

Removal of heavy metals from sandy soil using CEHIXM process

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Received 5 November 1999; received in revised form 21 August 2000; accepted 22 August 2000

Abstract

This paper presents the results of a new process of soil decontamination termed as couple electric-hydraulic gradient assisted by ion exchange medium (CEHIXM) in which a hydraulic gradient is coupled with electric gradient in a non-conventional arrangement for the purpose of electrolysis and ion transport. A suitable ion exchange medium was used to capture and subsequently recover the cations. In this process, heavy metals no longer precipitated in the treated soil near the pretreatment zone. The cations were transported out of the soil and captured in the ion exchange medium. Several laboratory tests were conducted to examine the removal of Pb, Cd, Zn and Mn from sandy soils. The experimental results demonstrated the removal efficiencies more than 97% for all the four heavy metals at an energy expenditure of 345 kW h/m³ of soil. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Soil remediation; Heavy metals; Electrolysis; Sandy soil; Ion exchange resin

1. Introduction

The contamination of soil and groundwater resources by hazardous wastes is a problem around the globe that poses a serious threat to life and the environment. During the past several decades, the need has grown for developing cost effective and efficient techniques for in situ remediation of large volumes of contaminated soil. Recently, electrokinetic decontamination (EKD) technology has received considerable attention which offers the possibility of transport and remediation of contaminants in the cases where conventional techniques are not feasible [1,2]. The EKD technique is applicable to soils of high surface charge and

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low permeability [3,4]. But in sandy/silty soils EKD is slow or ineffective due to the limited surface conductivity and high permeability of the soil.

In EKD technology, electroosmosis and ionic migration are the dominant transport mechanisms. Electroosmosis is defined as the movement of a fluid due to an applied electric field relative to a stationary soil mass due to the existence of the diffuse double layer at the soil particle surface–pore fluid interface. The second mechanism, ionic migration, is the movement of ions in the pore solution under the influence of an electric field. When an electric field is applied to a wet soil mass, positive ions are moved toward the negative electrode and the negative ions toward the positive electrode. The potential of electrokinetic soil decontamination has been described by many researchers [3–7]. The detailed description of the electrokinetic flow processes and the associated complicated features generated by electrochemical reactions are given by different authors [8–12].

An electric field is applied across the soil being treated in the conventional EKD technology. Therefore, the hydroxyls generated at the cathode are transported into the soil, causing an increase in soil pH near the cathode. Many heavy metals precipitate at high pH. Furthermore, a high pH favors the sorption of heavy metals onto the surface of the soil mass, causing high metal concentration in the cathode region after remediation. In this study, a new approach related to the technology has been proposed and examined by laboratory experiments. This approach eliminates the need for external chemicals and the precipitation of heavy metals in the cathode region. The schematic diagram of the approach is illustrated in Fig. 1. A detailed description of the apparatus is given in Section 5.2.

To demonstrate the proposed process, experiments were conducted with heavy metal contaminated sand, which cannot be decontaminated by hydraulic leaching or electroosmosis alone. Residual wastes like spent foundry sand fits the criteria for the type of waste targeted in this study. Khan and Alam [13] provided typical concentrations of heavy metals

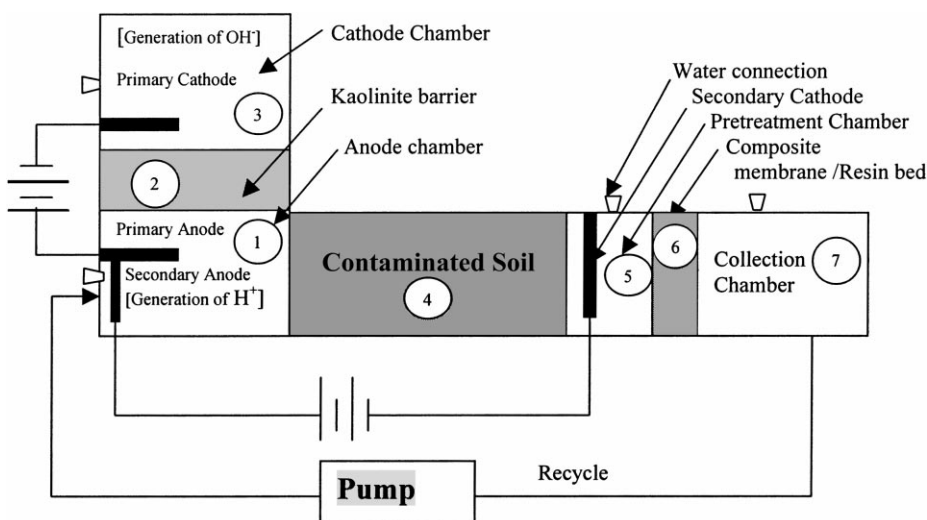


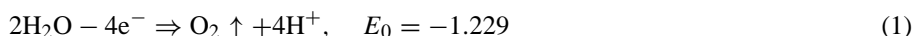
Fig. 1. Schematic representation of the CEHIXM process.

commonly present in this residual waste. This study was confined to primarily four heavy metals lead, cadmium, zinc and manganese. These metal contaminants are most abundant in the waste studied.

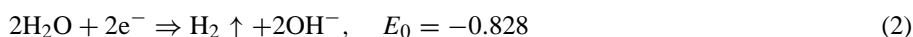
2. Theoretical background

When the electric voltage is applied, the electric current leads to electrolysis reactions at the electrodes, generating an acidic medium at the anode and an alkaline medium at the cathode. The electrolysis reactions of the primary electrodes are presented in the following equations:

Anode reaction:



Cathode reaction:



where E_0 is the standard reduction electrochemical potential, which is a measure of the tendency of the reactants in their standard states to proceed to products in their standard states. An elaborate description of the theoretical acid/base distribution that occurs during the electrokinetic soil processing is available in [14]. The acid medium (H^+ ions) generated at the anode advances through the soil toward the cathode by ion migration due to electrical gradient, pore-fluid flow due to any externally applied or internally generated hydraulic gradient and diffusion due to the chemical gradients developed in the system. In this study, a solution containing H^+ ions, is pumped through the soil sample. As the acid buffer capacity of soil is low, acid medium moves through the soil during the decontamination process and lowers the system pH. The average linear velocity, v , of the acidic solution through the porous soil sample under the hydraulic gradient can be expressed by Darcy's law:

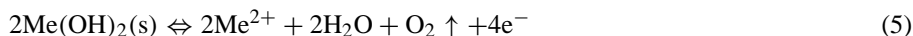
$$v = \frac{ki}{n} \quad (3)$$

where k is the coefficient of hydraulic permeability of the porous medium, i the hydraulic gradient, and n the porosity of the soil.

