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Effect of the Secondary Electrode Configuration in Removing Metal Contaminants from Soils by the CEHIXM Process

M. A. KARIM AND LUTFUL I. KHAN

The effect of the secondary electrode configuration in removal of metal contaminants from soils under coupled electric hydraulic gradient assisted by ion exchange medium (CEHIXM) process was investigated. Soil samples using a blend of spent foundry sand and millpond sludge were used to investigate the contribution and cost-effectiveness of the secondary electrode configuration in removal of primarily four heavy metals (Pb, Cd, Zn, and Mn). A number of tests were conducted at an optimum constant DC electric voltage of 50 V and an optimum constant flow velocity of 0.00713 cm/sec for a period of 200 hours. The experimental results demonstrated the removal efficiencies of approximately 89.84% of Pb, 96.63% of Cd, 92.89% of Zn, and 91.14% of Mn with the primary electrode (PE) configuration. In case of the secondary electrode (SE) configuration, the removal efficiencies were about 87.34% of Pb, 91.68% of Cd, 95.30% of Zn, and 90.44% of Mn. In the case of the combined PE and SE configuration, the removal efficiencies were about 90.16% of Pb, 93.27% of Cd, 96.34% of Zn, and 90.44% of Mn. The energy expenditures were about 480 kWh/m³ and 522 kWh/m³ of soil in the case of the PE and the SE configurations, respectively. It appeared that the use of the SE configuration and/or combination of the PE and SE configuration was not cost-effective and advantageous over the use of the PE configuration in removing heavy metals from the contaminated soils by the CEHIXM process.

Keywords Electrode configuration, electrolysis, coupled electric-hydraulic gradient, heavy metals, ion-exchange medium, soil decontamination

Introduction

Removal of heavy metal contaminants from soils has been a technological challenge for engineers and scientists for the past several decades. A variety of options exist to clean up a waste site; however, the efficiency and costs of these options may vary widely. Conventional ground burial and land disposal are often economical, but they do not provide a permanent solution, and in some cases they are not necessarily the most effective solution. For removing heavy metals from solid porous media, the most common *ex-situ* methods

employed include soil washing (USEPA, 1992) and ligand extraction (Raghavan et al., 1990; Shah et al., 1995). Apart from the generic problem of any *ex-situ* process, i.e., the need to excavate the soil and place it in an external reactor, the above-mentioned processes suffer from one or more of the following disadvantages:

- they require input of chemicals or high energy;
- they generate a liquid (in the case of soil-washing or ligand extraction) or solid waste (for incineration) disposal problem;
- they are not versatile enough to be applied to all cases (chemically non-interactive solid phase, chemically interactive solid phase, ion-exchange solid phase, and interaction with humic and fulvic materials) of soil compositions; and
- they are unable to concentrate the heavy metal for recycle/reuse.

Some *in-situ* methods include vacuum extraction (Hiller and Gudeman, 1989), thermal desorption (Iben et al., 1996), hydraulic fracturing (Leach, 1995), electrokinetic decontamination (including the “Lasagna” process) (Ho et al., 1995; Hamed et al., 1980), biotreatment (Baldi et al., 1990; Volesky, 1990; Neufeld and Herman, 1975), immobilization by encapsulation, and placement of barrier systems (Riley and Zachara, 1992; Evans et al., 1985). Most of these processes are employed for removal of organics present in soil. Soil washing is a chemical process for removing both organic and inorganic contaminants from the solid granular medium. Soil washing may be used in *in-situ* or *ex-situ* conditions. Primarily, the chemical treatment of the contaminated soil should reduce the heavy metal content in the solid medium so that these metals no longer lead to manage as hazardous waste and pose potential hazard to public health and the environment. These chemical treatment processes must be carefully controlled and contained, since in some cases the chemical treatment agent can itself pose an equal or greater potential hazard to the environment than the original pollutant. The factors which limit the effectiveness of the *in-situ* soil washing process include: complexity of the waste mixture; the high humic content of soil which inhibits solvent-metal reactions; and the presence of clay particles, which are negatively charged and bond with positive metal ions. Clay particles also decrease the permeability of the soil and thus prevent the washing solution from flowing through. Even though soil washing can successfully be undertaken commercially for sandy soils, most clay-containing-soil cleaning to date has been done in the laboratory or on a pilot plant basis (Pfister and Tsang, 1990).

