Proceedings of the Pakistan Academy of Sciences: A Physical and Computational Sciences 62(2): 165-173 (2025)
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ISSN (Print): 2518-4245; ISSN (Online): 2518-4253
http://doi.org/10.53560/PPASA(62-2)692

Pakistan Academy of Sciences

Research Article

Electro-remediation of Chromium and Associated Heavy Metals from Soils Affected by Leather Tannery Waste Effluents in Sambrial Town, Pakistan

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Abstract: A locally fabricated electrokinetic remediation apparatus was used for laboratory scale electrokinetic remediation of aqueous phase Cr and associated metals in coarse silty clay soil affected by waste effluents released from leather tanning factory located in the jurisdictions of Sambrial Town (Punjab), Pakistan. Acetic acid (0.1 M CH_3COOH: pH = 3.9 and EC = 0.4 mS/cm at the start of the experiment) was applied as electrolyte for electrokinetic washing of aqueous phase Cr and associated metal species in field collected test soil contained in an electrolytic soil cell by applying a constant 30 V DC (equivalent to 1 V cm^{-1}) across the cell for a period of 216 hours (~9 days). The pH and electrical conductivity of electrolytes (catholyte and anolyte) were measured at different time intervals during the course of electro-remediation. Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) has been employed to determine the contents of metals like Cr, Fe, Ni, Zn, Mn, Co, Pb and Sr in the test soil. Morphological changes in the test soil were observed through scanning electron microscope in response to electrokinetic washing of the soil. It is observed that after electro-remediation soil samples show that particles segregate and surface becomes more porous. It is noted that initially pH varies and then becomes constant, whereas electrical conductivity increases with time.

Keywords: Electro-remediation, Washing, Heavy Metals, Tannery Effluents, Waste Soils, Scanning Electron Microscopy.

1. INTRODUCTION

The leather tannery is the second largest export earning sector in Pakistan [1]. At present, there are over 250 tanneries functioning mainly in the Punjab Province of Pakistan. Most of these tanneries are situated in and around Sialkot city and alongside roads leading to Sialkot from Sambrial, Pasrur, Daska, and Head Marala. Most of these tanneries are working without any proper system of waste disposal [2]. In leather tanning industry, chrome is applied in the form of Basic Chromium Sulphate (BCS). About 60-70% of this chrome is reported to be absorbed by the hides and skins during process and the remaining is discharged as waste. The tannery effluents (wastewater) are reported to have Chemical Oxygen Demand (COD) values between 3800 mg/L to 41300 mg/L in contrast to the COD limit of 150 mg/L imposed by the National Environmental Quality Standards (NEQS) for the tannery wastewater [3]. The tannery effluents (wastewater) quality analysis along Sambrial-Sialkot road in the past for a range of parameters involving pH (3.1-3.4), COD (609-3413 mg/L), total dissolved solids (6456-91972 mg/L), and toxic metals including Cr (220-2877 mg/L) has clearly indicated an alarming soil contamination by effluents of leather tanning industry in the area [1, 3]. The continuous use of the contaminated potable groundwater (drinking water), causes various types of diseases, that are increasing rapidly and over 70% citizens are reportedly suffering from stomach and liver diseases, 60% from dysentery and 85% from stomach diseases in these areas [4]. The

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Received: October 2023; Revised: April 2025; Accepted: June 2025

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tannery effluents are, therefore, held responsible for the serious pollution threat to the soil-water and subsoil water adjacent to leather tanning industrial sites. It is feared that if adequate remedial measures are not taken promptly, the inhabitants living in the vicinity of tannery waste sites may eventually develop diseases like cancer and tuberculosis.

