



ChemTech

## International Journal of ChemTech Research

CODEN (USA): IJCRGG ISSN: 0974-4290  
Vol.8, No.5, pp 192-202, 2015

National conference on Nanomaterials for Environmental [NCNER-2015]  
19th & 20th of March 2015

### Removal of heavy metal ions from soil by electrokinetic assisted phytoremediation method

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**Abstract :** The focus of the present research work is on the monitoring of heavy metal pollution in water and soils of Ranipet, Tamil nadu India. The physico-chemical characteristics and heavy metals like Chromium and Cadmium were analysed for two polluted water and soil samples collected from Bharathi nagar (I) and Tandalam (II) villages of Ranipet surroundings. The soil sample of Tandalam was chosen for the remediation studies, due to its high levels of pollution. Electrokinetic remediation of Tandalam soil was carried at 50 V. The electrokinetic cell was sectioned into four compartments and analysed for the concentrations of Chromium and Cadmium. After electrokinetic remediation, the heavy metal contaminants get concentrated in different sections according to their charges and the soil in the four compartments of the electrokinetic cell was subjected to phytoremediation with Indian mustard (*Brassica juncea*) seeds. The efficiency of *Brassica juncea* was proved in remediating the heavy metals Chromium and Cadmium from the polluted soils.

**Key words:** Electrokinetic remediation, heavy metals, chromium, cadmium, phytoremediation.

#### 1 Introduction

Over the past years, numbers of sites are contaminated by heavy metals, and the pollution level of heavy metals is steadily increasing. Compared to organic pollutant, heavy metal is persistent in soil, and cannot be degraded by organism, which represents a serious threat to human beings and the environment [1]. Heavy metal contamination of soils is due to industrial activities and agricultural development can usually cause environmental problems. Elevated levels of heavy metals not only decrease soil microbial activity and crop production but also threaten human health through the food chain [2]. Hexavalent chromium is more readily absorbed by human body than trivalent chromium, regardless of the route of exposure. Extensive use of hexavalent chromium in various industrial applications has caused substantial environmental contamination.

Higher levels of cadmium may be found in soil or water near industrial area or hazardous waste sites. Soils near roads may contain high levels of cadmium from car exhaust. Surface water also contains low levels of dissolved cadmium in water which tends to sink and accumulate in bottom sediments. The form of cadmium encountered depends on solution and soil chemistry as well as treatment of the waste prior to disposal. The most common forms of cadmium include  $Cd^{2+}$ , cadmium-cyanide complexes, or  $Cd(OH)_2$  solid sludge [3].

Hydroxide and carbonate solids dominate at high pH whereas  $\text{Cd}^{2+}$  and aqueous sulphate species are the dominant forms of cadmium at lower pH (<8). Each fraction of the metals has specific interaction with the soil and pose different bioavailability strategies.

Electrokinetic (EK) remediation is a technology that was introduced for soil and groundwater remediation around 1980s. The technology applies direct-current (DC) electric field in soil to generate a voltage gradient that drives soluble pollutants out of soil by electromigration, electroosmosis and/or electrophoresis [4,5]. Phytoremediation is a developing innovative technique for heavy metal contaminated soil in recent years. The main advantage of phytoremediation is low expense and can be used for in situ application in large scales. There were few plants which could accumulate multiple heavy metals [6]. For phytoextraction to occur contaminants must be bioavailable (ready to be absorbed by roots). Bioavailability depends on metal solubility in soil pollution. Only metals present in soluble and exchangeable forms are readily available for plant uptake. So the study of EK-assisted phytoremediation process will be helpful for developing new combined remediation techniques. The objectives of this study were: (1) to study the change of soil heavy metal bioavailability during the electrokinetic-assisted phytoremediation; and (2) to investigate the processes of the combined technology on the heavy metal uptake by plant.

## 2 Materials and Methods

### 2.1 Sample collection

Water samples were collected from the lakes of Bharathi Nagar and Tandalam villages of Ranipet industrial town. Sub soil samples upto 15 - 30cm depth, were collected from the agricultural lands from the above mentioned sites. The soil samples were analysed for the following physico-chemical characteristics. Physico-chemical factors such as pH, Electrical conductivity, Total dissolved solids, Turbidity, Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Total alkalinity, Total Hardness, Total Nitrogen, Potassium, Phosphorous, Calcium, Sodium, Chloride, and heavy metals Chromium and Cadmium were analysed as per the methods of APHA (1990); [7].

### 2.2 Characterization of samples

Physico-chemical factors such as pH, Electrical conductivity, Moisture, Porosity, Alkalinity, Salinity, Organic matter, Total Nitrogen, Phosphorous, Sodium, and Calcium were analysed for the soil samples as per the method of APHA (1990). The heavy metals Chromium and Cadmium concentration were estimated using Atomic Absorption Spectroscopy (Varian AAA 220 FS). The soil sample collected from Tandalam site was chosen for further treatment.

