Reducing Agents Enhanced Electrokinetic Soil Remediation (EKSR) for Heavy Metal Contaminated Soil

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ABSTRACT: *Reducing agents-Enhanced electrokinetic Soil Remediation (EKSR) was performed for the removal of chromium (Cr), cobalt (Co) and nickel (Ni) from contaminated soil. The reducing agents oxalic acid and ascorbic acid were investigated under constant voltage gradient (2.0 V/cm), current changes, pH, redox potential, concentration changes and removal performance of Heavy Metals (HMs). The results indicated that the reducing agents were effective in the desorption of metals at the cathode with catholyte conditioning pH. The removal performance of heavy metals in reducing agents-enhanced EKSR was about 2-2.5 times more than in unenhanced treatment. The amount of HMs migrated to the catholyte was more than in the anolyte, which might be evidenced that the negatively charged metal-oxalate/ascorbate complexes migrated via electroosmosis. However, positively charged HM-oxalate/ascorbate complexes and free HM cations moved to the catholyte by electromigration action. Furthermore, the mass balance and cost analysis were performed for all EKSR experiments after 20 days of operation. The energy consumption per cubic meter of treated soil was 1104-18496 kWh/m³ and the total cost was about US$ 110.4-2095, including the cost of the enhancing agents. The study demonstrated that reducing agents-enhanced EKSR is cost-effective and efficient in the removal of HMs from contaminated soil.*

KEYWORDS: *Heavy metals; Electrokinetic remediation; Reducing agents; Ascorbic acid.*

INTRODUCTION

Heavy metal content generally occurs in the earth's crust in the various forms of rock fragments and sediments. Mining industries and allied metal ore milling operations are carried out in many countries. A large quantity of discharged waste will be generated and accumulated at overburden dumps particularly in the granite mining industry [1]. The discharged waste is the main source of potentially toxic Heavy Metals (HMs) such as lead (Pb), arsenic (As), cadmium (Cd), zinc (Zn), copper (Cu), manganese (Mn) and which may have

adverse effects on the environment. The heavy metals have an atomic density more than 4000 kg/m^3 or five times greater than water and they are natural components of earth crust [2]. Many studies are reported the significant role of organic acids on metal dissolution for silicate minerals and polluted soils, and discussed the feasibility of soil remediation using small molecular mass of organic acids, including acetic, citric, oxalic, ascorbic and succinic acid, particularly, in HM contaminated soils [3–7].

The electrokinetic remediation technologies can be used to remove the charged chemical species such as HMs, radionuclides and organic pollutants from contaminated soils [8]. The metal ions could be desorbed under acidic environment generated from the anode during electrokinetic process [9]. The acid conditioning environment was more prominent for the removal of cationic heavy metals [10]. The electrokinetic technology has been successfully used in the removal of HMs and organic pollutants from contaminated soils [11, 12]. The removal of HMs from clayey soil was investigated in many field applications using electric current [13]. During electrokinetic treatment, an electrical voltage is applied to accelerate the transport of organic or inorganic contaminants towards the electrode compartments. These ions are moved between the anode and cathode electrodes by electromigration and electroosmosis action [14]. The ElectroKinetic Soil Remediation (EKSR) technology can be used to remove the contaminants even, from low permeability soils in soil decontamination studies [15]. It is extremely difficult to remediate the soils with less permeability, an extreme cation exchange capacity and high buffering capacity. In order to cope up these problems, enhanced electrokinetics have been developed as more prominent for the remediation of HM contaminated soils [16].

Some researchers conducted the electrokinetic process in order to enhance the remediation efficiency with various applications such as catholyte conditioning pH, by using chemical reagents to increase the solubility of metals, use of ion selective membranes to exclude OH$^-$ ion transport from the cathode compartments to the soil matrix, and circulating the electrolytes to maintain the pH of electrolytes in electrode compartments [17–20]. An enhanced electrokinetic process was well explained in laboratory studies for the removal of copper(Cu) and nickel(Ni) from municipal sludge [21].

The aim of this study was to investigate the electrokinetic removal of chromium, cobalt, and nickel from contaminated soil. In this aspect, the reducing agents such as oxalic and ascorbic acid were used to enhance HM extraction from the soil. Furthermore, the mass balance was used to evaluate the removal and residual amounts of metal content in the soil before and after EKSR treatment. In the economical aspect, the cost analysis of EKSR system was used to determine the cost of enhancers and the electrical energy expenditure for 20 days of the operation. In this study, the targeted HMs (Cr, Co, and Ni) were utilized, due to their mobility and simply migrate from soil surface to the pore fluid under enhanced conditions.

EXPERIMENTAL SECTION
Characterization of soil

Mining dump soil was collected from the top layer of soil (0-30cm) from the granite industry at Chimakurthy, India. The collected samples were sieved through a series of 4.75-0.002 mm mesh nylon fibre sieves for the removal of any unwanted materials such as vegetation, fragments, and large material. Finally, samples were well homogenized and kept in inert zip plastic bags at ambient conditions for further study [22-24]. The physical and chemical characteristics of the tested soil, prior to electrokinetic remediation, are reported in Table 1.

Reducing agents

The removal efficiency of HMs depends on the presence of oxidising or reducing agents during electrokinetic remediation of contaminated soils [25-28]. In the case of high acid or base buffer capacity of the soil has more resistance to change its pH. It is extremely difficult to reduce the pH of the soil by the generation of H$^+$ ions in the electrolysis or incorporation of acids to the soil. Hence, other enhancement agents are to be used to desorb the HM contaminants from the soil particle surface and make them in the dissolved phase. The incorporation or injection of reducing agents during EKSR process of contaminated soil is equivalent to coupling electrochemical remediation with redox reactions to remediate the contaminated soils. Redox reactions can be used to enhance the extraction of contaminants or to reduce their toxicity from contaminated soils. The most common reducing agents such as Fe^{+2}, Fe^0, calcium polysulfide, or sodium dithionite are used to mitigate the contaminants [29]. Acid conditioning was effective in the removal of cationic heavy metals. Reducing agents have been

Table 1: The physical and chemical properties of soil used in this study.