With the advances in waste soil remediation technology, the conventional procedures such as flushing of waste soil by water admissible suitable solvents, and/or bioremediation are now being recognized as ineffective and costly tools for on-site remediation of contaminated soils [5]. In contrast, electro-kinetic decontamination process (also called electro-remediation process) has emerged as a very promising technology for on-site decontamination of aqueous phase/ leachable toxic species of a variety of contaminants including metals, radionuclides, organics from wastewater environment (e.g., contaminated ponds, sub-soil environment specially, low hydraulic permeability soils like clayey soils). The electro-kinetic remediation process utilizing the electro-kinetic phenomenon was initially reported way back in the beginning of eighteenth century [6-8]. During the past fifty years, the process of electro-remediation has been extensively studied, upgraded and effectively utilized for decontamination of a variety of waste soils, particularly the clayey soils hosting inorganic contaminants such as toxic metal ions etc. [1, 2], organic contaminants [9, 10], and radionuclides such as thorium and radium [11-14].

From practical view point, for electro-kinetic washing of contaminants from soil or water environment, it is necessary that these contaminants are present in the soil-water environment in ionic or nonionic form within the soil-water environment or these can be brought into aqueous phase using chelating agents for movement across the electrolytic soil geometry. The electro-kinetic process is actuated by applying low DC voltage or current across a set of two or more electrode systems installed at suitable depths and locations in a specific geometry across the contaminated soil geometry, whereby the ionic and nonionic contaminant species are transported to respective electrodes (anode or cathode) under the influence of DC voltage gradient across electrodes. As such, the electro-kinetic decontamination is actuated by the following three processes:

(i) The electrically induced (i.e., electrolytic) migration of ionic, non-ionic and/or polar contaminant species through the pore fluids in a soil-water environment as well as the transport of hydrogen ions (H^+) generated at the anode and the hydroxyl (OH^-) generated at the cathode toward opposite electrodes. Accordingly, the temporal migration of an acid front from the anode to the cathode is, therefore, an important feature of the electro-kinetic washing/remediation procedure in the contaminated soil-water systems [5-7, 15, 16].

(ii) Electro-osmosis, i.e., displacement of smaller significant layers of water molecules due to migration of ions toward an electrode in cases where the soil pore water has elevated ionic content. Significant flux of water produced by electro-osmosis may be able to move both the ionic and non-ionic species through soil-water system commonly mostly toward the cathode [17-19].

(iii) Electrophoresis, i.e., transport of charged colloids (containing contaminant species) in the soil-water environment towards electrodes for subsequent extraction above ground.

This paper documents the first ever laboratory scale electro-kinetic remediation of aqueous phase Cr and associated metal species from coarse silty clay soils in Sambrial Town affected by tannery waste effluents under the influence of low DC voltage. The key objectives of the present study are:

(i) To examine the practical efficacy and usefulness of an indigenously developed electro-remediation apparatus for laboratory scale electro-remediation of aqueous phase Cr and associated species in soil affected by effluents released from leather tanning industry in Sambrial Town.

(ii) To learn about the electro-remediation procedures and to overcome unforeseen issues that may arise during the course of electro-remediation (such as failure of DC supply across the electrochemical cell, leakage of electrochemical cell, etc.) and hinder the progress and efficiency of electro-remediation.

(iii) To quantify electro-remediation efficiencies of Cr and associated metal species in soil affected by tannery waste effluents.

2. MATERIALS AND METHODS

2.1. Soil Sampling

Coarse silty clay soil (hereafter referred to as SAMB Soil) was collected from a tannery waste effluent pond (Figure 1(a)) adjacent to Chromium Recovery Plant (Figure 1(b)), located on main Wazirabad-Sambrial-Sialkot road (Pakistan) within the jurisdiction of Sambrial Town. This plant was used for the treatment of effluents from the leather tanneries in the area.

2.2. Soil Analysis

For experimental purposes, the collected SAMB soil (Cr content: ~1054 mg/L) was sieved (Sieve No. 80, mesh size 180 µm) to attain a fine-grained soil. The morphological characteristics of the soil were determined with scanning electron microscope (Model: Leo 440I).