### 2.3 Electrokinetic remediation of soil collected from tandalam

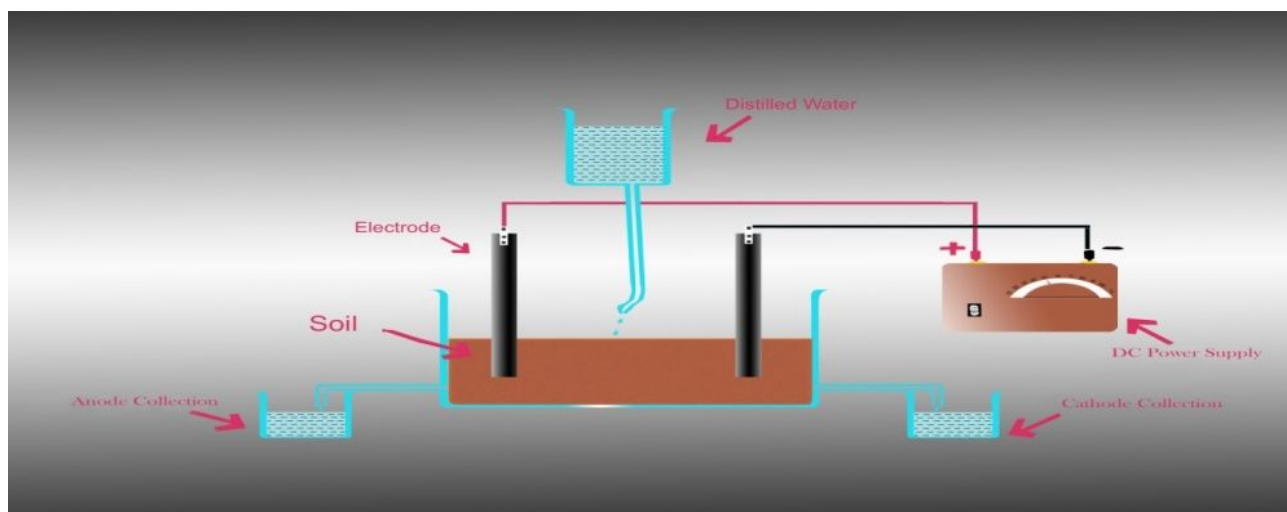
Contaminated soil sample, selected for this study, was obtained from Tandalam, Ranipet. The received soil sample was thoroughly homogenized. The homogenized soil sample was made into a slurry by mixing with deionised water in the ratio 1:10. The equilibrium pH of the slurry was measured with a pH meter. The experimental setup is as shown in the figure 1. The test setup mainly consists of an electrokinetic cell, two electrode compartments, a DC power source and a multimeter. Plexi glass cell having a total length of 25 cm, inside diameter of 15 cm and 50cm height was used as the electrokinetic cell. Each electrode compartment included an outlet valve and a wire mesh. The cell was divided into four compartments and labelled as anode, middle anode, middle cathode and cathode respectively. The outlet valves were connected to the reservoirs to collect the liquid that was removed along with the gases. A DC power source was used to apply a constant voltage to the electrodes, and a multimeter was used to monitor the voltage and measure current value through the soil sample during the test. Contaminated soil of about 3 Kgs in the form of homogenized slurry was packed in the electrokinetic cell. Deionised water was circulated inside to achieve the mobility of ions. Two graphite electrodes of dimensions 25 cms and 1.5cm outer diameter were inserted into the compartments. When DC electric fields are applied to contaminated soil via graphite electrodes placed into the soil packed in the electrokinetic cell and migration of charged ions occurs.

Contaminants from the different soil sections were extracted by acid digestion and the fluid samples were also digested. The samples were dried and the total concentrations of chromium and cadmium were determined using an Atomic Absorption Spectrophotometer (Varian4SAA).

Removal efficiency for each test was calculated dividing the total mass deposition in anolyte and catholyte by initial mass of contaminant of untreated soil.

The same type of electrokinetic treatment was carried out with artificially spiked soils. OECD artificial soil was prepared according to the composition 70% sand, 20% kaolin clay and 10% finely ground peat (OECD, 1984). The artificial soil was infused with potassium dichromate to study chromium removal, cadmium chloride to study cadmium removal. The samples were dried and the concentrations of the heavy metals chromium and cadmium were calculated.

### Electrokinetic cell set up



### 2.4 Phytoremediation of electrokinetically treated soil using indian mustard

The soil sample extruded from the electrokinetic cell is transferred into four pots and labelled accordingly as anode, middle anode, middle cathode and cathode. Plants of *Brassica juncea* grown in the electrokinetically treated soil were analysed for heavy metal concentration.

## 3 Results and discussion

A large number of tanneries and chemical industries situated in the study area, Ranipet Industrial Town, Vellore District have caused irreversible damage to the environment. Regular monitoring of the situation is highly necessary to stop the damage caused by the industries. Hence in the present work, an attempt has been made to analyse the physico-chemical factors and heavy metals in soil and water of various sites in Ranipet.