Most heavy metals are soluble in an acidic environment, and the lowering of pH promotes desorption of heavy metals from the soil surfaces and solubilization of metal ions. Ionized metals can be removed effectively by the combined actions of electroosmosis and ion migration in conventional electrokinetics, and by the hydraulic gradient in the CEHIXM process. When the H^+ rich solution is pumped in a soil sample containing heavy metals, the acid front facilitates the dissolution of the heavy metal precipitates (hydroxide, carbonate or sulfate, etc.) according to the following reaction:



The overall reaction (combining Eqs. (1) and (4)) may be represented as:



Thus, free heavy metal cations, Me^{2+} , are generated and move toward the direction of influent flow. For the cases of both chemically non-interactive and interactive solid phase species, the heavy metal precipitate will be dissolved along with the calcium, Ca^{2+} , from the CaCO_3 in the soil. If the heavy metal cations are bound to the ion exchange sites of the soil, the H^+ in the solution will strip the heavy metal cations from the sites and force them to move toward the ion exchange medium. In the scenario for the case of interaction of metals with humic and fulvic materials, where the heavy metal is complexed with organic ligands in the solid phase, the acid front converts the anionic ligands into uncharged molecules, thus freeing 2Me^{2+} . Therefore, the acid front generated at the anode is suitable for decontamination in all possible cases mentioned here. In this study, the performance of the coupled electric-hydraulic gradient assisted by ion exchange medium (CEHIXM) process has been assessed only for chemically non-interactive solid phase species. A detailed description along with the essential benefits of the CEHIXM process is given in Section 3.

In the current study, the electric field is not applied across the soil being treated but across a compacted kaolinite barrier. The fluid from the anode chamber is pumped through the soil to decrease the soil pH as illustrated in Fig. 1. Under these conditions, electrolysis creates a low pH front, and the hydraulic gradient transports the pH front and ions through the soil. This makes the process self-contained, requiring no external chemicals.

3. CEHIXM process

The CEHIXM is an in situ process, which couples an electrical gradient with a suitable hydraulic gradient to extract, and subsequently, recover the heavy metal contaminants from porous soil/sediments. The electric gradient is used to generate acid and the hydraulic gradient is used to pump this acid through the contaminated soil. The process involves placing the contaminated soil in an apparatus where water can be electrolyzed to acid and pumped through the contaminated soil, as shown in Fig. 1. The arrangement shows that electric gradient is applied across a compacted kaolinite barrier. The kaolinite barrier separates the anode and the cathode electrodes promoting the electrolysis process. The electric field creates oxidizing conditions at the anode resulting in electrolysis. The acid front generated during electrolysis is combined with a hydraulic gradient to force heavy metal cations and non-toxic cations towards an ion exchange medium. In the CEHIXM process, electrolysis is a dominant phenomenon in creating an acid front in the anode chamber, and the hydraulic gradient is the main driving force transporting the acid front and ionic species through the soil (Fig. 1). In addition, chemical gradient might be another driving force for transporting the species.

Because of the unique heavy metal selectivity of the ion exchange medium used in the CEHIXM process, the ion exchange medium selectively removes the heavy metal cations. The heavy metal loaded ion exchange medium may be withdrawn from the system and placed in an acidic environment. The heavy metal is obtained as a concentrated acidic solution, with the potential of recovery. The ion exchange medium may be ready for another service cycle. The process involves the following steps:

1. Generation of acidic solution by electrolysis of water at the anode region by a low direct current voltage gradient (<20 V/cm of distance between electrodes) or low current density (<100 mA/cm² of cross sectional area between electrodes).
2. Pumping the acid into the contaminated soil by a hydraulic gradient.
3. Dissolution of heavy metals in contaminated porous medium with the generated acid.
4. Transport of heavy metal cations (and other innocuous metal cations in the system) towards the composite membrane, or resin bed by a hydraulic gradient.
5. Selective recovery of the heavy metal cations by composite sorptive/desorptive ion-exchange heavy metal selective membranes, or resin beds.
6. Electric or chemical regeneration of the ion exchange medium.

As it may be noted from the steps (1) through (6), the process is closed loop and allows the heavy metal to be concentrated in acidic solution and removed. The remaining soil becomes free of heavy metals and can, thus, be classified as non-hazardous. Also, the generation and use of acidic solution by electrolysis eliminates the need for introducing aggressive chemicals in the soil. This process can be tailored to simultaneously remove heavy metals that may exist as precipitates in a contaminated sandy/silty soils. The essential benefits of this process may be listed as:

- it does not require external chemical, and thus, a *chemical-free* process;
- it is able to selectively remove heavy-metals from a coarse-grained soils;
- it enables the heavy metals to be recovered in a concentrated solution for possible recycle/reuse; and
- it can be employed in all coarse-grained contaminated soil situations.

4. Field application of the CEHIXM process

For the application of the process at a contaminated site, the acid may be produced by electrolysis of water in a small trench with a clay barrier in between. The flow should be generated perpendicular to this trench by placing collection wells at convenient distances. The plan view of the conceived field application is illustrated in Fig. 2. The trench will house the primary electrodes. The anode and the cathode electrodes will be separated by the clay

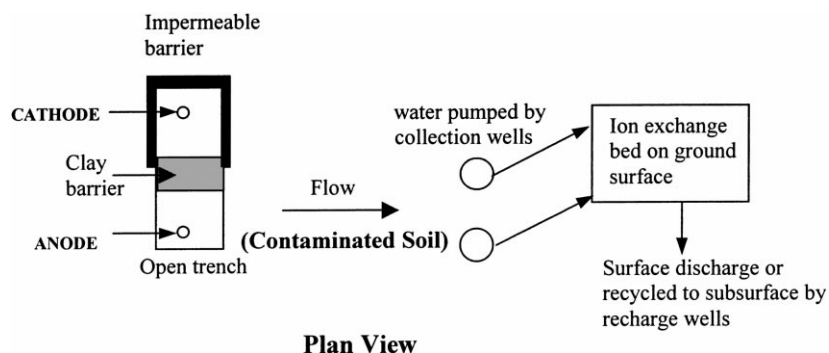


Fig. 2. Illustration of the field application.

barrier in the trench. The cathode electrode region should be lined with an impermeable barrier to prevent flow of OH^- in the soil. Metal contaminated water will be pumped out at the collection wells, which will then be treated in an ion exchange resin bed located on the ground surface. The treated water may be recycled to the groundwater by recharge wells or discharged on the surface.

5. Experimental

5.1. Materials

The spent foundry sand with a specific gravity 2.59 and negligible organic content was used in the experiments. The grain size distribution curve of the sample is shown in Fig. 3. The average particle size D_{50} was 0.55 mm. The concentrations of heavy metals in the residual wastes were Pb \sim 3 mg/kg, Cd \sim 1 mg/kg, Zn \sim 6 mg/kg and Mn \sim 113 mg/kg [13] which were not high enough to represent the prevailing conditions in the superfund sites. Lead carbonate, zinc chloride, cadmium chloride and manganese chloride salts were used to artificially contaminate the soil samples. The initial concentrations of Pb, Cd, Zn and Mn in the sample, with respect to the dry weight of the soil, were 482, 502, 1930 and 765 mg/kg, respectively.