2.3. Metal Analysis

The concentrations of metals (Cr, Fe, Ni, Zn, Mn, Co, Pb, and Sr) in test soil sampled before and after electro-remediation process, and in aliquots of anolyte (A) and catholyte (C) sampled during the course of electroremediation were determined by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES/iCAP 6500 Thermo Fisher) technique.

2.4. Electro-remediation Apparatus

Figure 2 shows the locally fabricated experimental electrokinetic remediation apparatus used in the present study. The detailed schematics and design of the apparatus are given elsewhere [12, 13]. Briefly, the experimental device consisted of the following key apparatuses: (a) One electrokinetic soil cell (dimentions: 30 × 13 × 10 cm^3) and two electrolyte compartments made by 1 cm thick acrylic sheet (dimentions: 13 × 10 × 3.6 cm^3); (b) Two 1mm thick titanium (99.9% pure) plates; (c) Five Tungsten wire electrodes (length = 15 cm, thickness = 0.1 cm); (d) Two Pyrex glass reservoirs (700 mL); and (e) One DC Power Supply (100 V and 2 Amps.). The electrokinetic soil cell was sandwiched between the electrolyte compartments while the titanium plates were inserted in the electrolyte compartments and used as anode and cathode. Similarly, the Tungsten wire electrodes were interspaced across the test soil bed to measure voltage gradient in the soil cell and used as dummy electrodes to measure potential across the soil cell. The Pyrex glass reservoirs were used to supplement electrolyte solutions (anolyte and catholyte) to respective electrolyte compartments as well as to measure the water volume transported across the soil cell.

Fig. 1. Soil sampling site near Sambrial (Punjab), Pakistan (a) Waste effluent pond near plant and (b) Chrome recovery plant.

Other tools included a multi-meter used to gauge the current and voltage across the electrokinetic soil cell during the electrokinetic washing of soil; a pH meter (Model PP– 201 K); an electrical conductivity meter (Model WTW–LF 95) used to measure electrical conductivity (including H^+ ion concentration) of the electrolytes (anolyte and catholyte) and the test soil; and plastic syringes were used to extract electrolyte samples for chemical analysis and to purge the electrolytes for the purpose of homogeneity of solutions in the anolyte and catholyte compartments.

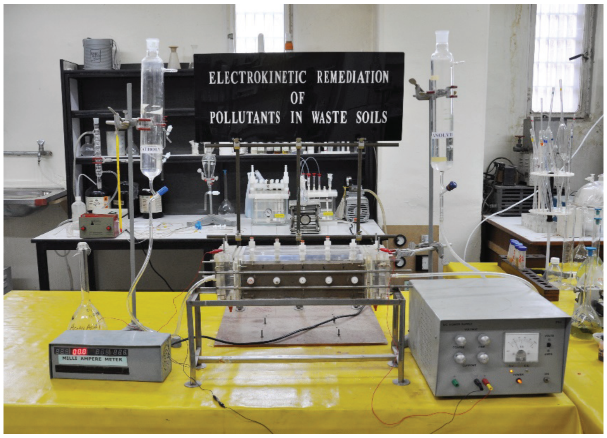

Fig. 2. Indigenous laboratory scale electrokinetic remediation apparatus.