In general, soil may be classified into two broad categories: fine-grained and coarse-grained. Removal of contaminants from fine-grained soils—primarily clay—is difficult because of their inherent low permeability and the physico-chemical interactions such as adsorption, ion exchange, and complexation between the soil particle and contaminants. In such cases, Electrokinetic Decontamination (EKD) may be an effective process. Several studies (Jacobs et al., 1994; Runnells and Wahli, 1993; Alshawabkeh and Acar, 1992; Pamukcu and Wittle, 1992; Mitchell, 1986) have shown that electroosmosis is the dominant phenomenon in the *EKD* process and that the process can be used to remove heavy metals from fine-grained soils. The transport phenomena and the associated electrochemical reactions in fine-grained soils have been studied by many researchers (Reddy and Shirani, 1997; Schultz, 1997; Shapiro and Probst, 1993; Acar and Alshawabkeh, 1993; Acar et al., 1990). However, in coarse-grained soils *EKD* is slow or ineffective due to the limited surface conductivity and the high permeability of the soil.

An *in-situ* decontamination process, namely coupled electric-hydraulic gradient assisted by ion exchange medium (CEHIXM), was developed at the Cleveland State University. This process had been proven to be efficient for removing and recovering the metal

Figure 1. Schematic representation of the CEHIXM decontamination process.

contaminants from coarse-grained soils having limited surface charge and relatively high permeability where electro-osmosis and ionic migration effect is negligible (Karim and Khan, 2001a; 2002), whereas electro-osmosis and ionic migration are the basic clean-up mechanisms in the case of conventional electrokinetic extraction of contaminants from fine-grained soils having low permeability and high surface charge (Yeung and Datla, 1995). In the CEHIXM process, an electric gradient is coupled with a suitable hydraulic gradient in an innovative fashion. A suitable ion exchange medium (heavy-metal-selective composite membrane or resin) is used to capture and subsequently recover the heavy metals. The exhausted ion exchange medium may be regenerated and reused. As shown in Figure 1, electrodes across a semi-permeable barrier, designated as the primary electrode (PE) configuration, and across the soil sample, designated as the secondary electrode (SE) configuration, were used to apply voltage. The effectiveness of the SE configuration in removing heavy metal contaminants from soils by the *CEHIXM* process has been evaluated and presented in this article.

Process Description

The proposed *CEHIXM* is an *in-situ* process, which couples an electric gradient with a hydraulic gradient along with a suitable ion exchange medium to extract and subsequently recover the heavy metals from porous (permeable to fluids) soils/sediments. The electric gradient is used to generate acid and the hydraulic gradient is used to pump the 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 soil, as shown in Figure 1. The arrangement shows that the electric gradient can be applied both across a semi-permeable barrier and the soil sample being treated. Low-voltage direct current (DC) electric field application is enough to perform the electrolytic reactions (Alshawabkeh et al., 2004). Application of DC results in redox reactions at the electrodes. If the inert electrodes are used, water oxidation generates an acid (H^+) and oxygen gas at the anode while water reduction produces a base (OH^-) and hydrogen gas at the cathode:

Separation of the electrodes (by an ion exchange medium such as soils) causes acid production and drop in the pH at the anode below 2.0. At the same time, the base increases the cathode pH to above 10.0.

The low pH front (H^+), generated in the anode, is pumped through the contaminated soils to force the heavy metal cations and non-toxic cations towards an ion exchange medium. In the *CEHIXM* process, electrolysis is a dominant phenomenon in creating acid in the anode chamber and the hydraulic gradient is the main driving force to transport acid front and ionic species through the soil (Figure 1). In addition, chemical gradient might be another driving force for transporting the species. The detail description the *CEHIXM* process can be found in Karim and Khan (2001a).

The adsorption of cations and anions to soil surfaces can be described by the following complexation reactions according to the surface complexation model (Reddy et al., 1997; Sposito, 1989):

where $S - OH$ represents a typical surface functional group, M^+ and L^- represent a cation and an anion, respectively. These complexation reactions are highly dependent on solution pH. Metals have different sorption characteristics and mechanisms that are also dependent upon the adsorbents. The adsorbents show differences in selectivity sequence for different metals. Desorption of heavy metals from the soil surfaces is essential for the decontamination to be efficient in contaminated soil deposits. The adsorption/desorption mechanism depends on the surface charge density of soil mineral, cation exchange capacity, characteristics and concentration of the cationic species, and existence of organic matter and carbonates in the soil. Furthermore, the adsorption/desorption mechanism is pH dependent. An increase in H^+ concentration associated with a decrease in pH results in desorption of cations by an amount controlled by the soil type (Yong et al., 1990)

When the H^+ rich solution is pumped through the 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 Equations 1 and 4) may be represented as:

Thus, free heavy metal cations, Me^{2+} , are generated and move toward the direction of influent flow.