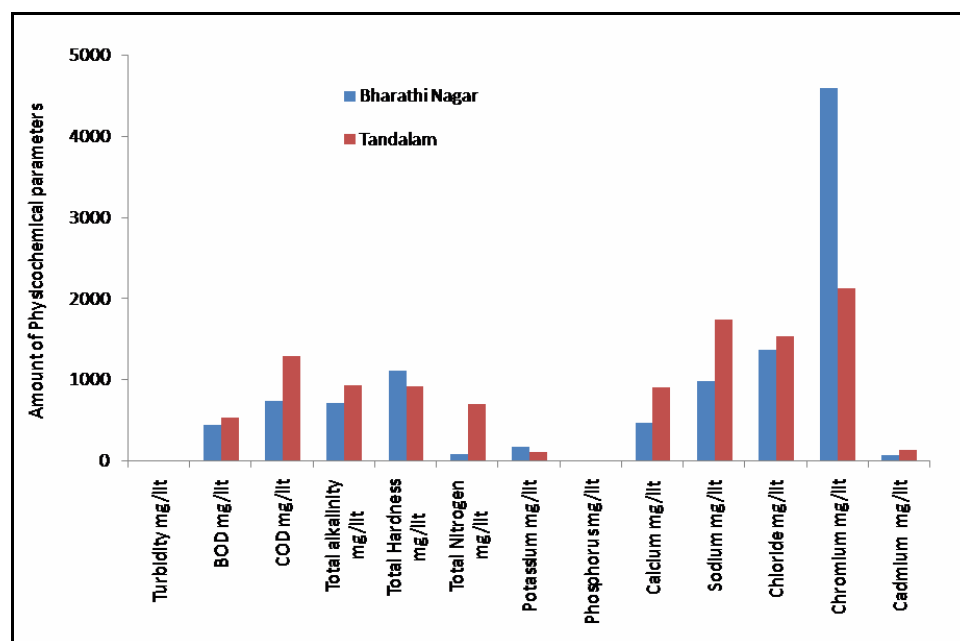
Table -1 and Figure-1 shows remarkable increase in the electrical conductivity of all the water samples and the accepted limit prescribed by WHO is 75-200  $\mu$  mhos/cm. The electrical conductivity (EC) of water collected from Bharathi Nagar lake was found to be very high (EC- 7480  $\mu$ mhos/cm). Bharathi nagar is contaminated by Malladi drugs and Pharmaceuticals and Thirumalai Chemicals Limited; Tandalam (EC- 3150 $\mu$ mhos/cm) is contaminated by Malladi drugs and Stahl India private Limited. EC of Maniyambat (726 $\mu$ mhos/cm) is significantly lower than the other samples but higher than the values prescribed by WHO (75- 200  $\mu$ mhos/cm). Increased conductance has been caused by the presence of ionic species in the effluents.

The analysis of the BOD and COD reveals that values of all the water samples are found to be high. The total heavy metal content namely Cd and Cr in the water sample implies that the effluents from various industries are not treated well before their discharge. Bharathi nagar I (4594 mg/L) and Tandalam II (2125 mg/L) shows high concentration of heavy metal chromium since basic sodium dichromate is used as a tanning agent in the chrome tanning process. Tandalam water sample showed more cadmium content than the other samples.

In a river polluted by base metal mining, Cd was the most mobile and potentially bioavailable metal and was primarily scavenged by non-detrital carbonate minerals, organic matter and iron-manganese oxide minerals.

**Table 1: Physico-chemical parameters of water samples**

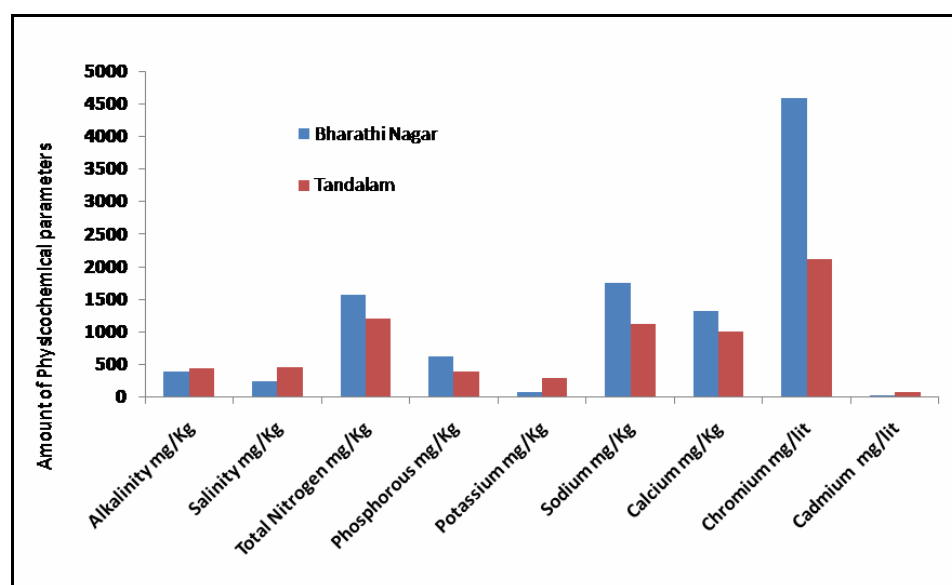
| Parameters                                   | I.Bharathi Nagar | II.Tandalam |
|--|------------------|-------------|
| pH   | 7.65             | 7.5         |
| Electrical conductivity ( $\square$ mhos/cm) | 7480             | 3150        |
| Turbidity mg/lit                             | 3                | 2           |
| BOD mg/lit                                   | 450              | 539         |
| COD mg/lit                                   | 745              | 1290        |
| Total alkalinity mg/lit                      | 724              | 936         |
| Total Hardness mg/lit                        | 1110             | 920         |
| Total Nitrogen mg/lit                        | 86               | 710         |
| Potassium mg/lit                             | 184              | 112         |
| Phosphorus mg/lit                            | 0.04             | 0.05        |
| Calcium mg/lit                               | 475              | 912         |
| Sodium mg/lit                                | 989              | 1748        |
| Chloride mg/lit                              | 1370             | 1540        |
| Chromium mg/lit                              | 4594             | 2125        |
| Cadmium mg/lit                               | 78               | 147         |

**Figure – 1: Physico-chemical parameters of water samples**

The physico-chemical properties of soil samples collected from five different sites of Ranipet Industrial area were studied by measuring the following parameters viz. pH, Electrical conductivity, moisture, porosity, alkalinity, salinity, organic matter, nitrite, ammonia, nitrate, phosphorous, potassium, sodium, calcium, and the heavy metals Chromium and Cadmium. The results are presented in the Table 2 and Figure 2.