Soil characteristics		Units	Value	Method
Gravel (>4.75 mm)		%	36	Sieve analysis
Sand	Coarse (4.75-2.00 mm)	%	12.81	Sieve analysis
	Medium (2.00-0.425 mm)	%	13.06	Sieve analysis
	Fine (0.425-0.075 mm)	%	11.91	Sieve analysis
Slit (0.075-0.002 mm)		%	13.02	Sieve analysis
Clay (<0.002mm)		%	14.12	Sieve analysis
Porosity		-	0.44	Permeability method
pH		-	9.8	1:2.5 soil/water slurry
Electrical Conductivity		μS/ppm	147.97	1:5 soil/water slurry
Zeta Potential		mV	-26.5	Electokinetic method
Total dissolved salts (TDS)		mS/ppm	173.18	1:5 soil/water slurry
Moisture		%	0.92	Drying method at 125^0C
Total Inorganic Matter		%	97.57	Drying method at 500^0C
Total Organic Matter		%	1.44	Drying method at 500^0C
Chromium		mg kg^{-1}	192	Acid digestion
Cobalt		mg kg^{-1}	175	Acid digestion
Nickel		mg kg^{-1}	204	Acid digestion
Copper		mg kg^{-1}	363	Acid digestion
Zinc		mg kg^{-1}	505.1	Acid digestion
Manganese		mg kg^{-1}	704	Acid digestion

effectively used to extract the heavy metals bound to the soil. Therefore, Strong reducing agents such as 0.1 M of dithionite was effective in the extraction of HMs strongly bound to the soil, while weak reducing agents such as 0.01 M of a dithionite or 0.1 M of oxalate/ascorbic acid were effective in the extraction of HMs that were relatively weakly bound to the soil [30].

Experimental apparatus

A laboratory-scale electrokinetic reactor was used in this study. The reactor was made of Plexiglas with dimensions of 30cm x 20cm x 15cm and two electrode compartments with dimensions of 5cm x 20cm x 15cm and soil matrix with dimensions of 20cm x 15cm x 5cm with a working volume of 1.5L. The two folded filter papers (Whattman 42) were placed between the soil matrix and the electrode compartments to avoid the outflow of the soil from the soil matrix to the electrode

chambers. The graphite electrodes with dimensions of 15cm in height and 1.5cm in diameter were used as anode and cathode. Multi-meter was used to measure the current intensity and voltage drop during EKSR process. Digital pH meter was used to test the pH of the anode reservoir, cathode reservoir, and different soil sections periodically during the course of the operation. Regulated DC power supply with voltage ranged from 0 to128V and 5A maximum current flow in output was used during EKSR experiments. As seen in Table 2, the electrode compartments were filled with prior prepared processing fluids. Fig. 1 represents the schematic experimental design set-up for EK reactor.

Experimental design

In this study, four EKSR experiments were carried out for four electrokinetic manipulation patterns as shown in Table 2. For unenhanced-EKSR Exp.1, both electrode

Table 2: Experimental conditions of four EKSR experiments.

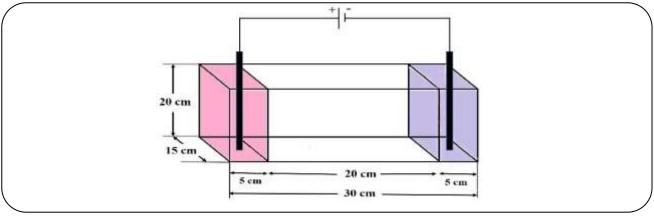| Exp.No	Anolyte purging solution	Soil saturation	pH	Catholyte purging solution	Duration (Days)	Voltage potential (V/cm)
1	Distilled water	Distilled water	9.7	Distilled water	5,10,15,20	2
2	Distilled water	0.1M Oxalic acid	4.5	0.1M Oxalic acid	5,10,15,20	2
3	Distilled water	0.1M Ascorbic acid	5.5	0.1M Nitric acid	5,10,15.20	2
4	Distilled water	0.1M Oxalic acid+0.1M Ascorbic acid	5.5	0.1M Nitric acid	5,10,15,20,	2

Fig.1: Experimental design set-up for EKSR reactor.

(anode and cathode) compartments were filled with double distilled water. In the case of oxalic acid-enhanced EK Exp.2, the soil was saturated with 0.1M of oxalic acid and pH was adjusted to 4.5 prior to the experimentation. The anode compartment was filled with double distilled water and the cathode compartment was filled with 0.1M of oxalic acid of 500 mL. In the case of ascorbic acid-enhanced EKSR Exp.3, the soil was pre-saturated with 0.1M of ascorbic acid and pH was adjusted to 5.5. Both the electrode (anode and cathode) compartments were filled with double distilled water and 0.1M of nitric acid about 500 mL. In Exp.4, the soil was pre-saturated with 0.1M of ascorbic acid and 0.1M of oxalic acid and pH was adjusted to 5.5. Both electrodes (anode and cathode) compartments were filled with double distilled water and 0.1M of nitric acid to supress the alkali environment at the cathode side. The anolyte and the catholyte solutions were replaced by freshly prepared solutions everyday once, in order to maintain the uniformity in the properties of electrolytes during the electrokinetic process. Prior to experimenting, approximately, 2000 g of dry soil mixed with1000 mLof distilled water in a separate plastic tray and stirred manually for several minutes to achieve homogeneity for Exp.1. In Exp.2,

approximately, 2000 g of dry soil mixed with1000 mL of oxalic acid and in Exp.3, 2000 g of dry soil mixed with1000 mL of ascorbic acid, and Exp.4, 2000 g of dry soil mixed with 500 mL of each oxalic acid and ascorbic acid to reduce the soil pH and stirred manually for 30 minutes to achieve homogeneity.

