

The hindering effect of experimental strategies on advancement of alkaline front and electroosmotic flow during electrokinetic lake sediment treatment

Jurate Virkutyte, Mika Sillanpää*

University of Kuopio, Laboratory of Applied Environmental Chemistry, P.O. Box 181, FIN-50101 Mikkeli, Finland

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Abstract

The current study focused on the hindering of alkaline front during electrokinetic copper migration in artificially contaminated lake sediments and the effect of several experimental strategies on electroosmotic flow. Fourteen laboratory scale experiments in triplicates were performed using plastic container where the distance between electrodes was 30 cm at 40 mA, 60 mA and 120 mA electric currents (under density of 0.15 mA cm⁻², 0.23 mA cm⁻² and 0.53 mA cm⁻², respectively) with different Cu concentrations (500 mg kg⁻¹, 1000 mg kg⁻¹, 1500 mg kg⁻¹, 2000 mg kg⁻¹ and 2500 mg kg⁻¹) for 14 days. Tests were conducted with/without electric current and with/without the employment of membranes or barriers. Selected membranes and barriers proved to be efficient in hindering the alkaline front and thus improving copper migration in the sediments. During electrokinetic treatment and the use of the nylon membrane 85% of Cu was removed from sediments. Additionally, 80% and 70% of Cu was removed when cation exchange membrane and filter paper barrier were used. During the electrokinetic treatment Cu as well as the electroosmotic flow was always directed towards the cathode. The highest electroosmotic flow was observed with the lowest (500 mg kg⁻¹) Cu concentration. Moreover, the electroosmotic flow and electrical gradient increased with the increase in electric current and was found to be the highest at 120 mA. When there were no membranes, barriers or acid used, severe pH jump was observed at a normalized distance of 0.5–0.6 from the anode. However, when membranes or barriers were employed, there was no pH jump present in the sediments.

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1. Introduction

Contamination of the environment with heavy metals, radionuclides and hazardous organic compounds is growing every year and may finally result in the loss of entire ecosystems agricultural productivity or cause serious damage to human and animal health problems [1]. Due to increased environmental pollution, there is a continuous search for the most efficient, sustainable and environmentally friendly technique to remediate contaminated media.

Remediation schemes are usually used to reduce the amount of contaminants in the soil or sediments [2]. In the past few years there was a constant search for remediation methods which are technologically sound, cost and time efficient. Lin and Lin [3] described several chemical, engineering and biological meth-

ods for the remediation of soil contaminated with heavy metals. However, chemical methods may destroy soil structure and result in a more severe contamination. In addition, these methods usually require the removal of contaminated soil and replacing it after the remediation process is over creating a secondary disposal problem [1].

One of these emerging technologies are electrokinetic remediation techniques, which offer a great potential for the removal of charged contaminants from sludge [4,5], soil [6], sediments [2] and copper chromated arsenate (CCA)-treated timber waste [7,8]. The electrokinetic phenomenon employs a low-level direct current across the contaminated medium, which induces the mobility of charged contaminants due to electromigration and electroosmotic flow [9]. There are also many chemical or physical reactions such as ion diffusion, ion exchange, mineral decomposition, precipitation of salts, hydrolysis, oxidation, reduction, physical and chemical sorption that usually occur during the electrokinetic remediation process [10].

* Corresponding author. Tel.: +358 15355 6201; fax: +358 15355 6363.
E-mail address: mika.sillanpaa@uku.fi (M. Sillanpää).

When contaminants are present in ionic form, they migrate towards oppositely charged electrodes. Several methods are proposed to enhance the migration of heavy metals under the applied low-level direct electric current. These include the addition of enhancement solutions (citric acid, EDTA and HEDPA) to assist in the solubilization of contaminants from the matrix [11–13], the use of ion exchange membranes, which allow the transport of contaminants present in the matrix [12,14], the conditioning catholyte pH with agents such as acetic acid, lactic acid with sodium hydroxide and acetic acid with EDTA [15] and applying sulfur oxidizing bacteria for copper removal experiments from soils [16].

Lake sediments were chosen as experimental medium because it may act as a sink for contaminants if the industrial site is close to the lake. For example, if contaminant plume is released, sediments may become contaminated with heavy metals and organic pollutants therefore endangering lake's flora and fauna. Contaminated sediments have to be treated or disposed at landfills. However, landfilling is very expensive and therefore alternative treatment methods, which are more economically and environmentally sound, should be implemented.

The current study provides innovative approach regarding lake sediments to hinder alkaline front during electrokinetic treatment, which can be used as efficient *in situ* treatment method, by applying barriers and ion selective membranes. Also, the study involves an experimental approach, aiming to obtain better insights of heavy metal mobilization and migration fundamentals. Additionally, the effect of various electrokinetic remediation strategies such as Cu concentrations and currents were evaluated with regard to electroosmotic flow and copper migration in artificially contaminated sample medium—lake sediments.