2.5. Electroremediation Procedure

Well homogenized moist SAMB soil (weight = 4.5 kg) was gradually loaded into the electrokinetic soil cell which was then gently vibrated/shaken on table to settle the soil and to remove the trapped air. Acetic acid (0.1 M (CH_3COOH), pH = 3.9, and EC = 0.4 mS/cm at the start of experiment) was used as electrolyte both for the anolyte and catholyte compartments. About 370 mL of 0.1 M CH_3COOH was added each to the anolyte and catholyte compartments. Similarly, 0.1 M CH_3COOH was added to the electrolyte storage reservoirs. Acetic acid was used as catholyte to avoid precipitation of transported cationic species in test soil because of high pH conditions in the immediate vicinity of the cathode compartment [6]. The levels of anolyte and catholyte in electrolyte compartments and the level of soil bed across electrolytic soil cell were kept similar for hydraulic reasons. The level of acetic acid in electrolyte compartments (mainly anolyte) was maintained by adding 0.1 M CH_3COOH solution from the relevant electrolyte storage reservoirs. A zero hydraulic head was maintained across the soil cell so as to ensure, ionic transport solely due to electro-kinetic mechanism. The current across anode and cathode and the voltage between anode, cathode and dummy electrodes (D1, D2, D3, D4, and D5) was monitored [20]. The electro-remediation process was initiated by applying constant 30 V DC (equivalent to 1 V cm^{-1}) across the soil compartment for a total period of 216 hours (~9 days). During the course of electro-remediation experiment, no pH control was applied in order to simulate natural hydrogeological conditions of the contaminated site. The electrolytes in the storage reservoirs and the electrolyte compartments were purged throughout the experiment to maintain homogeneity of electrolytes therein. Similarly, the electrical conductivity and pH of both anolyte and catholyte were monitored at various time intervals during the experiment.

3. RESULTS AND DISCUSSION

3.1. Characterization of Soil

The salient mineralogical phase analyses and physicochemical of SAMB soil are summarized in Table 1. The mineralogical phase analysis shows that the SAMB test soil consists of silicate minerals, mainly SiO_2 (Quartz) and $NaAlSi_3O_8$ (Albite), and clay minerals mainly: Chamosite [$(Fe,Al,Mg,Mn)_6(Si,Al)_4O_{10}(OH)_8$] and Muscovite [$KAl_2(AlSi_3O_{10})(OH)_2$]. Moderate contents of clay minerals namely Muscovite and Chamosite, and significantly high contents of Quartz show that the SAMB soil represents texture of coarse silty clay soil. Further, the fair proportion of Chamosite in the test soil gives a swelling character to the SAMB soil. The physicochemical analysis shows that the SAMB soil with pH = 6.72 is slightly acidic which might be due to the impact of acidic effluents from the close-by leather tanning factory in the soil sampling zone. The electrical conductivity of the test soil is 3.85 mS/cm which shows high proportion of soluble mineral contents. The bulk density of the test soil is 1.064 g/cm^3, while its specific gravity ranges from 1.87 to 1.93 which is quite low. Similarly, the moisture content of the test soil is also very low (θ = 8.4%). The porosity of the test soil ranges between 31.9% to 36.6% which is on the high soil porosity, reflecting large inter-granular spaces in the coarse silty clay soil which is also quite visible in SEM images of the SAMB soil. The acidic buffering capacity of the test soil ranges between 0.33 mM/g to 1.77 mM/g which is mildly on the lower side. In general, soils containing high contents of exchangeable ions like Ca, Mg, Na, and Al possess high buffering capacity. The moderately

Table 1. Physicochemical characteristics of experimental soil (SAMB Soil).

Analysis Type	**Value**
Mineralogical Phases	**% of bulk soil**
Quartz (SiO_2)	74 - 77
Albite ($NaAlSi_3O_8$)	4.7 - 13
Chamosite [$(Fe,Al,Mg,Mn)_6(Si,Al)_4O_{10}(OH)_8$]	04 - 5.9
Muscovite [$KAl_2(AlSi_3O_{10})(OH)_2$]	07 - 11.6
Physicochemical	
Cr content mg/L	1054
pH	6.72
Moisture Content (%)	8.4
Bulk Density (g/cm^3)	1.064
Porosity (%)	31.9 - 36.6
Specific Gravity	1.87 - 1.93
Organic Content (%)	0.43 - 0.64
Acidic Buffering Capacity (mM/g)	0.33 - 1.7
Electrical Conductivity (mS/cm)	3.85

low buffering capacity of SAMB soil signifies that the test soil may slightly impede to the production and/or transport of acidic front throughout the electro-kinetic remediation process.