A uniform voltage gradient 2 V/cm was provided to the slurry soil matrix for all the experiments and treated for twenty days. Two graphite electrodes as anode and cathode were placed within the electrokinetic cell and supplied with the electric current. The current intensity and the pH were continuously monitored daily by inserting multi-meter and pH probes directly in to the anode and cathode reservoirs under steady state conditions. The anolyte and catholyte were drained once each day and kept aside for the analysis of HM concentrations. The extracted 1g of soil and 5 mL of distilled water were placed in a 50mL beaker and stirred with glass rod for 10min., and then the pH was recorded, similar trend was repeated for other sections of extracted soil from soil matrix. Soil samples were collected from four soil sections of the soil matrix after 5, 10, 15 and 20 days of treatment in order to determine the heavy mental concentrations.

Research Article

Determination of heavy metals concentration

The HM concentrations in the soil before and after EKSR treatments were measured by the strong acid digestion process. The soil of 2g was weighed accurately and digested with aqua regia (20 mL of HCl and HNO_3) and heated at 100^0C over hot plate chamber for 30 min. Then diluted with 100 mL distilled water to acid digested samples and simultaneously filtered through 42 Whatman filter paper [31]. The liquid extracts were analysed for HMs concentration by means of Atomic Absorption Spectroscopy (AAS) using Varian AA110 spectrophotometer. Similar phenomena were repeated for two more replicates and the mean values were recorded. Further, the removal performance of HM ions during EKSR process was determined using the following expression [12, 32–34]:

$$\text{Removal efficiency (\%):} \quad \frac{C_0 - C_f}{C_0} \times 100 \tag{1}$$

Where, C_0, C_f are initial and final concentrations (mg/kg) of the soil before and after EKSR treatment.

Determination of electrical energy consumption

The cost of the process is directly proportional to the cost of the electrical energy expenditure and the cost of the enhancing reagents used in the process. The energy expenditure is directly related to the integral time of the electric current passing across the electrokinetic cell [35, 36]. *Ma et al.*, 2010; and *Pedersen et al.*, 2015 used the equation (2) to calculate the electrical energy consumption during electrokinetic removal of heavy metals from contaminated soils. We modified the equation (2) into equations (4 and 5) and proposed to determine the cost of electrical energy and the total cost of EKSR process including the cost of enhancers by incorporating Equation (3). The cost per volume of treated soil can be expressed by using the economic models for enhancers, electrical energy, and the total cost of the process as:

$$\text{Energy expenditure } (E_e) = \frac{P}{V_S} = \frac{1}{V_S} \int_0^t VI dt \tag{2}$$

$$\text{Cost of the enhancers } (E_C) = \frac{1}{V_S}\left[\sum_i^n (m_i \times c_i)\right] \tag{3}$$

Cost of the electrical energy (EE_C) (4)

$$= \frac{1}{V_S}\left[\left(10^{-3}\int_0^t VI dt\right)C_c\right]$$

Total cost of the process (T_C) (5)

$$= \frac{1}{V_S}\left[\sum_i^n (m_i \times c_i) + \left(10^{-3}\int_0^t VI dt\right)C_c\right]$$

Where T_C is the total cost of the process, V_S is the volume of the soil (m^3), m_i is the consumption of enhancing reagent (kg), c_i is the cost of enhancing reagent (U\$/kg), C_c is the cost of the electrical current (U\$/kWh), and t is the remediation time (h).

RESULTS AND DISCUSSION

Current density variation during EKSR process

The variation of current density depends on the operating time as shown in Fig. 2. The current density was observed at a relatively low level in unenhanced EKSR experiment (Exp.1) due to the scale formation of metal hydroxides as precipitates at the surface of the cathode electrode and leads to high resistance zone to the passage of current. In case of the enhanced EKSR experiments from Exp.3 to Exp.4, the current density suddenly raised from 0 to 6.5 mA/cm^2 and then slowly decreased to zero again. During the first 24 hours of EKSR process, Exp.2 reached about 3.5 mA/cm^2, Exp.3 reached about 5.5 mA/cm2 and Exp.4 reached about 6.5 mA/cm2 after 2h. Then, attaining a maximum peak level, the current density curve started to decrease for four EKSR experiments and reached to zero. The current density gradually reducing in the course of time, might be caused by reduction of electrolytes, scale formation due to salts of metal hydroxide complexes and polarization of electrodes. The enhancing electrolytes were replaced every day once for all the four EKSR treatment processes for Exp.2-4. The use of 0.1M oxalic acid and nitric acid as pH controlling electrolytes at the cathode suppressed the developing high pH environment and as well as to reduce the scale formation due to metal hydroxide complexes close to cathode compartment. Moreover, bulk quantity of ions was incorporated to catholyte and the soil, leading to increase the current density across the soil matrix. The result shows that pre-treatment of soil or soil saturated with oxalic and ascorbic acid solutions caused
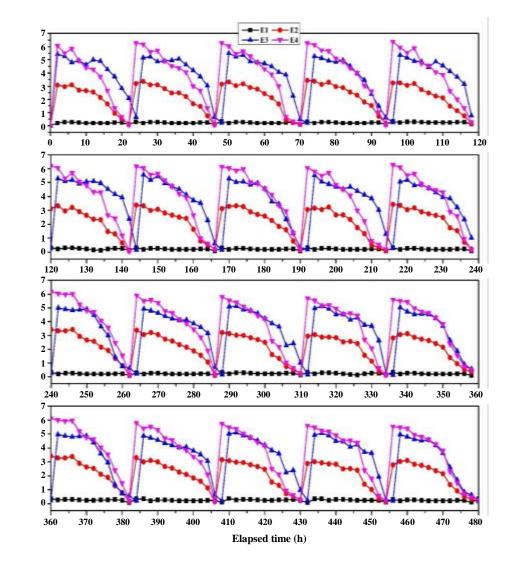
Fig.2: Time course of current density during EKSR treatment. Exp.1: Unenhanced EKSR;
Exp.2: oxalic acid-enhanced EKSR; Exp.3: Ascorbic acid-enhanced EKSR;
Exp.4: Oxalic acid+ascorbic acid -enhanced EKSR; Variation of soil pH during EKSR process.

an increase in the electrical conductivity of the soil. This solution improved desorption of metal ions onto the surface of the soil into the pore solution and accelerate the current density at uniform applied electric potential. Generally, oxalic and ascorbic acids act as moderate reducing agents and provide migration of ions for the soil.