2. Materials and methods

2.1. Preparation of artificially contaminated sediments

The amount of sediments, collected from a lake in Oulu (Finland) was 3000 g and was initially homogenized *in situ*. At the laboratory, sediments were sieved and the fraction smaller than 2 mm was used for experiments [17]. The initial Cu concentration was below the detection limits of 0.05 ppm (Perkin-Elmer 300). 3.58 g of $\text{Cu}(\text{NO}_3)_2$ was dissolved in deionized water ($0.055 \mu\text{S}$, $18 \text{ m}\Omega$, $T = 22 \pm 1^\circ\text{C}$, $\text{pH} 7.1$) to achieve 1000 mg kg^{-1} copper concentration. Additionally, to test the effect of Cu concentration on the electroosmotic flow, different $\text{Cu}(\text{NO}_3)_2$ concentrations were used: 500 mg kg^{-1} , 1500 mg kg^{-1} , 2000 mg kg^{-1} and 2500 mg kg^{-1} of Cu.

To homogenize sediment–contaminant mixture, it was stirred for an hour and was kept 48 h away from a direct sunlight to achieve consistent contaminant concentration and moisture content as described by Altin and Degirmenci [18]. Contaminated sediments were mixed with KNO_3 solution to fill the pores to keep the moisture content of 20–28%. Prepared mixture was relocated into the electrokinetic cell and compacted by the consolidation method [19]. Table 1 presents the main characteristics of experimental sediments.

Table 1
Main characteristics of pre-contaminated lake sediments

Parameter	Amount in sediments
Contaminant	Cu
Cation exchange capacity (CEC) ($\text{cmol}_c \text{ kg}^{-1}$)	1.51
Organic content (%)	2.9
Carbonate content (%)	10.2
Water content (%)	20–28
Clay (<0.002 mm)	6
Silt (0.002–0.06 mm)	16
Sand (0.06–2 mm)	78
pH	7.3

2.2. Experimental design

Laboratory scale electrokinetic experiments were conducted in a rectangular $40 \text{ cm} \times 17 \text{ cm} \times 15 \text{ cm}$ plastic container (Fig. 1). Three litres of 0.05 M KNO_3 conductive solution was supplied initially to the electrokinetic cell to prevent drying of the sediment cake. KNO_3 was chosen as a conductive solution due to its higher conductivity than demi-water for higher current to pass through sediments to facilitate the migration of ions. Also, KNO_3 does not produce hazardous by-products when electric current is applied. Additionally, if treatment is performed *in situ*, there is always some concentration of nitrates available and there is no need to add additional solutions. Moreover, addition of KNO_3 may also facilitate better understanding of nitrate migration and hence its removal by electric current. Table 2 presents experiments conducted in triplicates in the present study.

Electrokinetic set up consisted of DC power supply (Hewlett-Packard 613 Altai, Germany), which was used to constantly maintain a 0.15 mA cm^{-2} , 0.23 mA cm^{-2} and 0.53 mA cm^{-2} DC, plastic container, connection cables and electrodes. The voltage fluctuations were monitored with a Fluke 112 multimeter (Fluke, Eindhoven, The Netherlands).

Graphite plate anode was placed directly into the sediments and the cathode was immersed into the conductive solution. The sediment cake was supported by a porous plastic wall covered

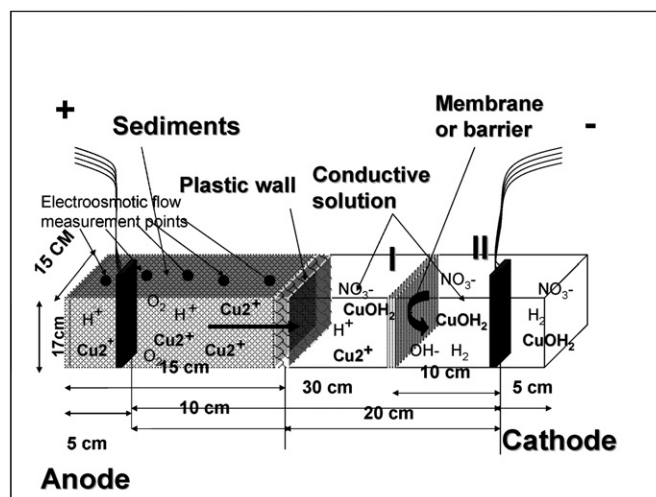


Fig. 1. Schematic representation of electrokinetic cell, where I and II are catholytic compartments.