The base front (OH^-) generated by electrolysis at the cathode may cause precipitation of most of the heavy metals and actinides if this base front can be pushed through the soil being treated. In the *CEHIXM* decontamination process the cathode is not in contact with the soil sample, especially in case of the PE configuration and the base front generated at the cathode will not be pushed through the soil sample. So there is no scope for the metal to precipitate in the system during the decontamination process. Dissolution of precipitated

metal salts is performed by the acid front according to Equation (5). However, in the case of the SE configuration, an inert cathode is placed in the pretreatment chamber, as shown in Figure 1, and the soil sample is in contact with the base front generated at the secondary cathode. This base front may be pushed through the soil sample, which is a common phenomenon in the conventional *EKD* process (Khan and Alam, 1994).

Experiments

The experiments were conducted with soil samples containing heavy metal contaminants. In order to investigate the effects of secondary electrode configuration, four sets of experiments were conducted applying an optimum operating voltage of 50 V with soil samples having characteristics as described under materials and methods. A number of tests were conducted, using a range of voltages (25, 50 and 100 V), for a duration of 50 hours. Based on these experiments an optimum operating voltage, for considerable decontamination rate and controllable gas production, was found to be 50 V. The selection of the optimum operating voltage is beyond the scope of this article and has been presented elsewhere (Karim and Khan, 2002). The experimental program undertaken for this study is illustrated in a flowchart (Figure 2).

As illustrated in Figure 2, the first set of experiments was conducted by applying the optimum electric voltage across the semi-permeable barrier, i.e. at the PE configuration at different flow rates for 24 hours in order to select an optimum operating flow rate to be used in the subsequent experiments. Kaolinite clay has been used to create a semi-permeable barrier. The second set was conducted by applying the electric voltage across the soil sample to be treated, i.e. at the SE configuration, using the same voltage and the optimum operating flow rate, selected from the first set of experiments, for a period of 200 hours. The third set was conducted by applying the electric voltage across the semi-permeable barrier, i.e. at the PE configuration, keeping all other operating parameters the same as the second set. The fourth set was conducted by applying the electric voltage both across the semi-permeable barrier and the soil sample simultaneously, i.e. at the combined PE and SE configuration,

Figure 2. Flow-chart for the experimental program.

also keeping all other operating parameters the same as the previous experiment sets. Duplicate and in some cases, as necessary, triplicate runs of the experiments were done and the average of the values, falling *within 0 to 10%* of the individual run, were used to generate the experimental data.

Apparatus

A schematic representation of the apparatus is shown in Figure 1. The apparatus consists of two segments. The first segment has three chambers, one of which contains a semi-permeable barrier. The second segment consists of five chambers, with a common chamber similar to 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 to create a semi-permeable barrier, which is identified as a semi-permeable barrier chamber. This barrier prevents intermixing of acidic and basic solutions generated in the anode and the cathode chambers. Chamber 3 holds the primary 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, is the pretreatment chamber. Chamber 6, next to the pretreatment chamber, is filled with ion exchange medium and is named the ion exchange chamber. Chamber 7 collects the effluent from the ion exchange chamber and is named the collection chamber. Clear Plexiglas (1.25 cm thick) and Eaton Product brand porous stones of 1.25 cm thick and grade 55 microns were used for constructing the apparatus to provide visibility and detect gas generation at the electrodes. An E332 Consort DC power source was used to provide a constant electric potential source during the experiment. Water circulation, through the soil sample, was accomplished with an Ismatec IPC-8 (8-channel) cassette-tubing pump. The Sybron IONAC C-249 ion exchange resin with a functional group of $\text{R-SO}_3^- \text{-Na}^+$ was used, as an ion exchange medium, to capture and subsequently recover the heavy metals. The detail description of the apparatus and the ion exchange resin can be found in Karim and Khan (2001a, 2003).