Variation of soil pH during EKSR process

The variations of pH in different soil sections depend on time and space during EKSR experiments as depicted in Fig. 3. The pH of the soil gradually increased with time near the cathode compartment and decreased

to about 3.0 or lower near the anode compartment because of production of H^+ ions due to water electrolysis at the anode compartment. In case of Exp.1, the anolyte and catholyte purging solution used as distilled water with a pH of 6.88, initially the soil pH was 9.7, at the end of EKSR experiment, the soil pH near the cathode compartment was reached 13.5, and it was declined step by step in a horizontal phenomenon and reached about 7.0 at the anode chamber. The soil pH was reduced from 9.7 to 6.9 near the anode, which was 5cm from anode zone, while soil pH was raised from 9.7 to 13.5, which was 20cm from anode zone, while the anolyte and catholyte pH ranged from 6.88 to 3.5 and 6.88 to 14
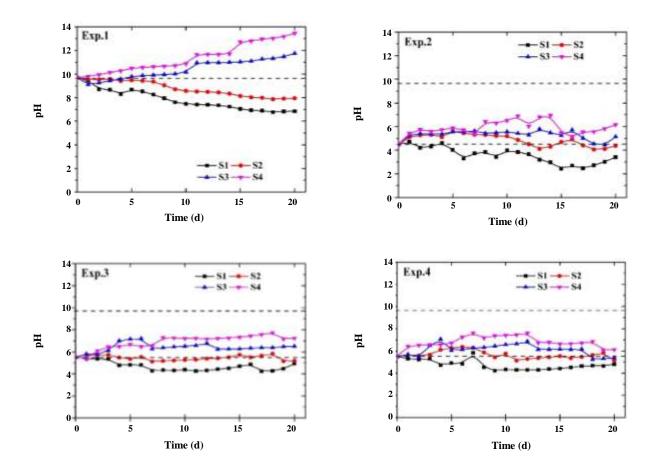
Fig. 3: pH change in time. Exp.1: Unenhanced EKSR; Exp.2: Oxalic acid-enhanced EKSR;
Exp.3: Ascorbic acid-enhanced EKSR; Exp.4: Oxalic acid+ascorbic acid-enhanced EKSR; S1, S2, S3 and
S4: 5, 10, 15 and 20 cm from anode compartment, respectively.

at anode and cathode. The pH pattern is typical of unenhanced EKSR treatments and caused primarily due to an electromigration action of H^+, OH^- and HCO_3^- between the anode and the cathode zones. It can be seen from Fig. 3, Exp.2-4, that from Table 2, were carried out for four EKSR manipulation experiments with reducing agents such as 0.1M oxalic acid and ascorbic acid and HNO_3 used as catholyte purging solutions to maintain an acidic environment of the soil.

It is observed from Fig. 3, that the variation in pH of the soil at different soil portions near the cathode in these later EKSR treatments were dramatically different from those in Exp.1. From Fig. 3, the enhanced EKSR experiments (Exp.2-4) indicate that the soil pH was lower than untreated soil's initial value of 9.7. The soil pH values gradually decreased from anode compartments due to the generation of H^+ ions at the anode and migrated towards the cathode. As found in Exp.2, the pH of soil

fluctuated and changed to 3.4 from initial value of 4.5 at anode side, while it was close to 5-6 at cathode side, due to the catholyte conditioning pH with oxalic acid and the generation of acidic front over alkali environment. The same pattern of slowly decreasing in pH of soil to 4-5 at anode side, and gradually increasing from an initial value of 5.5 to 7 at cathode side, in Exp.3-4 were observed, this might have been the depletion of electrolytes and the generation of alkali front at the cathode compartment. In these Exp.3-4, the soil pH values changed lightly from 5.5 to 7 because of pH maintaining daily by replacing the catholyte purging of 0.1M nitric acid solution. The soil pH values gradually increased from cathode compartments due to the generation of OH^+ ions at the cathode and migrated towards the anode. The effect of pre-treatment or soil saturated with 01.M of oxalic acid and ascorbic acid solutions on final soil pH was significantly affected. The results indicated that the soil
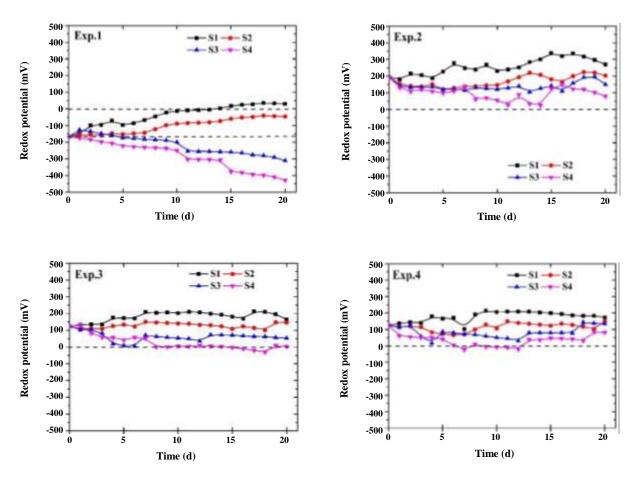
Fig. 4: Redox potential change in the course of time. Exp.1: Unenhanced EKSR; Exp.2: Oxalic acid-enhanced EKSR;
Exp.3: Ascorbic acid-enhanced EKSR; Exp.4: Oxalic acid+ascorbic acid-enhanced EKSR; S1, S2, S3 and
S4: 5, 10, 15 and 20 cm from anode compartment, respectively.

saturation with reducing agents (oxalic and ascorbic acid) and the catholyte replacing with nitric acid were effective in controlling pH of the soil.