Table 2
Experiments conducted in the present study (triplicates, differences in measurements 9–13%)

Experiments number	Description
1	Uncontrolled pH, no membranes used
2	No electric current, no membranes used
3	pH controlled with 5 ml 0.5 M HNO ₃ , no membranes, no HNO ₃ addition
4	Cation exchange membrane (CAT), no HNO ₃ addition
5	Filter paper barrier, no HNO ₃ addition
6	Nylon 6 membrane, no HNO ₃ addition
7	500 mg kg ⁻¹ Cu concentration, CAT membrane, no HNO ₃ addition
8	1000 mg kg ⁻¹ Cu concentration, CAT membrane, no HNO ₃ addition
9	1500 mg kg ⁻¹ Cu concentration, CAT membrane, no HNO ₃ addition
10	2000 mg kg ⁻¹ Cu concentration, CAT membrane, no HNO ₃ addition
11	2500 mg kg ⁻¹ Cu concentration, CAT membrane, no HNO ₃ addition
12	1000 mg kg ⁻¹ Cu concentration, 40 mA, CAT membrane, no HNO ₃ addition
13	1000 mg kg ⁻¹ Cu concentration, 60 mA, CAT membrane, no HNO ₃ addition
14	1000 mg kg ⁻¹ Cu concentration, 120 mA, CAT membrane, no HNO ₃ addition

with filter paper to avoid sediment penetration into the electrode compartments. Cathodic compartment was separated from sediments and catholyte I by cation-exchange (IC1-61CZL386) membrane (Ionics Inc., Watertown, MA, USA). To test the efficiency of different remediation strategies, nylon membrane with thickness of 5 mm (Nylon 6, obtained from Goodfellow Cambridge Ltd., UK) was used. Filter paper (particle retention 16 µm) was obtained from Millipore Inc., USA. The total length of the sediments was 15 cm. The electric field was applied for 14 days. Table 3 summarizes experimental design for the electrokinetic treatment process.

2.3. Analyses

At the end of the electrokinetic treatment, the power supply was turned off, the electrode wires were disconnected and

Table 3
Experimental design of laboratory scale electrokinetic treatment experiments

Parameter	Value
Contaminated sediment area (cm ²)	260
Length of sediments (cm)	15
Plate electrode area (15 cm × 3 cm) (cm ²)	45
Membrane area (cm ²)	225
Barrier or membrane location from sediments (cm)	10
Distance between electrodes (cm)	30
Applied currents (mA)	40, 60 and 120
Current densities (mA cm ⁻²)	0.15, 0.23 and 0.53
Duration of experiments (days)	14
Conductive solution	3 l 0.05 M KNO ₃
pH control solution	0.5 M HNO ₃

the electrokinetic cell was disassembled. After each experiment, electrodes and cation exchange membrane were immersed into diluted acidic solution to extract copper. Sediment samples were taken from the electrokinetic apparatus and sliced into five slices (3 cm thick) with a stainless steel serrated knife. Each sediment slice was thoroughly homogenized prior to analysis as suggested by Ottosen et al. [11]. The pH of the slices was measured by mixing 10 g of dry sediments and 25 ml 1 M KCl as reported by Alshawabkeh and Sarahney [20].

The total metal concentration in the homogenized samples (expressed as mg metal kg⁻¹ dry weight) after electrokinetic treatment was determined after microwave destruction and aqua regia (HCl/HNO₃, 3:1) digestion (Matthews CEM 2100, NC, USA) as described by Virkutyte et al. [4]. The digestion procedure was carried out in three steps (15 min at 100 °C, 15 min at 150 °C and 30 min at 200 °C). After digestion, Cu concentration was measured using Flame-AAS (Perkin-Elmer 300).

Organic matter content was measured by loss of ignition at 550 °C for 1 h as suggested by Nystroem et al. [2]. Water content in sediments was obtained after the drying of samples for 24 h in 105 °C chamber. The carbonate content was determined by a volumetric calcimeter method [21].

2.4. Electroosmotic flow determination

The electroosmotic flow was determined as described in details by Wick et al. [22]. One millilitre of phenolphthalein solution (0.5% in 50% aqueous ethanol) was injected in the sediments. The flow was determined after each day of experiments by removing of 5 ml of pore water at given locations (Fig. 1). The phenolphthalein concentration was determined spectrophotometrically at 555 nm after the addition of NaOH.