Experiments were conducted using ethylenediaminetetraacetic acid (EDTA) solutions at different molarities to study the effect of organic content in removing heavy metals from soils containing organic matter. However, the effect of organic content is beyond the scope of this article and has been presented elsewhere (Karim and Khan, 2001b).

Materials and Methods

A blend of spent foundry sand and millpond sludge (90:10 w/w ratio) with specific gravity of 2.62, organic content of 3.5%, and D_{50} of 0.25 mm was used as a contaminated source in the study. The characteristics of spent foundry sand and millpond sludge are available in Khan and Alam (1994). The concentrations of the heavy metal contaminants, such as lead (Pb), cadmium (Cd), zinc (Zn), and manganese (Mn) in the residual mixture with respect to dry weight of the mixture, were 163, 4, 1,705, and 587 mg/kg, respectively. To deal with a higher initial concentrations of heavy metals, the samples were spiked with a known amount of lead carbonate, cadmium chloride, zinc chloride, and manganese chloride followed by aging for a week before running the experiments. After contamination, the initial concentrations of Pb, Cd, Zn, and Mn in the sample were measured by digesting the contaminants out of the soil by the USEPA (1986) 1310 method. The initial concentrations of Pb, Cd, Zn, and Mn with respect to the dry weight of the soil were 640, 505, 3,630, and

1,140 mg/kg, respectively. The high initial metal concentrations represent the prevailing conditions in the superfund sites. Three representative soil samples were analyzed using a flame mode Atomic Absorption Spectrophotometer (AAS) of Perkin Elmer model M3100 and the average of the values, falling within 0 to 5% of the individual sample, was accepted as an initial concentration.

The soil samples were prepared by compacting the soil in the sample tubes of 10 cm long and 3.45 cm ID, in three layers, with 15 blows in each layer. After compaction, the permeability of the samples was in the range of 1.40×10^{-3} cm/sec and the porosity of the sample was about 41%.

Water samples were collected from all the chambers at certain time intervals. The pH and the metal concentrations of these samples were measured. The electric currents, through the kaolinite barrier (PE configuration) and the soil sample (SE configuration), were also monitored, at certain time intervals, with an auto range Radio Shack digital multimeter. The electric current data were used to estimate the energy expenditure. 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 AAS.

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 of each section was taken and the soil pH of each section was measured with the Cole-Palmer digital pH-meter and standard flat bulb probe. The sample was dried for 24 hours in an oven at 110°C according to ASTM D4959. The amount of metal remaining in the soil samples was also measured by leaching the contaminants out of the soil by the USEPA (1986) 1310 method.

The ion exchange resin was also taken out of the testing cell at certain time intervals and placed in concentrated nitric acid solution for about 24 hours. The supernatant was filtered and tested using AAS to measure the contaminants captured by the resin.

Results and Discussions

The optimum flow-rate was selected based on the recirculation pH (i.e. the pretreatment and collection chambers pH, as shown in Figures 3 and 4) as well as the metal removal

Figure 3. Variation of pretreatment chamber pH with time at different flow rate.

Figure 4. Variation of collection chamber pH with time at different flow rate.

efficiencies (the variations of the normalized concentrations (C/C_0) of Pb, Cd, and Zn remained in the soil samples as a function of flow-rate, after 24 hours of processing, as shown in Figure 5).

From Figures 3 and 4, it is observed that both the pretreatment and collection chambers pH decreased to below 2.0 at about first 13 hours of experiment run both for the flow-rates of 4 and 5 cm^3/min . From Figure 5, it is seen that the rate of decrease of C/C_0 was significant up to the flow-rate of 4 cm^3/min for Pb and Cd. But for Zn the rate of change

Figure 5. Variation of metal concentrations with flow rate.

was significant up to 5 cm³/min. No significant change of Pb and Cd was observed beyond 4 cm³/min. Increasing the flow rate beyond 4 cm³/min did not necessarily accelerate the decontamination process, at least for Pb and Cd. Either 4 cm³/min or 5 cm³/min may be considered as an optimum operating flow rate from pH point of view. However, based on the metal removal rates, lower flow rate, i.e., 4 cm³/min, seems to be the best fit. Also, running the experiments under higher flow-rate required more precautions and sometimes made it more prone to potential leakage. Therefore, it was reasonable to select 4 cm³/min (equivalent flow velocity ≈ 0.4278 cm/min. ≈ 0.00713 cm/sec) as an optimum operating flow-rate.