Variation of soil redox potential during EKSR process

The variation of redox potential profiles in the soil at different sections for all the experiments is shown in Fig. 4. The redox potential of the soil sections was continuously measured every day at four sections from the anode: 5, 10, 15 and 20 cm respectively. The distribution of redox potential of the soil depends upon the initial pH, acid buffer capacity, base buffer capacity, the chemical composition of soil and nature of the electrolytes and the direction of the electroosmotic action [37, 38].

Redox potential follow the variations of pH, within the soil matrix, oxidizing conditions prevailed near the anode compartment about 400mV, the middle of the soil matrix about 200mV and the soil section close to the

cathode was about -200mV, where the reducing conditions prevailed. Therefore, the more redox potential values near the anode are because of the reduction of electrons at the anode by applying external electric field, and less redox potential values near the cathode side are because of input of electrons from the external electric power supply [26, 37].The variation of redox potential significantly affected by electrolyte solutions such as oxalic acid, ascorbic acid, and nitric acid.

Unenhanced EKSR process

The acid-digestion derived heavy metal content residual within the soil cell varying with time during unenhanced EKSR treatment. Generally, HMs are moved between the anode and the cathode via electromigration and electroosmosis process [14]. As observed, the removal efficiency of HMs increasing with increasing the treatment time from 5 to 20 days. From this, for various
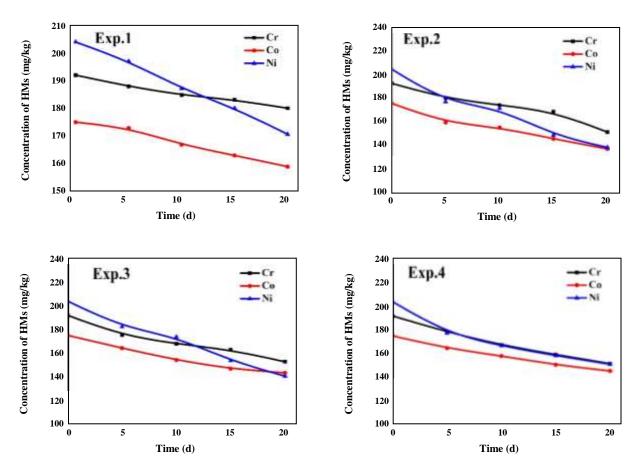
Fig. 5: Concentration change of HMs in the course of time for four EKSR experiments.

remediation times, it is observed that longer remediation times increases the removal of HMs within the soil close to the anode due to high acidic front formation. As seen in Fig. 4, in Exp.1, the concentration profiles of HMs are shown with a function of time. In the case of Exp.1, the catholyte pH controlling was not carried out for the EKSR process (20d), the concentration of HMs reduced for chromium from 192 mg/kg to 180 mg/kg, for cobalt 175 mg/kg to 158 mg/kg and for nickel from 204 mg/kg to 170 mg/kg, respectively. It can be seen from Fig.5, in Exp.1, the percentage removal of HMs for chromium about 6.22%, for cobalt about 9.2% and for nickel about 16.34% respectively after 20 days of operation. The removal percentage of HMs are higher in anolyte than catholyte due to high acidic front generated at anode compartment, where HMs were precipitated.

Reducing agents enhanced EKSR process

The reducing agents extracted HMs residuals in soil cell depends on time during enhanced EKSR process.

The concentration profiles and percentage removal of HMs are depicted in Figs. 5 and 6. In Exp.2, the catholyte conditioning was carried out using 0.1M of oxalic acid, at the end of the EKSR process (20d), the removal efficiency of HMs increasing over treatment time because of the migration of positive charge heavy metal ions towards cathode via electromigration. It is observed that the removal of all heavy metals was more in oxalic acid enhanced EKSR treatment than unenhanced treatment, because of easy desorption and quick migration of metal ions onto the soil surface to pore water at acidic environment. After 20d of the operation, it can be seen from Fig. 5, in Exp.2, the concentration of HMs are reduced for chromium from 192mg/kg to 150.62mg/kg, for cobalt 175mg/kg to 136.37mg/kg and for nickel from 204mg/kg to 137.66mg/kg, respectively. As seen in Fig. 6, in Exp.2, the percentage removal of HMs for chromium about 21.55%, for cobalt about 22.07% and for nickel about 32.52% respectively. The results demonstrate that the electrokinetic removal of HMs
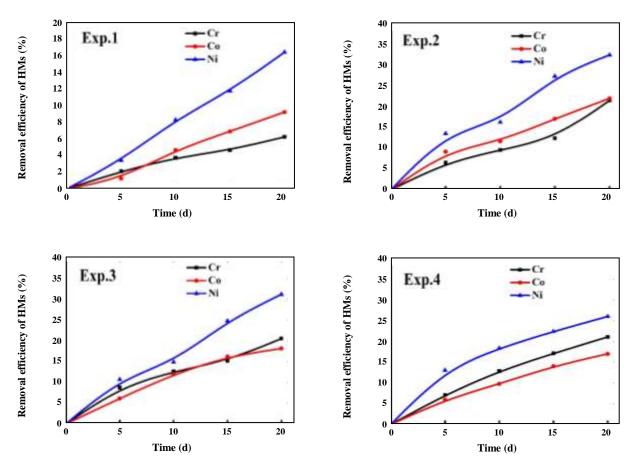
Fig. 6: Removal of HMs in the course of time for four different EKSR experiments.

in oxalic acid-enhanced EKSR was about 2.5 times when unenhanced process.

From Figs. 5 and 6, in Experiment 3, the soil was saturated by 0.1M ascorbic acid and catholyte pH controlling using 0.1M of HNO₃ solution were performed. The HMs migration was more significant due to the catholyte conditioning during EKSR treatment due to easy desorption of metal ions onto the soil surface to pore water under acidic environment. The concentration of heavy metals is rapidly decreased in the soil. After 20d of the operation, it can be seen from Fig. 5, in Exp.3, the concentration of HMs are changed for chromium from 192 mg/kg to 152.6mg/kg, for cobalt 175 mg/kg to 143.22mg/kg and for nickel from 204 mg/kg to 140.43mg/kg, respectively. As seen in Fig. 6, in Exp.3, the percentage removal of HMs for chromium about 20.5%, for cobalt about 18.16% and for nickel about 31.17% respectively. The removal percentage of HMs are higher in anolyte than catholyte due to high acidic front generated at anode compartment, where HMs

were precipitated. The results demonstrate that the electrokinetic removal of HMs in ascorbic acid-enhanced EKSR was about 2.2 times when unenhanced process.