**Table 2: Physico-chemical parameters of soils**

| Parameters   | I.Bharathi Nagar | II.Tandalam |
|--|------------------|-------------|
| pH   | 8.1              | 8.1         |
| Electrical Conductivity ( $\square$ mhos/cm <sup>2</sup> ) | 3450             | 3721        |
| Moisture %   | 26               | 28          |
| Porosity   | 3.4              | 2.24        |
| Alkalinity mg/Kg   | 403              | 441         |
| Salinity mg/Kg   | 252.4            | 460.1       |
| Organic matter %   | 2.5              | 9.1         |
| Total Nitrogen mg/Kg                                       | 1569.5           | 1202.2      |
| Phosphorous mg/Kg  | 627              | 396         |
| Potassium mg/Kg  | 91               | 301         |
| Sodium mg/Kg   | 1758             | 1124        |
| Calcium mg/Kg  | 1322             | 1010        |
| Chromium mg/lit  | 4594             | 2125        |
| Cadmium mg/lit   | 35               | 76          |

**Figure - 2: Physico-chemical parameters of soil samples**

Studies had been carried out in Ranipet Industrial area and the report showed that around 600 acres of the land area were irreversibly polluted due to the discharge of untreated effluents from the tanneries and leather processing units. Water and soil samples collected from MGR Nagar, Bharathi Nagar, Vanapadi and Vannivedu village of Ranipet Industrial area were analysed and subjected to speciation studies and the results were reported by Sarawathy and Sudha, (2010). Maintaining strict pollution control regulating measures alone can prevent further damage of the environment by the industries.

In the present study, it was proposed to conduct low voltage electrokinetic remediation followed by phytoremediation of the heavy metal contaminated soil.

### 3.1 Electro kinetic remediation of the soil samples

Approximately 3 kg of dry soil (Tandalam soil sample) saturated with 1.5L of deionised water was packed into the electrokinetic cell. A DC electric potential was then applied across the soil specimen through two graphite electrodes. Tandalam soil was found to be of sandy loam type of soil. As Tandalam soil has more organic matter percentage, the pollutants can easily bind with the organic matter of soil and can easily separate. The higher amount of organic matter and phosphates could probably result from long term cultivation activity.

As seen in Table - 2, the high content of organic matter as well as high concentration of exchangeable form of Chromium was estimated in Tandalam soil. Hence Tandalam soil was used for electrokinetic remediation treatment.

### 3.2 Removal of Chromium by EKR

It is likely that a sufficient cleaning efficiency could be reached in all soil types, if the duration of cleaning would be longer [8]. Each of these experiments lasted for 25 days. Treatment time can vary significantly depending on the properties of soil. It is likely that extension of process duration would ensure better results. Kristina Greiciute *et al* [8] reported that cleaning efficiency was very good at 29V than at 24 V for a sandy loam soil. Fan Sheng Meng *et al* [9] have done an experimental study on the effect of applied voltage on the electrokinetic removal of Chromium from kaolin and reported that the removal efficiencies increase with the increase in applied voltage.

Treated soil was sectioned into four parts. 0.5g of soil sample was collected from each compartment and digested with conc. Nitric acid. Aqueous solutions collected from the electrode reservoirs were also digested and tested for heavy metal concentration. The concentration of **Chromium** in the soil samples collected from various compartments after **ekr** treatment at 50 V and the same in the water effluents collected from the electrokinetic cell are tabulated in Table - 3. The values showed that the removal rate gradually increased as the duration of treatment increased and after 25 days of **ekr** treatment, 17% of chromium was leached out into the water collected from the anode terminal and 8.5% of chromium was leached out into the water collected from the cathode terminal.

The water samples collected from anode and cathode outlets on the 5<sup>th</sup> day of **ekr** treatment showed 2.35% and 1.33% of Cr removal. The soil near anode deposited (77.6ppm) 3.65% of total Chromium, the cathode compartment accumulated (37ppm) 1.74% of Chromium and about (middle anode 53.36 ppm, middle cathode 42 ppm) 4.46% remained in the middle compartments. On the 10<sup>th</sup> day of **ekr** treatment, the water collected from anode, soil from anode, middle anode, middle cathode, cathode compartments and the water from the cathode outlet showed (124.34 ppm 5.85%, (196ppm) 9.22%, (117.12 ppm) 5.5%, (67.24 ppm) 3.16%, (40.56 ppm)1.9%, (33.08ppm)1.55% Chromium percentages respectively.