3.2. SEM Analysis

Figure 3 shows the SEM images of SAMB soil before and after electro-remediation. It is observed that before electro-remediation, the particles are well connected and have larger grain size (Figure 3(a)). However, after electro-remediation, the clay morphology changes, the particles are segregated and porosity is increased size (Figure 3(b)). This could be due to the washing of soil with 0.1 M CH_3COOH (acetic acid: pH = 3.9), there may be some dissociation of clay minerals in the test soil resulting in partial destruction of some of the soil particles and/or precipitation of mineral phases at low soil pH, thereby altering the morphological nature of the soil particles.

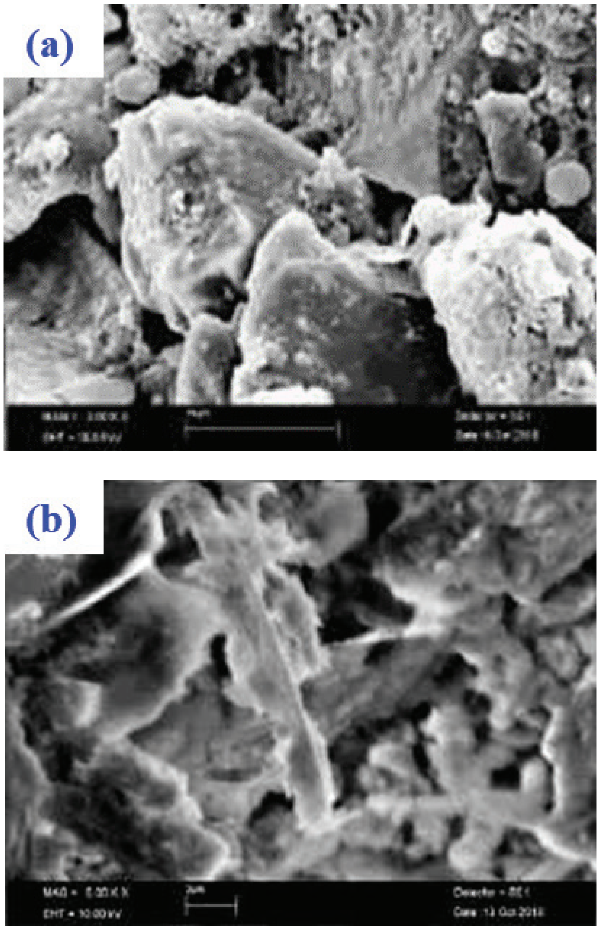

Fig. 3. SEM images of SAMB soil (a) before electroremediation and (b) after electroremediation.

3.3. Variations in the Electrolytes pH and Electrical Conductivity

The overall variations in the pH and electrical conductivity (EC) of the electrolytes (0.1 M CH_3COOH with initial pH = 3.9 and EC = 0.4 mS/cm) in the catholyte and the anolyte compartments during the course of electro-kinetic washing of SAMB soil in the electro-kinetic cell are illustrated in Figure 4 and Figure 5, respectively. Interestingly, the rate of decrease or increase in the pH of electrolytes was quite rapid during the first 20-25 hours of electro-remediation process and after this the pH kept almost constant till the experiment was terminated [1].

Figure 5 shows a rise in the electrical conductivity of catholyte from 0.4 mS/cm up to 28.8 mS/cm was observed during the course of electro-remediation. Whereas, the anolyte electrical conductivity increased from 0.4 mS/cm to 22 mS/cm during electro-remediation.

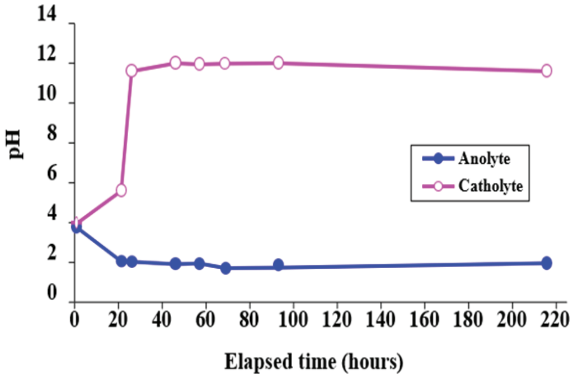

Fig. 4. Temporal variations of pH of catholyte and anolyte with time.