From Figs. 5 and 6, in Exp.4, the soil was saturated by 0.1M ascorbic acid and catholyte pH controlling using 0.1M of HNO₃ solution were performed. The HMs migration was more significant due to the catholyte conditioning during EKSR treatment due to the easy desorption of metal ions onto the soil surface to pore water under acidic environment. The concentration profiles of HMs are rapidly decreased in the soil. After 20d of the operation, it can be seen from Fig. 5, in Exp.3, the concentration of HMs are changed for chromium from 192 mg/kg to 151.47mg/kg, for cobalt 175 mg/kg to 145.25mg/kg and for nickel from 204 mg/kg to 150.88mg/kg, respectively. As seen from Fig. 5, in Exp.3, the percentage removal of HMs for chromium about 21.11%, for cobalt about 17.02% and for nickel about 26.04% respectively. The removal percentage of HMs are higher in anolyte than catholyte due to high acidic

Table 3: The removal efficiency (%) of HMs in Unenhanced Exp.1 and Reducing agents Enhanced Exp.2-4.

HM	Exp.1	Exp.2	Exp.3	Exp.4
Cr	6.22	21.55	20.52	21.11
Co	9.2	22.07	18.16	17.02
Ni	16.37	32.52	31.16	26.04
Avg.	10.60	25.38	23.28	21.39

front generated at anode compartment, where HMs were precipitated. The results demonstrate that the electrokinetic removal of HMs in the combination of oxalic acid and ascorbic acid-enhanced EKSR was about 2 times when an unenhanced process. The overall results demonstrate that the electrokinetic removal of HMs in reducing agents-enhanced EKSR was about 2-2.5 times when unenhanced process. Table 3 shows the average removal efficiency (%) of HM in Unenhanced Exp.1 and Reducing agents Enhanced Exp.2-4.

The relative concentration of HMs and removal efficiency of all EKSR experiments

The normalized concentration profile and removal efficiency of HMs for four different EKSR experiments are presented in Fig. 7. After all the EKSR experiments, the heavy metal ionic concentrations dramatically less than their initial concentration ($C/C_0 < 1$). For Cr(VI), all the four experiments after 20 days, the lowest residual concentration was 150.62 mg/kg and the highest removal efficiency was about 21.55% in Exp.2, it can be seen in Fig. 7 (a and b), when 0.1M of oxalic acid was used as conditioning catholyte solution. It was significant removal in Exp.4 as residual concentration and removal content were about 151.47mg/kg and about 21.11% respectively. In Exp.4, the removal content of Cr(VI) might have been reduced due to sodium complex precipitates formation. In the case of Exp.3, the removal content was about 20.52% due to high resistance to the current flow and desorption of ions from the soil because of excess sodium precipitates formation onto the surface of the cathode electrode.

In case of cobalt, after 20d operation in all the four experiments, the lowest residual concentration was 136.37mg/kg and the highest removal efficiency was obtained about 22.07% in Exp.2, As seen in Fig.7(c) and Fig. 7(d), when 0.1M of oxalic acid was used as conditioning catholyte electrolyte, which is a metal

complex formation with Co^{+2} ions and migrated towards the cathode side. It indicated that catholyte conditioning was favourable to the removal of Co^{+2} ions. It was found that the significant removal in Exp.3 as residual concentration and removal content were about 143.22mg/kg and about 18.66% respectively. In case of Exp.4, the removal content was about 17.02%, the removal content of cobalt might be reduced due to excess metal hydroxide complexes formation.

In case of nickel, at the end of 20d operation in all In the four experiments, the lowest residual concentration was 137.66mg/kg and the highest removal efficiency was achieved about 32.52% in Exp.2, according to Fig. 7(e) and Fig. 7(f), when 0.1M of oxalic acid was used as conditioning catholyte solution, which is a metal ability complex formation with Ni^{+2} ions and migrated towards cathode side via electromigration. In Exp.3 and Exp.4, nickel was removed about 31.17% and 26.045 respectively, the removal content of nickel might be reduced due to metal hydroxide complexes formation at cathode side.

In this study, the removal of HMs during EKSR has been enhanced by catholyte conditioning with reducing agents to control the pH of soil cell and complex metal ions formation. The removal of HMs was higher in the presence of reducing agents such as oxalic acid and ascorbic acid because HMs can be easily desorbed from surface of soil into pore solution under an acidic environment. However, the desorbed metal ions can be migrated towards the cathode by electromigration under constant applied electric voltage. During enhanced EKSR treatments, the soil cell pH values are less than initial soil pH 9.7, leads to formation of carboxylic groups ($-COO^-$) as deprotonation within the heavy metal complexes. Higher HMs removal efficiencies in Exp.2 and Exp.3 could be due to metal-oxalate/ascorbate ($OA/AscA-M^+$) complex formation being higher in oxalic acid than ascorbic acid, the reaction mechanism of reduced HM (M^{n+}) ions can be expressed as follows:
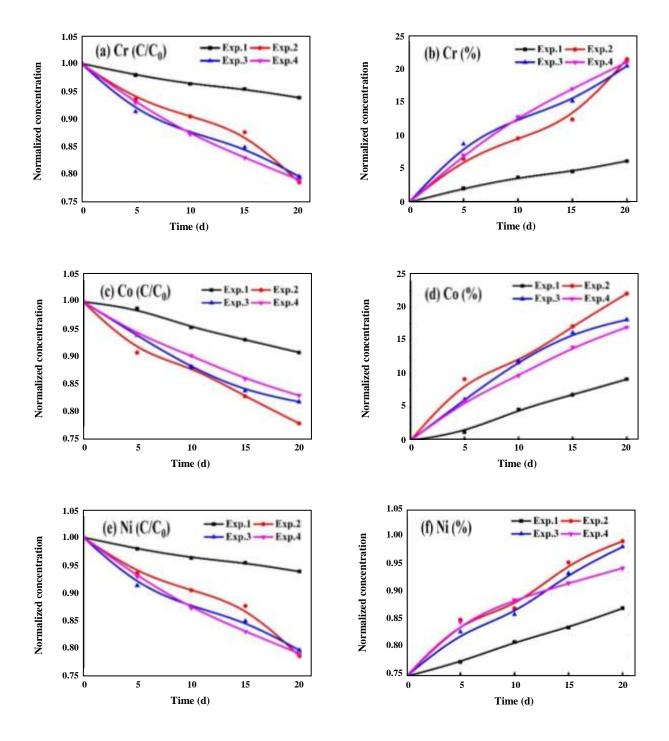
Fig. 7: Normalized concentration and removal of HMs in the course of time during four EKSR experiments..