The ion exchange resin, IONAC C-249 manufactured by Sybron chemicals Inc., was used in this study as an ion exchange medium to capture and subsequently recover the heavy metals. The salient properties of the ion exchange resin are presented in Table 1.

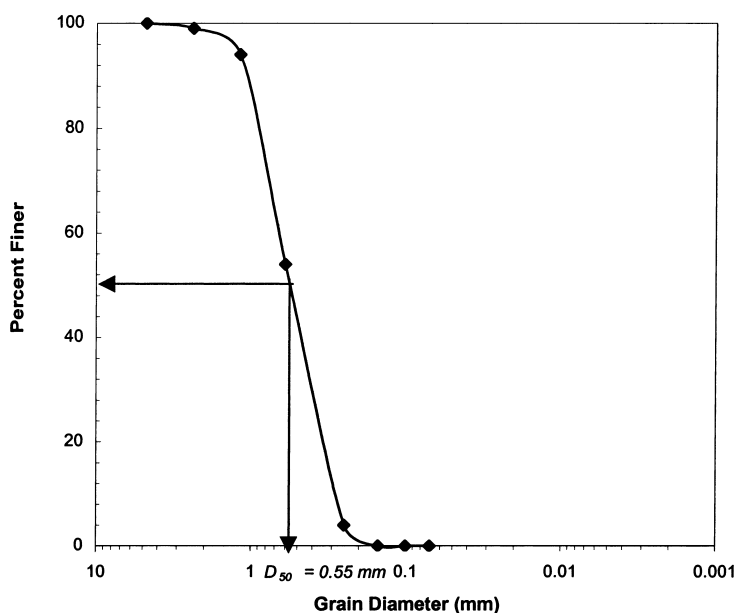


Fig. 3. Grain size distribution curve for spent foundry sand.

Table 1
Salient properties of IONAC C-249 ion exchange resin

Property	IONAC C-249
Polymer structure	Styrene-dyvinylbenzene copolymer
Functional groups	R – SO ₃ ⁻ – Na ⁺
Ionic form	Sodium, Na ⁺
Physical form	Spherical beads
Reversible swelling (H to Na)	5% approx.
Particle size distribution	0.4–1.2 mm
Effective size	0.47–0.53 mm
Specific gravity	1.3
Backwash expansion	50–75%
Regenerant:	
NaCl	
Strength	5–15%
Quantity (100%)	5–15 lb/ft ³
Flow rate	0.25 g/m ft ³
Solubility	Insoluble in all common solvents
pH range (stability)	0–14
Operating temperature	280°F (max.)
Service flow rate	3 g/m ft ³ (max.)
Freeboard requirement (H form)	80–100%
Minimum bed depth	Approx. 60 cm
Operating pH	2.0–6.0
Water retention	45–47%
Regenerant contact time	20–40 min
Conditioning step:	
NaOH	
Concentration	2%
Quantity (100%)	3.5 lb/ft ³

The arrangement of the instrument used in the research is schematically shown in Fig. 1. The contaminated sand was placed in a clear acrylic tube of 10 cm long and 3.45 cm i.d., connecting to the anode chamber at one end and to the pretreatment chamber at the other end. Porous stones with permeability greater than the soil were used at the ends of the sample tube. Voltage of 50 and 100 dc V were applied to the primary electrodes. The water from the collection chamber was pumped to the anode chamber to produce a constant hydraulic flow-rate of 10 cm³/min.

5.2. Apparatus

A schematic representation of the CEHIXM apparatus is shown in Fig. 1. The apparatus consists of two segments. The first segment has three chambers, one of which contains semi-permeable kaolinite barrier. The second segment consists of five chambers, with a common chamber with the first segment. As shown in this figure, chamber 1 holds the primary and the secondary anode electrodes and is named as the anode chamber. Chamber 2 is filled with compacted kaolinite, which is named as kaolinite barrier chamber.

Chamber 3 holds the cathode electrode and is named as the cathode chamber. Chamber 4 holds the sample tube. The sample tube is attached with the help of two tie bars. Chamber 5 following the sample tube holds the secondary cathode electrode and is named as the pretreatment chamber. Chamber 6 is filled with ion exchange medium (composite membrane/resin bed) and is named as ion exchange chamber. Chamber 7 collects the water from the pretreatment and the ion exchange chambers and is named as the collection chamber. Clear Plexiglas (1.25 cm thick) and porous stones of 1.25 cm thick and grade 55 μm were used for constructing the apparatus to provide visibility and detect gas generation at the electrodes.

The secondary electrodes were included in the instrument with the expectation that they would create OH^- ions in the pretreatment chamber and reduce the H^+ ions. As a result, the competition of absorbing the cations by the ion exchange medium would be minimum. The second purpose was to compare the cost with the primary electrode configuration. However, the effects of the secondary electrodes are beyond the scope of this article.

5.3. Procedure

The samples were prepared by compacting the soil in the sample tube in three layers, with 15 blows in per layer. After compaction the hydraulic permeability of the soil sample was in the range 1.39×10^{-2} cm/s and the porosity of the sample was about 45%. After assembling the sample tube in the cell, all chambers were filled with tap water. Then the desired dc voltage was applied across the primary electrode and the water from the collection chamber was pumped to the anode chamber at a constant flow-rate of $10 \text{ cm}^3/\text{min}$. During the experiments, water samples were collected from all the chambers at certain time intervals. The pH and metal concentrations of these samples were measured. The electric current through the kaolinite barrier was also monitored with a Radio Shack auto range digital multimeter. The pH was measured with a Cole-Palmer digital pH meter and standard bulb probe. Metal concentrations were measured according to Standard Method of Examination of Water and Wastewater using Atomic Absorption Spectrophotometer (AAS) of Perkin-Elmer model M3100. The amount of metals removed was calculated on the basis of the measured concentration, volume of the solution in the chamber, and the dry weight of the soil sample.

At the end of the experiment, the soil sample was taken out of the sample tube and divided into five equal segments. The wet weight and pH of each segment was measured. The sample was for 24 h in an oven at 110°C according to ASTM D4959. The moisture content of all samples was calculated. The heavy metals remained in the soil samples were also measured by digesting the contaminants in the soil by the USEPA [15] method. The procedure followed had four steps: (1) exactly 5 g of the sample were placed in of 20 ml of 10% nitric acid solution, making sure that the solution pH was approximately 2.0; (2) the samples for the leaching experiments were kept in nitric acid solution for around 24 h to achieve the complete desorption of contaminants from the soil surfaces; (3) the mixture was filtered with a suction filtration system using $0.45 \mu\text{m}$ filter paper; (4) the filtered liquid was tested with AAS. The final concentration of the contaminants per kg of the soil was calculated.