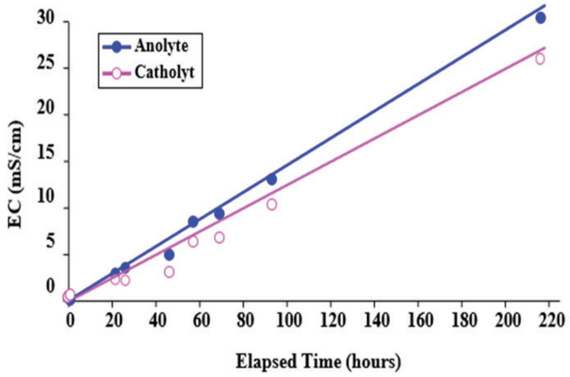

Fig. 5. Temporal variation of electrical conductivity of catholyte and anolyte.

It is observed that electrical conductivity of both anolyte and catholyte increased with time, that might of due to the accumulation of metallic ions in both electrolyte compartments.

3.4. Transport of Contaminant Across the Electrolytic Soil Cell

Both anolyte and catholyte were initially colorless. However, during the process of electro-remediation, the color of anolyte and catholyte changed along with occurrence of osmotic flow. The change in color of electrolytes depended upon the type of species received at respective electrolyte compartments. The change in color of electrolytes and the occurrence of osmotic flow from the anolyte compartment to the catholyte compartment in fact provided an indication of successful electro-kinetic washing of the soil matrix. Throughout the experiment, the anolyte colour constantly changed. Approximately, after 22 hours of electrokinetic washing, the color of the anolyte turned to yellow. After 24 hours of the electrokinetic washing, the color of the anolyte turned to dark red. After 30 hours of the electrokinetic washing, the color of the anolyte turned to slightly violet; while after 48 hours it turned to reddish colour and ultimately to green color towards the end of experimentation with a corresponding decrease in pH from 3.9 to 1.95. Likewise, after 22 hours of electro-remediation, slight yellowish turbidity was noticed in the catholyte compartment. After 26 hours of electro-remediation, the yellowish turbidity turned to deep yellowish red. With the progression of electro-remediation experiment, a yellow precipitate started settling at the bottom of the catholyte compartment and towards the end of the electro-remediation experiment, the catholyte solution started becoming colorless again with a change in pH from 3.9 to 11.6.

The heavy metals like Co, Cu, Ni, Pb, Cd, etc. may coexist with Cr within the contaminated aquatic and/or hydrogeological system in the form of cationic species [9, 21-23]. Figure 6 shows the variation in the concentrations of Cr, Fe, Ni, Zn, Mn, and Co in anolyte, measured during the course of electro-remediation of SAMB soil. It may be observed that Fe, Cr and Ni were more efficiently remediated at anode as compared to Mn and Zn. The remediation efficiency of Fe was much higher as compared to Cr and Ni. In contrast, no appreciable concentration of the metal ions, Cr, Mn, Ni, Pb, Sr, and Zn were detected in the catholyte compartment during the course of electro-remediation. This may also be attributed to precipitation of these metals as different mineral phases in the catholyte compartment in response to increasing trend of pH during the first 20-25 hours of electro-remediation process.