**Table 3 : Chromium in the Experimental soil after Electrokinetic treatment at 50 Volt**

| No. Of Days Of Treatment | Water from Anode   | ANODE              | MIDDLE ANODE       | MIDDLE CATHODE     | CATHODE          | Water from Cathode |
|--------------------------|--------------------|--------------------|--------------------|--------------------|------------------|--------------------|
| 5                        | 50.08<br>(2.35%)   | 77.6<br>(3.6%)     | 53.36<br>(2.5%)    | 42<br>(1.96%)      | 37<br>(1.74%)    | 28.34<br>(1.33%)   |
| 10                       | 124.34<br>(5.85%)  | 196<br>(9.22%)     | 117.12<br>(5.5%)   | 67.24<br>(3.16%)   | 40.56<br>(1.9%)  | 33.08<br>(1.55%)   |
| 15                       | 275.89<br>(12.98%) | 364<br>(17.13%)    | 249.52<br>(11.74%) | 145.5<br>(6.84%)   | 111.2<br>(5.23%) | 74.34<br>(3.49%)   |
| 20                       | 325.23<br>(15.3%)  | 409.24<br>(19.26%) | 289.4<br>(13.62%)  | 241.64<br>(11.37%) | 205.8<br>(9.68%) | 156.06<br>(7.34%)  |
| 25                       | 375<br>(17.65%)    | 461.3<br>(21.71%)  | 389<br>(18.31%)    | 294.4<br>(2.35%)   | 253<br>(11.9%)   | 181<br>(8.5%)      |

The water and soil samples collected from the various compartments on the 15<sup>th</sup> and 20<sup>th</sup> days showed regular increase in the concentrations near anode. The Chromium removal efficiency calculated on the 15<sup>th</sup> day was (825.5ppm) 38.85% and 18.59% remain in the soil in the middle compartments. Out of the 38.85% collected from various compartments, approximately 29% remains near the anode and water collected from anode and the remaining 8 to 9 % accumulate near cathode terminal. The result obtained on the 20th day was as follows: water from anode 15.3%, anode soil 19.26%, middle soil 13.62%, middle cathode 11.37%, cathode 9.68% and the water from cathode 7.34% respectively.

On the 25<sup>th</sup> day, the percentage accumulation of Chromium near anode was 461.3ppm (21%) and at cathode it was 253 ppm (11.9%). The middle anode and middle cathode areas showed (389 ppm) 18.31% and

(294.4ppm) 2.35% of total Chromium respectively. Hence the removal efficiency on the 25<sup>th</sup> day of **ekr** treatment was 59.78%.

Ageing of contaminated soil can be an important factor for the mobility of metal contaminants present in soil. With ageing of contaminants in soil, co-precipitation and incorporation with inorganic minerals will occur; cavities inside mineral lattices will be filled and solid solutions may occur. Metals that have been diffused and incorporated into minerals will be less prone to desorption and are thus less available for plants, reducing toxicity levels, but are also less mobile, reducing removal efficiencies during remediation attempts.

The results are compared with heavy metals Chromium and Cadmium spiked in OECD artificial soil under similar experimental conditions. From the electrokinetic treatment of spiked soil (Table- 4) the following observations were made. On the 25<sup>th</sup> day, 23.13% of chromium was leached out into the water collected from the anode terminal and 7.74% of chromium was detected in the water collected from the cathode terminal. The percentage accumulation of chromium near anode was (490.4ppm) 23% and at cathode was (242 ppm) 11.4% in the spiked soil. Spiked soil showed remarkable changes compared to experimental soil on the same durations viz., 5<sup>th</sup>, 10<sup>th</sup>, 15<sup>th</sup>, 20<sup>th</sup> and 25<sup>th</sup> days of treatment. The removal efficiency on the 15<sup>th</sup> day was 39.18% and that on the 25<sup>th</sup> day was 65.28%. Results of **ekr** carried out with spiked soil showed higher removal efficiencies of the metal Chromium. The reason may be attributed to the presence of sand used in the spiked soil preparation and to the absence of other possible contaminants in spiked soil as in the experimental soil. Sandy loam and sand have a most coarse grain structure as compared with other types of soil, which ensures a better movement of metal ions and thus better results of cleaning [8].

In the **EKR** treatment carried out on both the experimental and spiked soils, showed that the concentration of chromium in various compartments gradually decrease in the following trend **Anode > Middle anode > Middle cathode > Cathode**.

Previous researches have shown that chromium is available in hexavalent form as soluble chromium and hence it is leached out. On further analysis, it is seen that concentration of chromium is more towards anode than at the cathode confirming the presence of chromium in its anionic forms like  $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{CrO}_4^{2-}$ ,  $\text{HCrO}_4^-$ . In addition to dissolved metal complexes, metals also may associate with mobile colloidal particles. Colloidal size particles are particles with a diameter ranging from 0.01 and 10 $\mu\text{m}$ . Gschwend and Reynolds (1987) reported that colloidal particles of intermediate diameter, 0.1 $\mu\text{m}$  to 1 $\mu\text{m}$ , were the most mobile particles in a sandy medium. The chemical forms of heavy metals in soils can greatly influence their fate in terms of leaching and subsequent transport.