The variations of the influent and the effluent pH for different electrode configurations as a function of time are presented in Figures 6 and 7. Figure 6 did not show any significant differences in the anolyte pH at different electrode configurations. It was expected to decrease the pH in the anode chamber more in the case of combined PE and SE configuration, as the electric voltage was applied both in the primary and the secondary electrodes simultaneously. But the pH value did not decrease as expected.

One reason for the anode pH not decreasing as expected could be the rate of H^+ ion production stopped when the anode solution became saturated with H^+ ions. The second reason could be the production of OH^- ions in the pretreatment chamber due to the electrolysis at the SE that tend to increase the pH of the pretreatment chamber which eventually flows to the collection chamber. As a result the pH of the collection chamber increased and the fluid from the collection chamber was recycled to the anode chamber. Figure 7 represents the effluent pH as a function of time both in the pretreatment and the collection chambers at different electrode configurations. After 100 hours of the processing, both the pretreatment and the collection chambers pH ~ 3.50 were higher in cases of the SE configuration and the combined PE and SE configuration than that in the case of the PE configuration (pH ~ 1.50). Therefore, the recycling of fluid from the collection chamber

Figure 6. Variation of anode and cathode pH with time at different electrode configurations.

Figure 7. Variation of pretreatment and collection chambers pH with time at different electrode configurations.

might tend to increase the anode pH in cases of the SE configuration and the combined PE and SE configuration.

The distribution of soil pH along the length of the specimen at different electrode configurations is presented in Figure 8. The soil pH near the anode was close to 2.0 and in the other end of the sample the soil pH was close to 3.5 in case of SE configuration. A similar trend was observed in the case of PE and SE configuration, where pH was about 1.75 at the anode end and close to 3.0 at the other end, whereas, in the case of the PE configuration, the soil pH was approximately 1.00 throughout the sample specimen. This

Figure 8. Distribution of soil pH along the length of the specimen at different electrode configurations.

Figure 9. pH distribution at $t = 9$ days. Comparison of model and experiments (after Jacobs et al., 1994).

scenario resembles the conventional EKD process (DC supply is used across the soil sample to be treated) to some extent where a pH jump is obvious at the cathode end, as shown in Figures 9 (Jacob et al., 1994) and 10 (Hicks and Tondorf, 1994).

The distributions of metals along the length of the specimen, at different electrode conditions, are illustrated in Figures 11 and 12. No significant accumulation of metals

Figure 10. Distribution of pH at the end of 9-day run (after Hicks and Tondorf, 1994).

Figure 11. Distribution of Pb and Cd along the length of the specimen at different electrode configurations.

($C/C_o > 1.0$) was observed at the far end of the anode electrode although a moderate pH jump (from 2.0 to 3.50) was observed (Figure 8) in the soil in the cases where the SE configuration was used. This was because the final pH at the far end of the soil sample was less than 3.5, and the metals used in this study were fairly soluble at that pH level, as shown in Figures 13 and 14. The C/C_o values for Pb, Cd, Zn, and Mn were higher in the case of the SE configuration, followed by the combined PE and SE configuration, and it was

Figure 12. Distribution of Zn and Mn along the length of the specimen at different electrode configurations.

Figure 13. Variation of metal hydroxide concentration $p[M^{2+}]$ in aqueous phase with pH.

higher than that in the case of the PE configuration. This is understandable according to Figures 13 and 14, as the average pH ~ 3.0 of the soil in the cases of the SE configuration and the combined PE and SE configuration was higher than that of the PE configuration (pH ~ 1.0).

The average concentrations of metals remaining in the soil, after 200 hours of the process run at different electrode configurations, are listed in Table 1. The mass balance of the metals at the PE configuration is listed in Table 2. From Table 1, it is seen that the average concentration of Pb that remained in the soil at the PE configuration was

Figure 14. Variation of total metal concentration $p[M']$ in aqueous phase with pH (partially after Khan and Alam, 1994).