$$OA/AscA + M^{n+} \rightarrow nH^+ + OA/AscA - M^+$$

(Metal complex)

The HM-ascorbate complexes could be expected to hold a net positively charged ions and be migrated towards the cathode via electromigration. The migration of these HM-ascorbate complexes from soil cells toward the cathode by the major driving force of electroosmosis action. Therefore, overall movement of disorpted and dissolved complex metal ions was from the anode compartment to the cathode compartment via electromigration force and electroosmosis action.

Table 4: Mass balance of HMs in EKSR system.

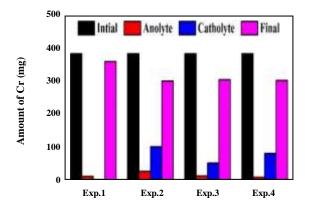| Exp. No	Intial con(mg/kg)	[a]Intial (mg)	[b]Catholyte (mg)	[c]Anolyte (mg)	Residual con(mg/kg)	[d]Soil (mg)	[e]Removal	[f]Mass balance
Mass balance of Cr								
Exp.1	192	384	11.74	1.68	180.05	360.1	6.22%	97.27%
Exp.2	192	384	102.35	28.02	150.62	301.24	21.55%	112.39%
Exp.3	192	384	52.3	13.8	152.6	305.2	20.52%	96.70%
Exp.4	192	384	81.73	9.54	151.47	302.94	21.11%	102.65%
Mass balance of Co								
Exp.1	175	350	14.75	13.42	158.9	317.8	9.20%	98.85%
Exp.2	175	350	106.11	22.07	136.37	272.74	22.07%	114.55%
Exp.3	175	350	16.54	74.38	143.22	286.44	18.16%	107.82%
Exp.4	175	350	53.17	18.42	145.21	290.42	17.02%	103.43%
Mass balance of Ni								
Exp.1	204	408	27.04	12.55	170.6	341.2	16.37%	93.33%
Exp.2	204	408	152.6	16.08	137.66	275.32	32.52%	108.82%
Exp.3	204	408	62.11	47.56	140.43	280.86	31.16%	95.72%
Exp.4	204	408	143.5	21.41	150.88	301.76	26.04%	114.37%

$$^*e = \left(1 - \frac{d}{a}\right) \times 100, \quad ^*f = \left(\frac{b+c+d}{a}\right) \times 100$$

Mass balance of EKSR system

After 20 days of operation, the mass balance of HMs was performed for anolyte, catholyte and soil collected electrokinetic cell. The calculated mass balances for three HMs for four experiments Exp.1-4 have been shown in Table 4. The mass balance of Cr (the amount of Cr in the initial, anolyte, catholyte and final) can be seen in Fig. 8. The amount of Cr(VI) desorbed from anolyte was about 9.54 to 28.02 mg, which indicates that 2.5% to 7.3% of the Cr(VI), in the soil was desorbed. It was desorbed from catholyte was about 1.68 to 102.35 mg, which indicates that 0.44% to 26.65% of the soil was desorbed. In the case of Co^{2+}, the mass balances were 98.85%, 114.55%, 107.82%, and 103.43% respectively for four EKSR experiments Exp.1-4.The mass balance of Co (the amount of Co in the initial, anolyte, catholyte and final) can be seen in Fig. 9. The amount of Co^{2+} desorbed from anolyte was between 14.75 and 74.38mg, which indicates that 4.21% to 21.25% of the Co^{2+} in the soil was desorbed. It was desorbed from catholyte was between 13.42 and 106.11mg, which indicates that 3.83% to 30.31% of the soil was desorbed. In the case of Ni^{2+}, 93.33%,

108.82%, 95.72% and 114.37% respectively for four EKSR experiments Exp.1-4.The mass balance of Ni (the amount of Ni in the initial, anolyte, catholyte and final) can be seen in Fig. 10. The amount of nickel desorbed from anolyte was between 27.04 and 47.56 mg, which indicates that 6.63% to 11.65% of Ni^{2+} in the soil was desorbed. It was desorbed from catholyte was between 12.55 and 152.6 mg, which indicates that 3.07% to 37.40% of the soil was desorbed.

In the case of Cu^{+2}, 87.05%, 83.26%, 86.25%, and 92.75% respectively for four EKSR experiments Exp.1-4. The mass balance of Cu (the amount of Cu in the initial, anolyte, catholyte and final) can be seen in Fig. 11. The amount of Cu^{+2} desorbed from catholyte was between 29.23 and 183.37mg, which indicates that 4.02% to 25.25% of the Cu^{+2} in the soil was desorbed. It was desorbed from anolyte was between 45.01 and 164.05mg, which indicates that 6.2% to 22.6% of the soil was desorbed. In the case of Zn^{2+}, the mass balance of 97.23%, 91.08%, 85.56%, and 87.04% respectively for four EKSR experiments Exp.1-4. The mass balance of Zn (the amount of Zn in the initial, anolyte, catholyte and final)
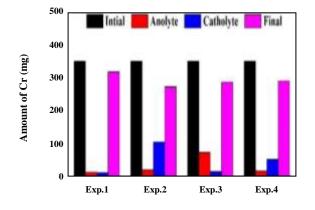
Fig. 8: Mass Balance of Cr.