**Table 4: Chromium in spiked soil after Electrokinetic treatment at 50 Volts**

| No. of Days | Water from Anode | Anode          | Middle Anode   | Middle Cathode | Cathode      | Water from Cathode |
|-------------|------------------|----------------|----------------|----------------|--------------|--------------------|
| 5           | 75.45(3.55%)     | 80.02(3.76%)   | 56.12(2.64%)   | 44.04(2.07%)   | 39.24(1.85%) | 30.04(1.4%)        |
| 10          | 150.2(7.06%)     | 206.03(9.69%)  | 201.24(9.47%)  | 74.08(3.48%)   | 50.24(2.36%) | 56.32(2.65%)       |
| 15          | 290.37(13.66%)   | 382.15(17.98%) | 256.64(12.07%) | 148(6.94%)     | 85.4(4.02%)  | 74.65(3.5%)        |
| 20          | 386.3(18.18%)    | 442.28(20.81%) | 297.32(13.99%) | 252(11.85%)    | 220(10.35%)  | 144.34(6.79%)      |
| 25          | 491.6(23.13%)    | 490.4(23.07%)  | 402.4(18.94%)  | 300(14.17%)    | 242(11.38%)  | 164.46(7.74%)      |

Also, as the soil was found to be basic, the Chromium present in the soil could have also been existing as complex species. Hence the metals move from more towards anode than towards cathode. The presence of complex species in the soil solution can significantly affect the transport of metals through the soil matrix relative to the free metal ion in the environmental samples. Metals applied with sewage sludge may be retained in the soil as a result of their adsorption on hydrous oxides, clays, and organic matter; the formation of insoluble salts; or the presence of residual sewage sludge particles [10]. The role of carbonates on Cu and Zn retention has been pointed out by other authors and has been partly attributed to the formation of metals carbonates in soils [11]. The chemical forms of heavy metals in soils can greatly influence their fate in terms of leaching and subsequent transport.

The behaviour of Cr in the environment is complex. The mobility of Cr is dependent on the speciation of Cr, which is considerably affected by the conditions of the environment. Cr (III) is primarily present in a reducing environment, whereas an oxidizing condition favours Cr (VI) species.

Trivalent Cr (III) and hexavalent Cr (VI) are the two stable species in the environment. Under natural conditions, Cr (III) is readily adsorbed on solid phase, while most Cr (VI) solids are relatively soluble and, therefore, Cr (VI) is generally considered to be more mobile and consequently more bioavailable than Cr (III) in soil-water systems.

The concentration of metals in the soil solution, at any given time, is governed by a number of interrelated processes, including inorganic and organic complexation, oxidation reduction reactions, precipitation/dissolution reactions, and adsorption/desorption reactions. Metals will form soluble complexes with inorganic and organic ligands. Common inorganic ligands are  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{OH}^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{NO}_3^-$  and  $\text{CO}_3^{2-}$ . Soil organic ligands include low molecular weight aliphatic, aromatic, and amino acids and soluble constituents of fulvic acids.

### 3.3 Removal of Cadmium by EKR

The concentration of **Cadmium** in the soil samples collected from various compartments after **ekr** treatment at 50 V and the same in the water effluents collected from the electrokinetic cell are tabulated in Table - 5. The values showed that the removal rate gradually increased as duration of treatment increase and after 25 days of **ekr** treatment, (5.75ppm) 7.56% of cadmium was leached out into the water collected from the anode terminal and (14.65ppm) 19.26% of cadmium was leached out into the water collected from the cathode terminal. Cadmium was available as soluble cadmium hydroxide, cadmium chloride or cadmium sulphate and hence it was leached out. It was seen that concentration of cadmium was more towards cathode than to the anode confirming the presence of cadmium as its  $\text{Cd}^{2+}$  forms. Results obtained on 5<sup>th</sup>, 10<sup>th</sup>, 15<sup>th</sup>, 20<sup>th</sup> and 25<sup>th</sup> days showed that cadmium moved towards cathode. 2.19% of Cadmium was detected near anode and 2.78% was found near cathode on the 5<sup>th</sup> day of **ekr** treatment.

**Table-5: Cadmium in Experimental soil after Electrokinetic treatment at 50 Volts**

| No. of Days | Water from Anode | Anode        | Middle Anode | Middle Cathode | Cathode       | Water from Cathode |
|-------------|------------------|--------------|--------------|----------------|---------------|--------------------|
| 5           | 0.8 (1.05%)      | 1.06 (1.39%) | 1.3 (1.71%)  | 1.54 (2.03%)   | 1.76 (2.32%)  | 1.82 (2.39%)       |
| 10          | 1.71 (2.24%)     | 2.347(3.07%) | 2.7(3.55%)   | 6.32(8.31%)    | 7.45(9.79%)   | 6.72(8.83%)        |
| 15          | 3.613(4.75%)     | 4.37(5.7%)   | 6.085(8%)    | 10.65(14%)     | 12.65(16.63%) | 9.257(12.18%)      |
| 20          | 4.25(5.58%)      | 7.2(9.46%)   | 7.9(10.38%)  | 11.35(14.92%)  | 13.235(17.4%) | 11.27(14.82%)      |
| 25          | 5.752(7.56%)     | 7.65(10.06%) | 8.43(11.09%) | 13.32(17.52%)  | 20.27(26.65%) | 14.65(19.26%)      |

The water samples collected from anode (1.34%) and cathode terminals (3.48%) on the 5<sup>th</sup> day showed more accumulation Cadmium is near cathode than at anode. Thus, the removal efficiency on the 5<sup>th</sup> day was 7.15%. On the 15<sup>th</sup> day, 4.75% of Cadmium was leached out in the anode terminal and 12.18% was leached out in the cathode terminal. The percentage removal efficiency of Cadmium on the 15<sup>th</sup> day was 39.32%. There was a regular increase in the values, following a similar trend. On the 25<sup>th</sup> day, the percentage accumulation of Cadmium near anode is (7.65ppm) 10.05% and at cathode (20.27 ppm) 26.65%. The Cadmium removal efficiency at the end of the experiment duration was 63.58%. Srinivasa et al., 2007 has reported the Cadmium removal efficiency for a five days treatment on a soil with pH 8.36 and organic content as 6.25% to be 4.15% under unenhanced conditions whereas our results has shown 7.15%. This may be due to a higher organic content of 9.1%. Significant accumulation of Cadmium was observed in the area close to the cathode.