Table 1
Metal concentrations remaining in the soil at different electrode configurations

Metals	PE Configuration Only	SE Configuration Only	Combined PE and SE Configuration
Pb, mg/kg	41 (6.41)*	81 (12.66)	63 (9.84)
Cd, mg/kg	21 (4.16)	42 (8.32)	34 (6.73)
Zn, mg/kg	116 (3.17)	172 (4.70)	134 (3.66)
Mn, mg/kg	74 (6.49)	109 (9.56)	109 (9.56)

*Values in the parentheses are in %.

about 41 mg/kg (~6.41%), followed by 63 mg/kg (~9.84%) at the combined PE and SE configuration. At the SE configuration, the concentrations of Pb that remained was about 81 mg/kg (~12.66%), which is twice as much as at the PE configuration. Similar trends were observed for Cd and Zn. The average concentration of Mn remaining in the soil, both at the SE configuration and the combined PE and SE configuration, were about 109 mg/kg (~9.56%), whereas at the PE configuration it was about 74 mg/kg (~6.49%).

From Table 2, the corresponding removal efficiencies of the four heavy metals demonstrated to be approximately 89.84% of Pb, 96.63% of Cd, 92.89% of Zn, and 91.14% of Mn with the PE configuration. From this table, it is seen that the mass balances for Pb, Cd, Zn, and Mn varied from 95 to 102%. Approximately 2 to 5% of metals were unaccounted for during the processing. One reason for the unaccounted metals could be due to the non-uniform distribution of the cations in soil (Figures 11 through 14); after the processing, small samples of the soil specimens were analyzed and the weighted average of the metal concentrations was reported. The second reason could be the adsorption of metal ions on the graphite electrodes and porous stones during the processing. Therefore, it is reasonable to anticipate that this unaccounted loss could be eliminated to some extent if the whole specimen is analyzed for metal concentrations. From Table 1, in the case of the SE configuration, the removal efficiencies were about 87.34% of Pb, 91.68% of Cd, 95.30% of Zn, and 90.44% of Mn. In the case of the combined PE and SE configuration, the removal efficiencies were about 90.16% of Pb, 93.27% of Cd, 96.34% of Zn, and 90.44% of Mn. No mass balance was performed for the latter two electrode configurations.

Table 2
Mass balance of metals at the PE configuration

Metal	Remaining in soil	Removed in pretreatment chamber	Captured in resin	Total removed	Mass balance, %
Pb, mg/kg	41 (6.41)*	85 (13.28)	490 (76.56)	575 (89.84)	96.25
Cd, mg/kg	21 (4.16)	56 (11.09)	432 (85.54)	488 (96.63)	100.79
Zn, mg/kg	116 (3.20)	352 (9.70)	3,020 (83.20)	3,372 (92.89)	96.09
Mn, mg/kg	74 (6.49)	95 (8.33)	944 (82.81)	1,039 (91.14)	97.63

*Values in the parentheses are in %.

Figure 15. Energy expenditure as a function of time at different electrode configurations.

Evaluation of energy expenditure is an important component to estimate the total cost of the process. Energy expenditure is evaluated per unit volume of soil treated in kWh/m³. The energy expenditure per unit volume of soil processed may be given by the following equation for tests with constant electric potential conditions. It is directly related to the time integral of the electric field across the cell

$$E = \frac{1}{1000V_s} \int VI(t)dt \quad (6)$$

where E is the energy expenditure per unit volume of soil in kWh/m³, V_s is the volume of soil being processed in m³, V is the applied electric field in Volt, $I(t)$ is the electric current passing through the kaolinite barrier in amp, and dt is the time integral operator in hour. The currents across the primary electrodes, obtained from the experiments at 50 volts, were plotted as a function of time and fitted in a 3rd order regression curve. The following equation was obtained.

$$I(t) = -4.0 \times 10^{-7}t^3 + 3.35 \times 10^{-5}t^2 + 4.131 \times 10^{-4}t + 0.0323 \quad (7)$$

Using Equation (6) and the equation of the regression curves (Equation 7), the energy expenditures, in kWh/m³ of soil, were calculated for different time period. Figure 15 represents the plots of the energy expenditure as function of time for both PE configuration and SE configuration. At the end of 200 hours of the processing, the energy expenditure of the decontamination process was about 480 kWh/m³ of soil at the PE configuration and about 522 kWh/m³ at SE configuration. At these energies, Pb, Cd, Zn, and Mn that remained in the soil were 41 mg/kg (~6.41%), 21 mg/kg (~4.16%), 116 mg/kg (~3.17%), and 74 mg/kg (~6.49%), at the PE configuration and 81 mg/kg (~12.66%), 42 mg/kg (~8.32%), 172 mg/kg (~4.70%), and 109 mg/kg (~9.56%), at the SE configuration, respectively, as shown in Table 3. Therefore, it is obvious from this discussion that to remove the same percentage of metal, cost is significantly higher in the SE configuration than that of the PE configuration.

