cr is in progress to evaluate kinetic parameters and remediation efficiencies for Cr ions. As such, the present studies will play a vital role in the development and application of electrokinetic technique for on-site remediation of contaminated soils in Pakistan.

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