The ion exchange resin was also taken out of the testing cell every 10 h and placed in concentrated nitric acid solution for about 24 h. The supernatant was filtered and tested

using AAS to measure the contaminants captured by the resin. The removal efficiencies were calculated on the basis of the mass balance between the metal removed in the pretreatment chamber, metal captured in the ion exchange resin and metal remained in the soil. Fifteen sets of experiments were conducted at the electric potentials of 0, 50 and 100 V and for the duration of 10, 20, 30, 50 and 100 h.

6. Results and discussion

As mentioned earlier, the proposed method has been tested for the removal of Pb, Cd, Zn and Mn from residual wastes. The results, shown in Table 2 indicate that high metal removal efficiencies were achieved. The experimental results are discussed and presented in the following subsections.

6.1. Variation of soil pH, influent pH and effluent pH

The post experiment soil pH values are presented in Figs. 4–6. Fig. 4 represents the variation of soil pH with time at 0, 50 and 100 V of electric potentials. Figs. 5 and 6 represent the distribution of soil pH along the length of the specimen. Figs. 7 and 8 represent the variation of the anode, the cathode, the pretreatment and the collection chambers pH with time, at 50 and 100 V. It is essential to measure the pH changes across the soil and in the anode chamber solution during removal of toxic metals since pH is a master variable in chemical equilibrium and desorption/precipitation reactions. It is observed in Figs. 4–6 that the soil pH with the hydraulic gradient alone was always close to the neutral value. At that time tap water with pH ~6.90 was pumped through the sample and not expected to decrease the soil pH. However, the soil pH decreased to approximately 2.0 within the first 50 h of experiment, both at 50 and 100 V. This was expected as the oxidation at the anode chamber decreased the pH to approximately 2.0. Most of the pH changes were realized within the first 20–30 h of the processing at 100 V, and 30–50 h at 50 V (Fig. 7). In Figs. 4 and 5, no pH jump (high pH) was observed at the pretreatment end of the specimen as reported by

Table 2
Mass balance of metals after 100 h of the processing

Metal and electric voltage	Remaining in soil, (mg/kg)	Removed in pretreatment chamber (mg/kg)	Captured in resin, (mg/kg)	Total removed, (mg/kg)	Mass balance (%)
Pb at 50 V	22 (4.58) ^a	45 (9.34)	405 (84.02)	450 (93.36)	97.94
Pb at 100 V	22 (4.58)	50 (10.37)	405 (84.02)	455 (94.39)	98.97
Cd at 50 V	5 (1.03)	60 (11.95)	430 (85.66)	490 (97.61)	98.64
Cd at 100 V	4 (1.00)	70 (13.94)	430 (85.66)	500 (99.60)	100.66
Zn at 50 V	13 (0.67)	122 (6.32)	1770 (91.71)	1892 (98.03)	99.00
Zn at 100 V	11 (0.65)	135 (6.99)	1775 (91.97)	1910 (98.96)	99.61
Mn at 50 V	28 (3.66)	52 (6.80)	668 (84.12)	720 (94.12)	97.78
Mn at 100 V	19 (2.48)	52 (6.80)	685 (89.54)	737 (96.34)	98.82

^a The values in parentheses are measured in percent.

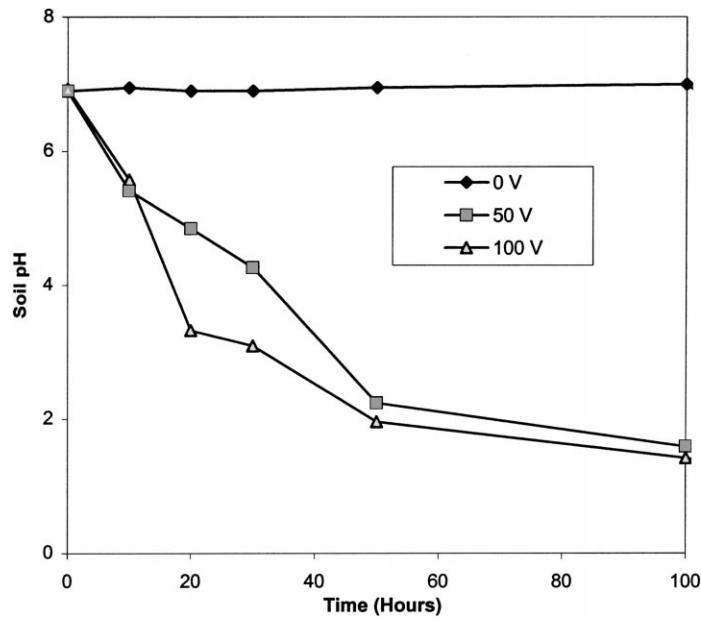


Fig. 4. Variation of soil pH with time at different voltages.

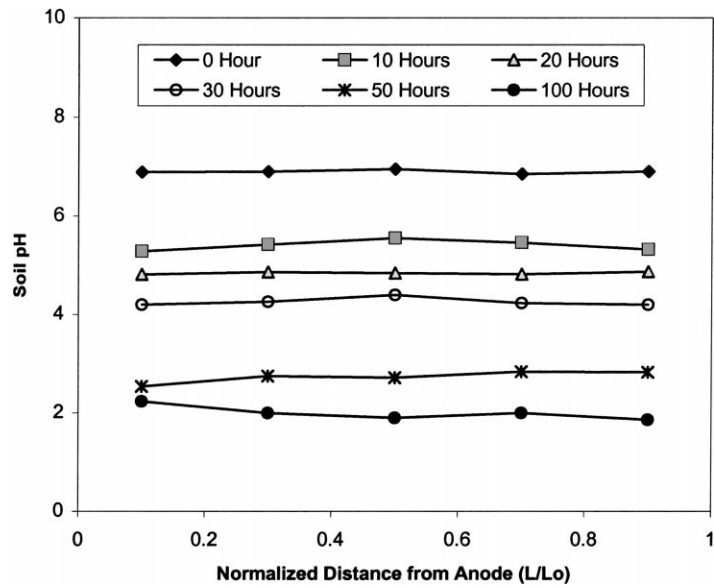


Fig. 5. Distribution of soil pH along the length of the specimen at 50 V. The initial pH for all conditions was 6.85.