Table 3

Energy expenditure in kWh/m³ of soil with metal concentrations remaining in the soil at different electrode conditions

Metals	PE Configuration Only		SE Configuration Only	
	Metal remaining mg/kg	Energy kWh/m ³	Metal remaining mg/kg	Energy kWh/m ³
Pb	41 (6.41)*	~480	81 (12.66)	~522
Cd	21 (4.16)	~480	42 (8.32)	~522
Zn	116 (3.17)	~480	172 (4.70)	~522
Mn	74 (6.49)	~480	109 (9.56)	~522

*Values in the parentheses are in %.

The amount of metals in mg/kg remaining in the soil, as a function of energy expenditure, at the PE configuration, is presented in Figure 16. The ratio of metal concentration remaining in the soil to the initial concentration of metals available in the soil (C/C_0), as a function of energy expenditure, at the PE configuration, is also presented in Figure 17. From these figures, it is apparent that the metal removal rate was higher up to energy expenditure of 100 kWh/m³ for Pb and Cd. Beyond 100 kWh/m³, the removal rate was very slow and around 380 kWh/m³ of energy was required to reduce approximately 40 mg/kg of Pb and 30 mg/kg of Cd (Figure 16). The curves for Zn and Mn showed a similar pattern and progressive removal rate up to the end of the experiment (i.e. up to 480 kWh/m³ of energy), as shown in Figure 16. Figure 17 showed significant percentages of metal removal

Figure 16. Metal concentrations remaining in the soil versus energy expenditure at the PE configuration.

Figure 17. C/C_o versus energy expenditure at the PE configuration.

up to 100 kWh/m³ for all the four heavy metals. After that energy, a significant amount of energy was required to remove small percentage of the metals.

Summary and Conclusions

A laboratory study was conducted to investigate the effect of secondary electrode configuration in removing heavy metals using the CEHIXM process. A blend of spent foundry sand and millpond sludge (90:10 w/w ratio) containing Pb, Cd, Zn, and Mn was used as a contaminated source. Four sets of experiments were conducted applying an optimum operating voltage of 50 V with soils samples having characteristics as described under Materials and Methods. The first set of experiments was conducted by applying the optimum electric voltage across the semi-permeable barrier at different flow rates for 24 hours to select an optimum operating flow rate to be used in the subsequent experiments. Based on the first set of experiments, an optimum operating flow rate was selected to be of 4 cm³/min (equivalent flow velocity $\approx$ 0.00713 cm/sec). The second set of experiments was conducted by applying the electric voltage across the soil sample to be treated to assess the effectiveness of the SE configuration in removing heavy metals from soils and the corresponding energy expenditure using the same voltage and the optimum operating flow rate, selected from the first set of experiments, for a period of 200 hours. The third set was conducted by applying the electric voltage across the semi-permeable barrier to assess the effectiveness of the PE configuration in removing heavy metals from soils and the corresponding energy expenditure and to compare with the effectiveness of the SE configuration. The fourth set was conducted by applying the electric voltage both across the semi-permeable barrier and the soil sample to assess the effectiveness of the combined PE and SE configuration in removing heavy metals from soils and to compare this with the effectiveness of the SE configuration. The removal efficiencies of the four heavy metals was demonstrated to be approximately 89.84% of Pb, 96.63% of Cd, 92.89% of Zn, and 91.14% of Mn with the PE configuration. In the case of the SE configuration, the removal efficiencies were about 87.34% of Pb, 91.68% of Cd, 95.30% of Zn, and 90.44% of Mn. In the case of the PE and SE configuration, the removal efficiencies were about 90.16% of Pb, 93.27% of Cd,

96.34% of Zn, and 90.44% of Mn. The energy expenditures were about 480 kWh/m³ and 522 kWh/m³ of soil in the case of the PE and the SE configurations, respectively. It appeared that use of the SE configuration or combination of the PE and SE configuration was not cost-effective and advantageous over the use of the PE configuration in removing heavy metals from the contaminated soils by the CEHIXM process. The order of metal removal appeared to be Cd > Zn > Mn > Pb with the PE configuration, Zn > Cd > Mn > Pb with the SE configuration, and Zn > Cd > Mn $\approx$ Pb in the case of combined PE and SE configuration.

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