Fig. 10: Mass balance of Ni.

Fig. 9: Mass Balance of Co.

Fig. 11: Mass Balance of Cu.

can be seen in Fig. 12. The amount of Zn^{2+} desorbed from catholyte was between 20.97 and 261.84mg, which indicates that 2.07% to 25.92% of the Zn^{2+} in the soil was desorbed. It was desorbed from anolyte was between 66.5 and 137.06mg, which indicates that 6.58% to 13.57% of the soil was desorbed. In the case of Mn^{2+}, the mass balance of 86.15%, 83.23%, 81.74%, and 88.59% respectively for Exp.1-4. The mass balance of Mn (the amount of Mn in the initial, anolyte, catholyte and final) can be seen in Fig. 13. The amount of Mn^{2+} desorbed from catholyte was between 80.26 and 354.05mg, which indicates that 5.46% to 24.12% of Mn^{2+} in the soil was desorbed. It was desorbed from anolyte was between 103.1 and 293.14 mg, which indicates that 7.02% to 19.96% of the soil was desorbed, which might be the reason, the oxalate/ascorbate-Mn^+ complexes moved toward cathode by electroosmosis and free manganese cations moved toward the cathode by the electromigration.
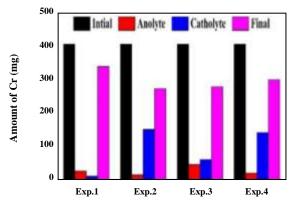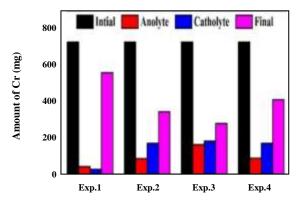
Cost analysis of EKSR process

The energy consumption is proportional to the integral time of the electric current passing across the electrokinetic cell. As seen from Table 5, for four EKSR experiments, the determined electrical energy consumption rates are 1104, 2304, 17616 and 18496 kWh/m^3 respectively. It can be seen from Table 5, the removal amounts of HMs were proportionally increasing with treatment time and enhancing solution cost, but the distilled water cost was excluded. Based on electric power consumption charges in India, the energy consumption per cubic meter of treated soil was 1104-18496 kWh/m^3, which is a cost of about US$ 110.4-1850, while adding the enhancing agents, the total cost becomes US$ 110.4-2095. The remediation cost either be increased or be decreased depending on the treatment time. Overhead costs such as capital costs, maintenance costs and other additional costs required in the field

Table 5: Cost analysis of EKSR system.

Exp. No.	Enhanced solution consumption						Electrical energy		Total cost($)
	Oxalic acid		Ascorbic acid		Nitric acid				
	consumption (kg/m³)	[a]Cost ($)	consumption (kg/m³)	[b]Cost ($)	consumption (kg/m³)	[c]Cost ($)	consumption (kWh/m³)	[d]cost($)	
1	0	0	0	0	0	0	1104	110.4	110.4
2	146.7	1027	0	0	0	0	2304	230.4	1257.4
3	0	0	26.7	320	2.8	13.4	17616	1761.6	2095
4	6.7	46.9	13.3	160	2.8	13.4	18496	1849.6	2070

[a] Cost of Oxalic acid: 7$/kg, [b] Cost of Ascorbic acid: 12$/kg, [c] Cost of Nitric acids: 4.8$/kg, [d] Average cost of electricity in India: 0.1$/k.
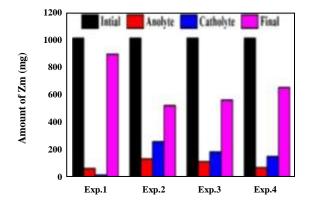

Fig. 12: Mass Balance of Zn.

Fig. 13: Mass Balance of Mn.

must be considered in to the account. Further reports on such costs will be conducted through the scale-up process at the field level.

CONCLUSIONS

In this study, Electrokinetic Soil Remediation (EKSR) technology was applied and investigated the removal of HMs from contaminated soil by using the reducing agents (oxalic acid and ascorbic acid), controlling catholyte pH with nitric acid. The removal performance of HMs in reducing agents-enhanced Exp.2-4 were about 2-2.5 times more than when unenhanced Exp.1. The amount of heavy metals migrated in the catholyte was more than in anolyte in case of in all electrokinetic experiments, which might be evidenced that the negative charged HM-oxalate/ascorbate metal complexes were migrated via electroosmosis action and positively charged metal ions (free cations) moved to the catholyte by electromigration action. The removal performance of heavy metals in enhanced conditions were more due to the common reducing properties of oxalic and ascorbic acid, included
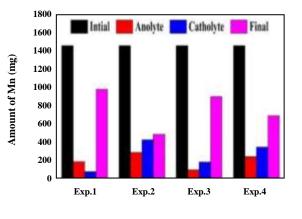
chemical binding, and the solubility enhancement in an acidic environment. It was concluded that Cr(VI), Co^{2+} and Ni^{2+} removal can be enhanced by oxalic and ascorbic acid as reducing agents and the catholyte controlling pH with nitric acid.

Furthermore, the mass balance of HMs was performed for all EKSR experiments before and after 20 days of operation. The calculated average mass balance of Cr(VI), Co^{2+} and Ni^{2+} are 102.25%, 106.16%, and 103.064% respectively with an error about 2-6%, which demonstrates that the maximum amount of Ni^{2+} was desorbed by both anolyte and catholyte under enhanced conditions. The energy consumption per cubic meter of treated soil was 1104-18496 kWh/m³ and the total cost was about US$ 110.4-2095, including the cost of the enhancing agents used in this study. Hence, the actual required cost of the electrical energy and enhancing agent's consumptions could vary depending upon the amount of HM contaminated soil and the treatment time. Further studies can be performed to attain a maximum elimination of heavy metals by using effective reducing

agents and combination with chelating agents at the same time to perform the cost optimization in order to reduce the cost of the process.

Acknowledgment

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