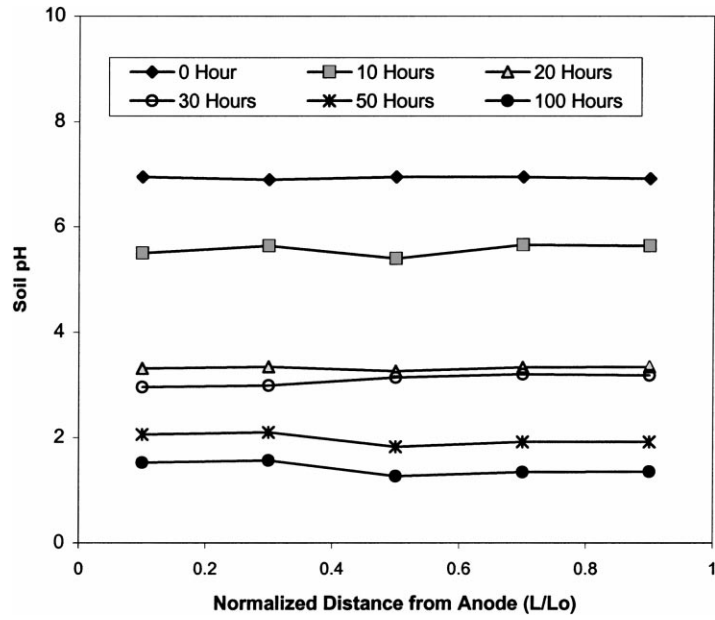


Fig. 6. Distribution of soil pH along the length of the specimen at 100 V.

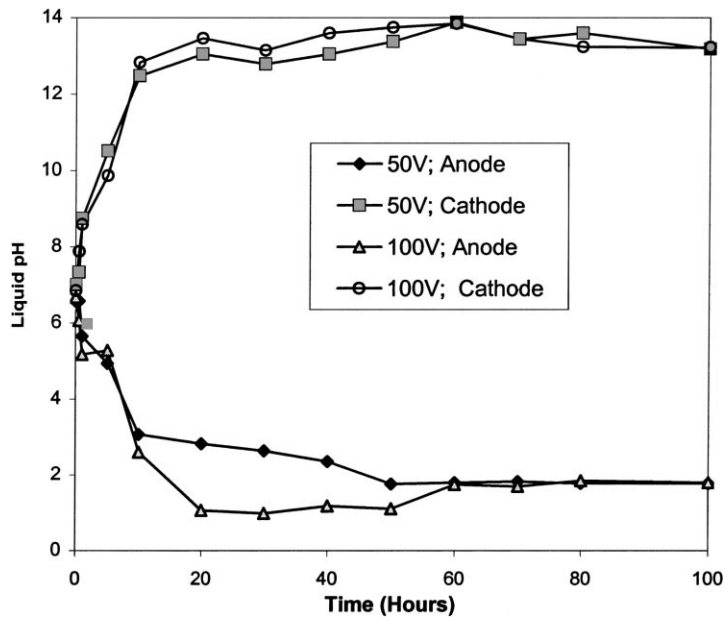


Fig. 7. Variation of the anode and the cathode chamber pH with time at 50 and 100 V.

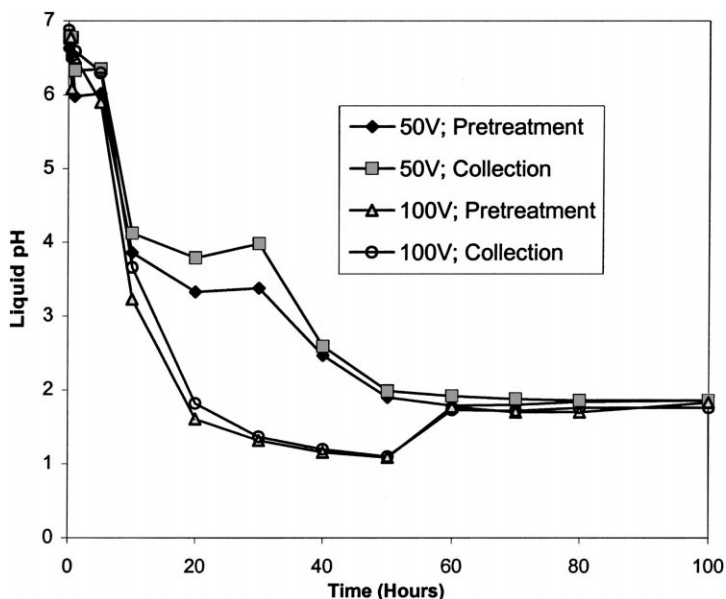


Fig. 8. Variation of the pretreatment and the collection chamber pH with time at 50 and 100 V.

many authors [16–18] in the conventional EKD process. Although the anode pH decreased to <2.0 within the first 20–30 h of the processing at 100 V, the soil pH did not decrease to that value within the time frame. This phenomenon may be due to the pH buffering capacity of the soil due to the presence of other ions in soil. Another reason could be an additional reaction of metal hydroxides (metal hydroxide dissolution) that may occur, which would tend to increase the pH of the pore water in the soil sample.



The rate of production of OH^- ions decreased as the amount of metal hydroxide decreased with time (due to the removal process). As a result, it took some time to reduce the soil pH below 3.0, at which the solubility of metal is maximized. A soil pH of 2.0 was realized within 50 h of the processing at 100 V, and within 70 h at 50 V, as shown in Fig. 4. In Fig. 8, it is seen that the pH of the pretreatment and the collection chambers decreased to approximately 2.0 within the first 20–30 h, at 100 V and within 30–50 h at 50 V. This observation confirms that the applied flow-rate of $10 \text{ cm}^3/\text{min}$ was effective in moving fluid from the anode chamber to the pretreatment chamber. The final pH in the pretreatment and the collection chambers remained approximately 2.0. As a result, the metal ions extracted from the solid medium remained in solution in the pretreatment chamber, facilitating the ion exchange resin to capture the cations. This yielded an effluent in the collection chamber virtually free of metal ions that may be recycled for wastewater volume reduction. Moreover, recycling of the collection chamber effluent will not increase the pH of the anode chamber water and will not reduce the efficiency of the process as it does for recycling of effluent from the cathode in the conventional EKD process [15].

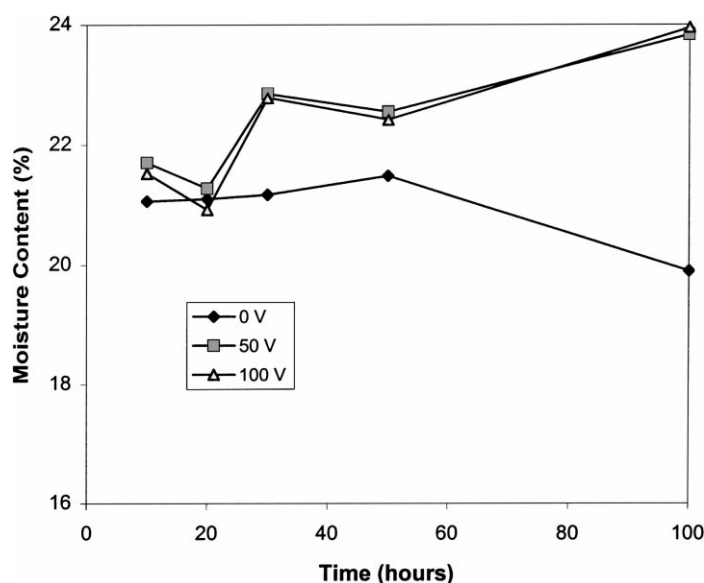


Fig. 9. Variation of soil moisture content with time at different voltages.