The accumulation of Cadmium was probably associated with a high pH environment, where migration of  $\text{OH}^-$  precipitated as  $\text{Cd}(\text{OH})_2$ . Cadmium metal was found electrodeposited on the cathode and/or precipitated on the cathode as cadmium hydroxide [12]. Tests of metal removal by electric field have shown that metal pollutant may concentrate at some intermediate region between the electrodes. The high pH near the cathode will favour the formation of metal precipitates and / or complexes, thus decreasing the mobility of heavy metals



[13]. A common problem encountered with *ekr* of heavy metals is the hindrance due to the formation of precipitates of the metal ions, which has been found close to the cathode. Heavy metals tend to form complexes with organic matter in the soil (humic and fulvic acids), which are different for each metal. The results obtained in the present study corroborated with the findings of Stevenson (1982) as the experimental soil has high organic matter content and hence a still higher removal efficiency was not attainable. Also, the migration and precipitation of calcium bicarbonates and hydroxides are observed to clog the pores preventing the transport of Cadmium. Danuta Leszczynska and Hafiz Ahmad (2006) have reported the overall removal efficiency of the heavy metal Arsenic by *ekr* treatment for 25 hours without any special augmentation solution as 39%.

The results of *ekr* treatment of Tandalam soil are compared with Cadmium spiked soil under similar experimental conditions and are tabulated in Table-6. Water collected from anode and cathode outlets contained 1.09% and 3.25% of Cadmium on the 5<sup>th</sup> day of *ekr* treatment. 1.59%, 1.91%, 3.51% and 3.81% was found in the soil samples collected from anode, middle anode, middle cathode and cathode compartments respectively. The removal efficiency on the 15<sup>th</sup> day was found to be 48.94% of total Cadmium 4.4% of cadmium was leached out into the water collected from the anode terminal and 13.6% of cadmium was leached out into the water collected from the cathode terminal on the 15<sup>th</sup> day of *ekr* treatment. The percentage accumulation of cadmium near anode was (7.34 ppm) 9.6% and at cathode (19.37 ppm) 25.47% in the spiked soil on the 20<sup>th</sup> day. On the 25<sup>th</sup> day of EKR treatment the concentration of cadmium in the anode compartment was (7.46 ppm) 9.8% and that at the cathode compartment was (25.42 ppm) 28%.

**Table – 6: Cadmium in spiked soil after Electrokinetic treatment at 50 Volts**

| No. of Days | Water from Anode | Anode        | Middle Anode  | Middle Cathode | Cathode        | Water from Cathode |
|-------------|------------------|--------------|---------------|----------------|----------------|--------------------|
| 5           | 0.83 (1.09%)     | 1.21 (1.59%) | 1.45 (1.91%)  | 2.67 (3.51%)   | 2.9 (3.81%)    | 2.47 (3.25%)       |
| 10          | 2.48 (3.26%)     | 3.02 (3.97%) | 3.37 (4.43%)  | 4.27(5.62%)    | 7.24 (9.53%)   | 6.4 (8.42%)        |
| 15          | 3.34 (4.4%)      | 7.25 (9.53%) | 7.9 (10.38%)  | 14.65 (19.26%) | 16.23 (21.35%) | 10.37 (13.64%)     |
| 20          | 4.5 (5.92%)      | 7.34 (9.65%) | 8.03 (10.55%) | 15.75 (20.71%) | 19.37 (25.47%) | 12.624 (16.6%)     |
| 25          | 4.02 (5.27%)     | 7.46 (9.81%) | 8.24 (10.83%) | 17.65 (23.21%) | 25.42 (33.44%) | 14.35 (18.87%)     |

The removal efficiency on the 15<sup>th</sup> day was found to be 48.94% of total Cadmium and that on 25<sup>th</sup> day, at the end of the experimental duration was found to be 67.43%. This showed that the stability in attaining maximum removal rate for cadmium is achieved within 15 to 20 days of *ekr* treatment. The concentration of cadmium in various compartments gradually decrease in the following trend

**Cathode > Middle cathode > Middle anode > Anode**

In these experiments, sand was used in making the OECD soil and the metals are artificially spiked into the sand, for which the removal was probably not as difficult as for real contaminated soils. Sandy loam and sand have a most coarse grain structure as compared with other types of soil, ensures a better movement of metal ions and thus better results of cleaning [8]. For Cadmium, both high and low remediation efficiencies have been reported for unenhanced treatment. It seems that the removal success is highly dependent on site and speciation. Citric acid seems to be a suitable leaching / complexing agent when treating soil with Cadmium and upto 85% Cadmium was removed when citric acid was used [14].

Plants are found to accumulate heavy metals and other pollutants in their cells. The process called as phytoremediation is an *in-situ* decontamination approach showing promise for addressing both organic and inorganic contaminants. It is the method of attenuation of pollution through the use of plants which impose minimal environmental disturbance and offer economic, agronomic and social benefits. Contaminated sites revegetated with plants, reduce wind and water erosion that spread materials containing heavy metals. Hence in the present research work, the electrokinetically treated soils were further subjected to phytoremediation using

*Brassica Juncea* (mustard) plant. Upon termination of electric power, the experimental soil specimen was removed from the cell according to their compartments into suitable pots.