Although, in the present investigations, Cr species were not analyzed/quantified chemically, it is important to reiterate the Cr redox chemistry to address the observed major transport of Cr towards the anolyte compartment (anode side) as compared to the feeble transport of Cr towards the catholyte compartment (cathode side). The kinetics and redox chemistry of chromium in terms of its distribution, speciation, and transformation in the saturated/unsatuarated contaminated posrous media (soils and aquifer sediments) have been extensively addressed by several researchers [24-30]. In nature, Cr is found to exist in valence states ranging from -2 to +6. However, in the subsurface soil-water environment, Cr is found to exist in the form of cationic species or anionic species depending upon its valence states +3 [Cr(III)/ trivalent chromium] and +6 [Cr(VI)/hexavalent chromium] [40]. Further, Cr(VI) is found to be much highly mobile as compared to Cr(III); due to existence of Cr in the above mentioned two different forms within the subsurface soil-water environment, the electromigaration of Cr in clayey soils can be quite a complex phenomenon [22]. For example, in the subsurface environment, naturally occurring substances like organic matter, sulfides, and ferrous iron may donate electrons and therefore, reduce hexavalent Cr to trivalent Cr. In laboratory scale electro-remediation of clays contaminated

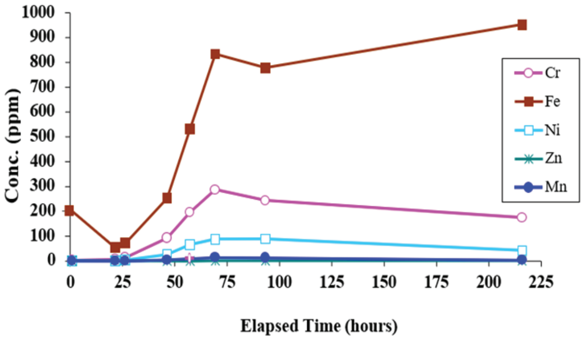

Fig. 6. Temporal variations in the concentration of metal ions in anolyte.

with electroplating wastes like Cr, Cd, and Ni, the transport of Cr(VI)/hexavalent chromium towards anode was attributed to be very much dependent on the soil type, soil mineralogy as well as presence of iron oxides in the soil [6, 9, 21, 22]. Depending upon the pH and redox conditions, Cr(VI) may exist as soluble oxyanions specifically in the form of hydrochromate ($HCrO_4^-$), dichromate ($Cr_2O_7^{2-}$) and chromate (CrO_4^{2-}) that remain in solution over a fairly wide range of pH and that these species can migrate towards anolyte compartment/anode during the electro-remediation process [25, 26, 31].

Reddy and Chinthamreddy [22] demonstrated that under applied electric field, the anionic hexavalent Cr species get easily migrated towards anolyte compartment/anode due to low adsorption of hexavalent Cr on to soil surfaces over a fairly wide range of pH. However, the cationic trivalent Cr species migrate a bit slowly towards the catholyte compartment due to higher adsorption of trivalent Cr and its precipitation as Cr(III) hydroxyl solids under slightly acidic to fairly alkaline conditions. The cationic trivalent Cr species such as $Cr(OH)^{2+}$, $Cr(OH)_2^+$ have been reported to exist over a wide range of low pH/acidic conditions and at comparatively low redox potentials, and that these may migrate towards cathode during the electro-kinetic remediation [7, 32]. At higher pH, Cr(III) precipitates as its hydroxides [$Cr(OH)_3$] between pH of 6.8 and pH of 11.3, while at higher pH values, the cationic trivalent Cr species may form anionic hydroxo-complexes like $Cr(OH)_4^-$, and $Cr(OH)_5^{2-}$ that may transport towards anode. It has also been reported that the reduction of chromium from Cr(VI)/hexavalent chromium to Cr(III)/trivalent chromium may occur before the process of electro-kinetic washing of soil depending upon amount and the type of reducing agents present in the soil [21, 32].