6.2. Variation of soil moisture content and electrical current

Fig. 9 represents the variation of soil moisture content as a function of time at 0, 50 and 100 V. The moisture content is in the narrow range 21–24% both at 50 and 100 V and in the range 19.5–21% at 0 V. Moisture content in all situations was close or above the saturation moisture content (19.45%) of the soil samples. The variation of current passing through the kaolinite barrier as a function of time, both at 50 and 100 V is represented in Fig. 10. The current was about 25 mA at the beginning of the experiment both at 50 and 100 V. Initially the current rose to approximately 50 mA then dropped and fluctuated between 20 and 115 mA, at 50 V and rose and fluctuated between 20 and 125 mA at 100 V. The fluctuation of the current might occur due to the changes of resistance in kaolinite during the experiments as the soil chemistry changes during the process.

6.3. Contaminant removal efficiency

The variation of normalized concentrations (C/C_0) of metals remained in soil after the experiments are shown in Figs. 11 and 12 for lead & cadmium and zinc & manganese, respectively. The distribution of metal concentration along the length of the specimen after 50 and 100 h of experiment at 50 and 100 V are presented in Figs. 13 and 14, respectively. The percentage of metal extracted in the pretreatment chamber, captured by the ion exchange resin and the total metal removed, at the end of the processing, are also shown in Figs. 15–18. As seen from Figs. 11 and 12, negligible amounts of metals were removed during the experiment of 100 h with hydraulic gradient alone. The concentrations of lead,

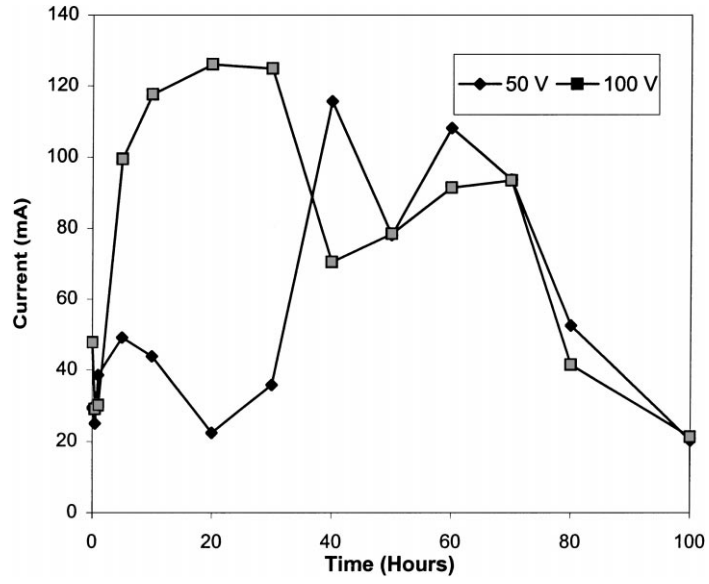


Fig. 10. Variation of current with time at different voltages.

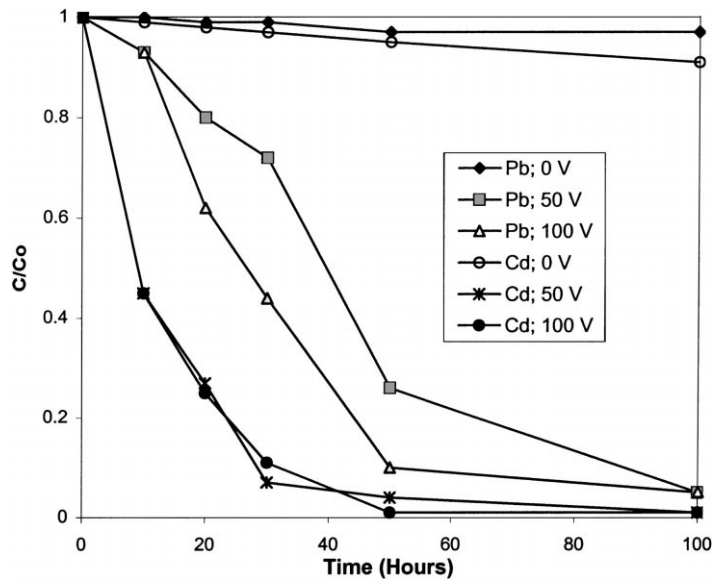


Fig. 11. Variation of normalized concentration of lead and cadmium with time at different voltages.

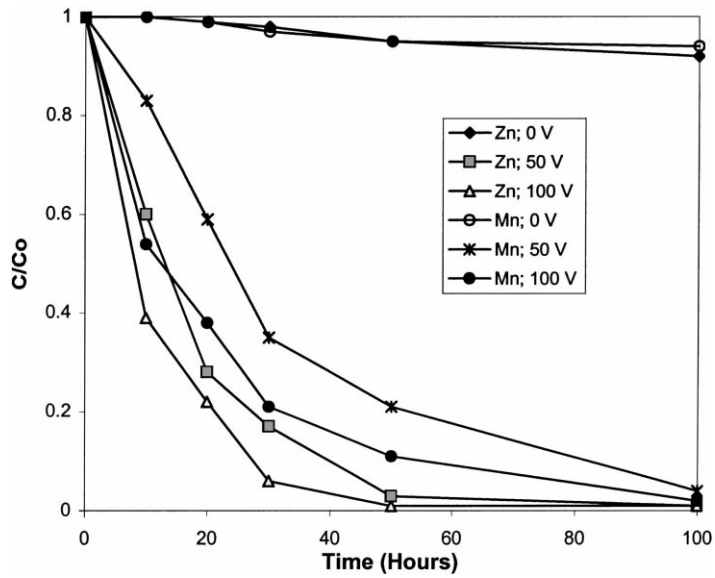


Fig. 12. Variation of normalized concentration of zinc and manganese with time at different voltages.

cadmium, zinc and manganese remained in soil were approximately 467, 459, 1,783 and 718 mg/kg (i.e. 97, 91, 92, and 94%, respectively). This removal might be due to the presence of sulfate and other salts of the metals in the soil that are soluble to water at or close to neutral pH under certain circumstances.