In the present research work an attempt had been made to utilise *Brassica juncea* (Indian Mustard) to remediate electrokinetically treated soil of Tandalam, Ranipet industrial area by phytoextraction technology. Fertile soil collected from Kaniyambadi village, Vellore district was taken as control. The various physico-chemical characteristics of the control and polluted soils were analysed. The impact of heavy metals Chromium and Cadmium on the biochemical factors, vitamins and mineral factors and antioxidant properties of the plants *Brassica juncea* grown in metal spiked control soil and polluted soils were investigated.

The soil extruded from the four compartments of the electrokinetic cell (viz Anode, Middle anode, Middle cathode and Cathode) were transferred into four pots. Another pot was filled with control soil. After a period of 21 days, the plants were harvested. Plants were harvested by cutting the shoots and roots and washed with deionised water. They were dried for 48 hours at 70°C.

Tables -7 shows the percentage bioaccumulation of Chromium and Cadmium metals by *Brassica juncea* exposed to heavy metal contaminated soil. The bioaccumulation of Chromium was found to be 0.041 ppm in the plants grown in control soil. The bioaccumulation of Chromium was 5.46% (25.2 ppm) in the plants grown in the anode soil which had 461.3 ppm of Chromium after **ekr** treatment, 5.68% (22.1 ppm) in the plants grown in the middle anode soil that had 389 ppm of Chromium after **ekr** treatment, 7.16% (21.1 ppm) in the plants grown in the middle cathode soil that contained 294.4 ppm of Chromium, and 7.59% (19.2 ppm) in the plants grown in the cathode soil which contained 253 ppm of Chromium after **ekr** treatment (Table 7).

**Table - 7: Heavy Metal accumulation in Indian mustard plant**

| Heavy metals | Control | Anode       | Middle Anode | Middle Cathode | Cathode     |
|--------------|---------|-------------|--------------|----------------|-------------|
| Cr           | 0.041   | 25.2(5.46%) | 22.1(5.68%)  | 21.1(7.16%)    | 19.2(7.59%) |
| Cd           | 0.001   | 2.2(28.75%) | 2.7(32%)     | 3.7(27.78%)    | 5.3(26.14%) |

The bioaccumulation of Cadmium was found to be 0.001 ppm in the plants grown in the control soil whereas the plants grown in the anode soil bioaccumulated 28.75% (2.2 ppm) of 7.65 ppm of Cd in the **ekr** treated soil, 32%(2.7ppm) of 8.43 ppm in the middle anode, 27.78% (3.7ppm) of 13.32 ppm in the middle cathode, and 26.14% (5.3 ppm) of 20.27 ppm in the cathode soil after **ekr** treatment for 25 days (Table 7). Several researchers have reported on the accumulation on metals by plants. Kumar *et al.*, 1995; Lee *et al.*, 2002 have shown that different varieties of *Brassica juncea* (Indian mustard) were able to take up and accumulate high concentrations of trace elements in intercellular spaces. Plant uptake of metals increased by the electrokinetic-assisted phytoremediation, and a medium voltage gradient of 2Vcm<sup>-1</sup> was the best due to the highest metal accumulation in the plant. Voltage gradient was the most important factor in affecting the plant growth, soil properties and metal concentrations in the soil and plant.

As per the results of **ekr** experiments more Chromium was deposited in anode soil and more cadmium has migrated towards cathode soil. 5.46% of Chromium was accumulated in the plants grown in the anode soil and 26.14% of Cadmium was accumulated in the plants grown in the cathode soil. This may be a function of lower phytotoxicity of Cadmium and also due to the increase in the concentration of labile Cadmium in the cathode part of the **ekr** cell. The experimental soil showed a pH value of 8.1 (Table - 2). The acid conditions generated at anode of the **ekr** cell represent unfavourable conditions for plant growth. pH is the major soil parameter which affects the plant growth. Brown *et al.*, reported that soil pH not only affects metal bioavailability, but also it affects the metal uptake by the roots. Sanders (1983) reported that the solubility of heavy metals is generally greater as pH decreases within the pH range of normal agricultural soils. The high pH values of soils could have accounted for a low transfer of metals from soil to plants.

Metal uptake by plants involves a series of processes such as metal desorption from soil particles, transport of soluble metals to root surfaces via diffusion or mass flow; metal uptake by roots and metal translocation from roots to shoot. The results show a promising accumulation of heavy metals Chromium and Cadmium in single harvest, which can further be increased in subsequent harvests. Plants for phytoextraction, i.e., metal removal from soil, should have the following characteristics: (i) tolerant to high levels of the metal,

(ii) accumulate reasonably high levels of the metal, (iii) rapid growth rate, (iv) produce reasonably high biomass in the field, and (v) profuse root system [15]. Hence Indian mustard has proved to be a good accumulator of heavy metal contaminants in soil in the present study.

#### 4 Conclusion

The two approaches were used in combination in the present research. Electrokinetic mobilization of metals in the soil increases the metal accumulation in a particular part of the field and availability to the plants and thus plant metal uptake and in further, the possibility of subsequent extraction by phytoremediation. Combined use of electrokinetic technology in conjunction with phytoremediation may possess greater potential in the future to treat industrially heavy metals contaminated soils.

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