Reddy and Chinthamreddy [21] and Saleh *et. al* [24] have extensively discussed the impact of soil geochemical composition on electro-migration of Cr species. These researchers reported that in the presence of humic acid, minimum reduction of Cr(VI) to Cr(III) occurred, whereas in the presence of sulfides, maximum reduction of hexavalent Cr to trivalent Cr was found to occur and therefore, the presence of sulfides significantly retarded the electro-migration of hexavalent Cr due to reduction of Cr (VI) to Cr(III) as well as due to increase in the soil pH. In addition, the naturally occurring organic matters, ferrous iron, and sulfides in the subsurface soil environment may contribute/donate electrons and reduce hexavalent Cr to trivalent Cr, the extent of which depends upon prevailing geochemical conditions such as pH, redox potential, etc., as well as on the type and concentration of reducing agent(s)/ligands [21, 24]. Kim *et al*. [29] also reported Chromium(VI) reduction by Hydrogen Sulfide in aqueous media. In experimental studies of hexavalent Cr reduction by the organic matter in various types of soils, it was reported that Cr(VI) reduction was higher in low pH soils [27]. Laboratory investigations on hexavalent Cr reduction in different subsoils containing small amounts of Fe(II) and organic matter revealed that only acidic subsoils caused reduction of hexavalent Cr [26]. The rate of reduction of Cr(VI) to Cr(III) was found to increase with decrease in pH below 4. Under acidic conditions, the reduction of Cr(VI) by Fe(II) and by organic matter were equally important. It was also reported that depending on pH, the Cr(VI) reduction in acidic subsoils also resulted in the precipitation of $(Fe,Cr)(OH)_3(am)$. The type of subsoil material, the content and the form of Fe as well as the solid to solution ratio may pose significant effect on the reduction of hexavalent Cr [27, 33]. Laboratory investigations revealed that Cr(VI) may be reduced in the presence of Mn^{2+} at pH values higher than 7.2 [27]. The reduction of anionic Cr(VI) to cationic Cr(III) species may be caused to various extents by different reducing agents present in the soil/water environment. In a sandy aquifer, about 30% of Cr(VI) was found reduced to Cr(III) [28]. Lastly, as mentioned earlier, mostly, heavy metals like Pb, Cd, Ni, Co, Cu, Cr, etc. may coexist in the form of cationic species within a specific contaminated hydrogeological system and that depending upon the soil type, there may be synergistic effects of co-existing Ni(II) and/or Cd(II) on removal of Cr(VI) [21, 33].

4. CONCLUSIONS

In the present study bench scale electrokinetic remediation experiment on SAMB soil collected besides tannery waste effluent pond in Sambrial town (Punjab Province, Pakistan) has been investigated. The electrokinetic remediation efficiency for Cr and associated metals such as Cu, Fe, K, Mn, Ni, Pb and Zn was established through mass balance calculations using the contents of these metals in the SAMB test soil contained within the electrolytic cell before and after electroremediation. Cr was mainly detected in the anolyte compartment and it was quite feebly detected in the catholyte compartment. This shows that Cr was present in the test soil in the form of Cr(VI) as well as Cr(III) depending upon the redox of the cell during the course of experiment. It is presumed that the reduction of Cr(IV) into Cr(III) might have been triggered by the presence of reducing agents like Mn and Fe, changes in redox conditions within the test soil (due to significant changes in the pH and redox potentials at the electrodes owing to electrolysis reactions under the influence of applied electric field); and soil moisture contents, which ultimately retarded the transport of Cr(III) due to high pH conditions in soil in the vicinity of catholyte compartment. It is concluded that further experimentation is recommended to identify the most appropriate recipe for efficient removal of Cr and associated contaminants from tannery waste affected soils such as in Sambrial (Pakistan) in a cost effective and environmentally safe manner.

5. ACKNOWLEDGEMENTS

Financial support provided by the Higher Education Commission (HEC), Islamabad to Ms. Maria Khalid facilitated accomplishment of field sampling, laboratory scale electro-remediation studies and metal analysis in soil and aqueous electrolyte samples in connection with PhD studies at the Institute of Geology as well as College of Earth & Environmental Sciences, University of the Punjab, Lahore, Pakistan. Metal analysis and SEM analysis at CAF Division and Physics Division, respectively, PINSTECH are gratefully acknowledged.

6. CONFLICT OF INTEREST

The authors declare no conflict of interest.

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