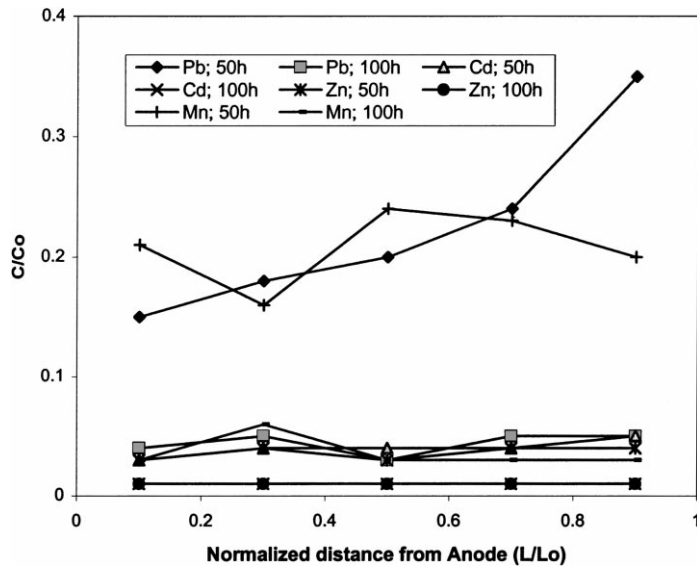


Fig. 13. Distribution of metal concentration in soil along the length of the specimen at 50 V.

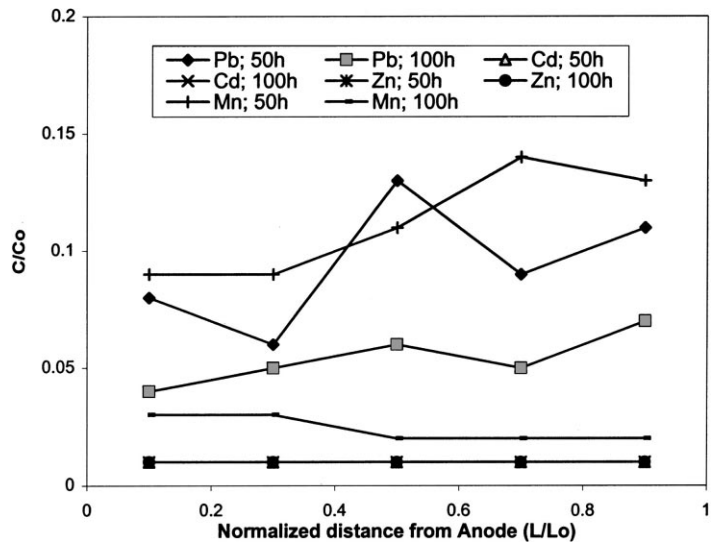


Fig. 14. Distribution of metal concentration in soil along the length of the specimen at 100 V.

From Figs. 11, 12 and 15–18, it is observed that at 50 V and at the end of 100 h of experimental duration, the concentrations of lead, cadmium, zinc and manganese remained in soil were 22, 5, 13 and 28 mg/kg, which correspond to 4.58, 1.03, 0.67, and 3.66% of initial metals in the soil, respectively. Total removal of the metals in the pretreatment chamber

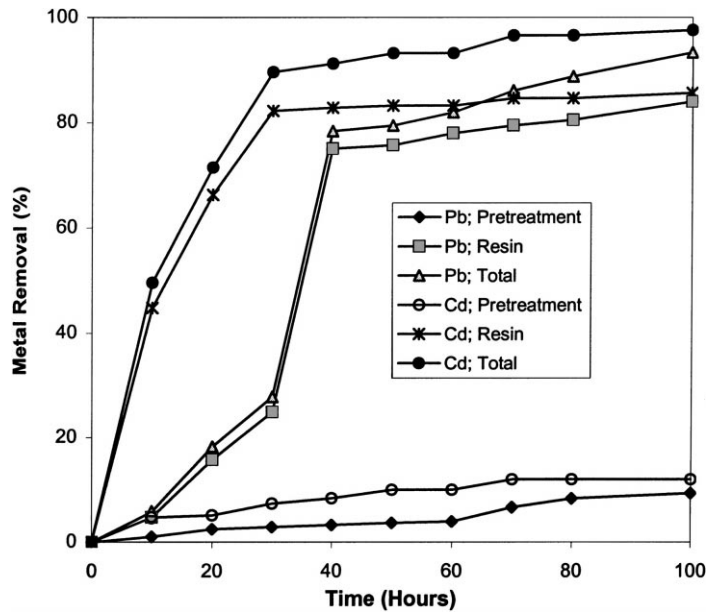


Fig. 15. Percentage of lead and cadmium removal with time at 50 V.

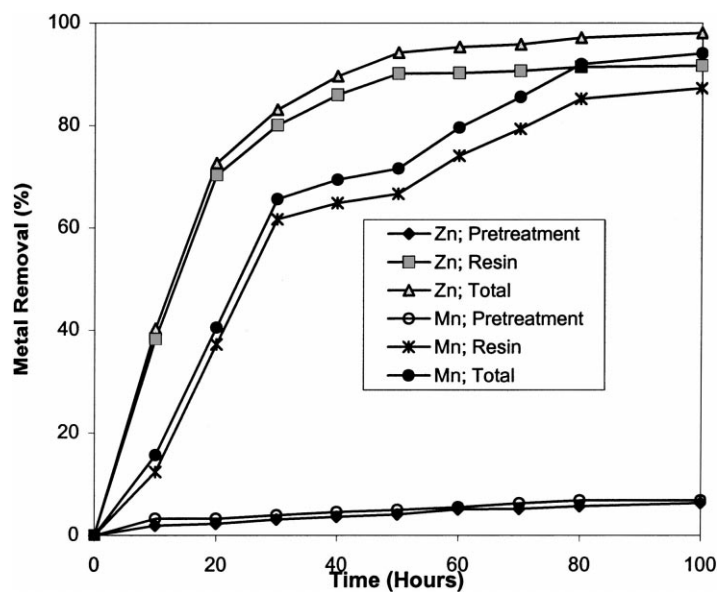


Fig. 16. Percentage of zinc and manganese removal with time at 50 V.

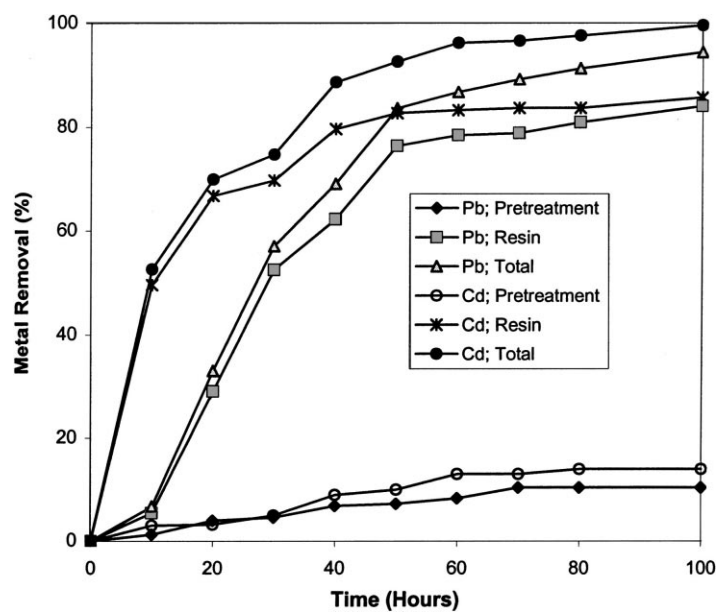


Fig. 17. Percentage of lead and cadmium removal with time at 100 V.

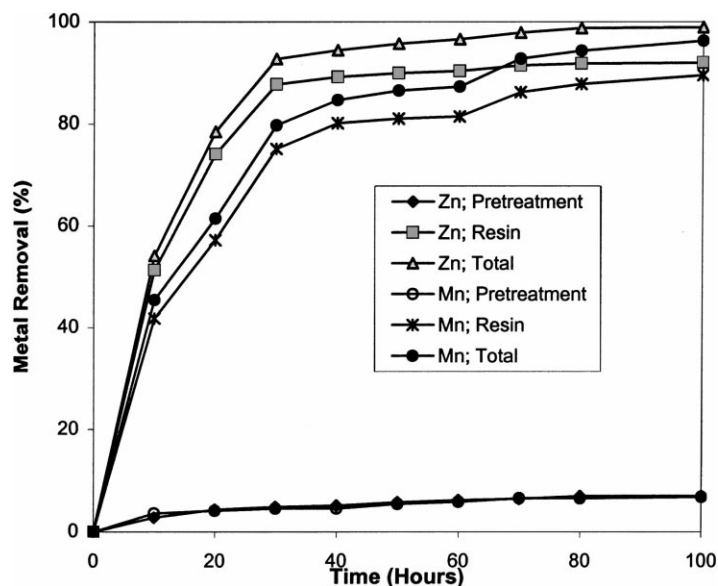


Fig. 18. Percentage of zinc and manganese removal with time at 100 V.

and the ion exchange resin at 50 V were 450, 490, 1892 and 720 mg/kg, which correspond to 93.36, 97.61, 98.03 and 94.12% (Table 2), respectively. At 100 V and at the end of the experimental duration, the concentrations of lead, cadmium, zinc and manganese remained in soil were about 22, 4, 11 and 19 mg/kg (i.e. 4.58, 1.00, 0.65, and 2.48%, respectively). The total concentrations of the metals removed in the pretreatment chamber and in the ion exchange resin at 100 V were 455, 490, 1910 and 737 mg/kg, which correspond to 94.39, 97.61, 98.96 and 96.34% (Table 2), respectively. From Table 2, it is seen that the mass balance for Pb, Cd, Zn and Mn varies from 97 to 100.66%. Approximately 3% of the metals were unaccounted following the process. One reason for the unaccounted loss of metals might be the non-uniform distribution of the cations in soil after the processing (Figs. 13 and 14). The second reason might be the deposition of metal ions on to the graphite electrodes and porous stones during the processing. From Table 2, it is also seen that the concentrations of metals remained in the soil after 100 h of the processing were 22, 4, 11 and 19 mg/kg for Pb, Cd, Zn and Mn, respectively. It is also reasonable to anticipate that additional removal of metals could be attained with a longer period of processing. In Figs. 13 and 14, no accumulation of metals was observed along the length of the specimen under the applied voltages. Many researchers [16–18] reported the high pH jump and the accumulation of metals near the cathode end of the soil specimen in conventional electrokinetic soil processing, which hinders the treatment process to some extent.

Comparisons of metal removals at different electric voltages are shown in Fig. 19. It is seen that more than 90% of Cd and Zn and more than 80% of Pb and Mn were removed within the first 50 h of the processing, both at 50 and 100 V, which is higher than the removal reported by Li et al. [19]. At the end of the experiment, the difference in metal removal at 50

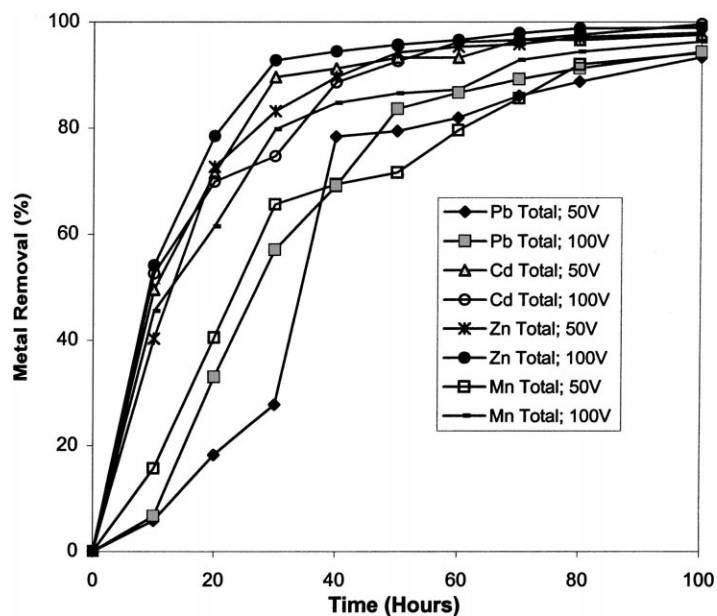


Fig. 19. Comparison of percentage of metal removal with time at 50 and 100 V.

and 100 V was negligible. This is perhaps because the soil pH decreased to <2.0 within 50 h for both the cases. The removal differences at 50 and 100 V were 1.0% for Pb, 2.0% for Cd, 0.9% for Zn and 3.0% for Mn. The order of overall metal removal rate at the equilibrium pH appeared to be $Zn > Cd > Mn > Pb$.

The energy expenditure during field application is largely dependent on the resistance and initial pH of the soil-water system. The economic cost data based on the bench-scale experiments and the actual costs at full-scale are expected to be significantly different. Assuming field conditions identical to the laboratory experiments conducted in this study, the field energy requirement for the process would be approximately 345 kW h/m^3 of soil.

7. Conclusions

The basic principles of contaminant extraction by the CEHIXM process from the sandy soil have been demonstrated to be feasible. The specific conclusions could be made in this study are as follows:

1. By using the proposed technique, more than 97% of Pb, Cd, Zn and Mn were removed after 100 h of the processing at an energy expenditure of 345 kW h/m^3 of soil.
2. The order of the mass of the heavy metal removal from the contaminated soil was $Zn > Cd > Mn > Pb$.
3. The low pH condition necessary for significant metal dissolution was achieved within the first 50 h of the processing both at 50 and 100 V.

4. Higher voltage did not result in significant higher metal removal beyond the first 50 h of the processing.
5. The effects of high pH jump and the accumulation of metals in the specimen near the pretreatment zone were eliminated.
6. The final pH in the pretreatment and the collection chamber remained approximately 2.0 during all experiments. As a result, the metals extracted from the solid medium remained in solution in the pretreatment chamber, facilitating the ion exchange resin to capture the cations.

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