2.5. Quality assurance and control

The analysis of samples followed the standard quality assurance and control (QA/QC) procedures [23]. According to Reddy and Chinthamreddy [24], to assure the reproducibility of testing procedure, following precautions should be taken into considerations: (1) new electrodes, cation exchange membranes and barriers were used for each experiment; (2) after electrokinetic treatment, plastic container was immersed into 0.05 M HCl solution for 24 h, rinsed with tap water and then with distilled water to avoid contamination; (3) all chemical analysis was performed in triplicates; (4) the AAS calibration was checked after five samples; (5) and a mass balance was calculated for each test.

2.6. Mass balance

Mass balance calculations of copper were done for each concentration (Table 4). The mass balances of copper were calculated from its concentrations in the liquid phase, in the sediments and the metal deposited onto the electrodes and membrane. The data of total copper concentrations were obtained from triplicates ($n = 3$).

Table 4
Mass balance calculated for laboratory scale experiments

Experiment	Electrode	Initial total amount	In sediments after experiment	Anode	Catholyte I	On membrane or barrier	Cathode	Catholyte II	Total final amount
CAT ^a	Cu	500 ± 52	75 ± 8.2	0.2	2.3	32 ± 3.2	4.5 ± 0.32	340 ± 42	507 ± 48
Nylon ^b	Cu	1000 ± 101	70 ± 8.5	0.1	1.8	55 ± 4.7	5.2 ± 0.31	820 ± 72	1035 ± 40
CAT			120 ± 10.1	0.1	1.6	40 ± 3.1	4.9 ± 0.42	730 ± 65	974 ± 72
Filter paper ^c			280 ± 16.5	0.1	2.2	66 ± 5.8	5.2 ± 0.42	540 ± 42	957 ± 85
CAT	Cu	1500 ± 112	250 ± 18.1	0.0	2.1	56 ± 5.1	4.6 ± 0.32	1080 ± 125	1460 ± 120
CAT	Cu	2000 ± 253	350 ± 27.5	0.1	1.7	67 ± 6.2	5.8 ± 0.45	1250 ± 138	1846 ± 185
CAT	Cu	2500 ± 285	420 ± 36.6	0.1	1.7	79 ± 6.7	7.2 ± 0.64	1750 ± 215	2516 ± 179

Values are presented for the experiments at 40 mA.

^a Cation exchange membrane.

^b Nylon mesh barrier.

^c Filter paper barrier.

3. Results and discussion

3.1. Variations in pH and the effect on the copper migration

When electricity is applied to the soil or sediments, electrolysis of water takes place at the electrodes where oxygen and hydrogen ions are produced at the anode and hydrogen and hydroxide ions are produced at the cathode. As could be seen from Fig. 2, compared to the initial pH values, which were circum-neutral, pH changed significantly in the areas close to the anode and the cathode in the experiment with no pH control. In addition, current study demonstrated that acidic front, developed at the anode was moving towards the cathode and alkaline front, developed at the cathode migrated towards the anode where they met at a normalized distance of 0.5–0.6 from the anode after 6 days of electrokinetic treatment (Fig. 2). This is in agreement with the findings of Chung and Kang [25] where they observed similar phenomenon when examining electrokinetic lead removal from contaminated marine clay.

It is observed that buffering capacity of the soil or sediments, i.e. the carbonate content influences the pH changes [26]. However, the carbonate content in the current study was only 10.2%, hence it was not sufficient to buffer the acidic generation at the anode. Thus the most evident pH changes occurred in the experiment without pH control (Fig. 2).

Altin and Degirmenci [18] have stated that changes in the pH profiles between the anode and cathode hinders contaminant

migration. Indeed, experiments conducted in the current study showed that pH has a significant impact on the Cu migration in the lake sediments (Figs. 2 and 3). Due to the low pH at the anode there was insignificant concentration of Cu found close to the anode, as it is well documented that Cu is the most mobile under acidic conditions in soils [14]. However, when the normalized distance from the anode reached 0.5, Cu concentration significantly increased without pH control. In addition, there was a visible increase in Cu concentration when several strategies were employed, due to the alkaline front coming from the cathode (Fig. 3).

In experiments with no pH control, a sharp change in pH occurred at a normalized distance of 0.5–0.6 from the anode within several days since initiation of the electric treatment (Fig. 2). Suèr and Allard [27] also found that after several days of electric treatment, the pH shift approached the cathode and mostly all the soil was found to be acidic. After the electrokinetic treatment, there was no well-defined copper migration in the lake sediments (Fig. 2), which could be attributed to the unfavorable pH conditions for efficient copper migration. However, as there were acidic conditions by the anode observed, it allowed insignificant release of copper from the sediments (Figs. 2 and 3). The pH started to increase at a normalized distance of 0.5 from the anode (Fig. 2), indicating that some OH⁻ ions were reaching the sediments and possibly interfering with the mobility of copper ions. It is similar to the observations by Suèr et al. [28], who found that increasing pH lowers

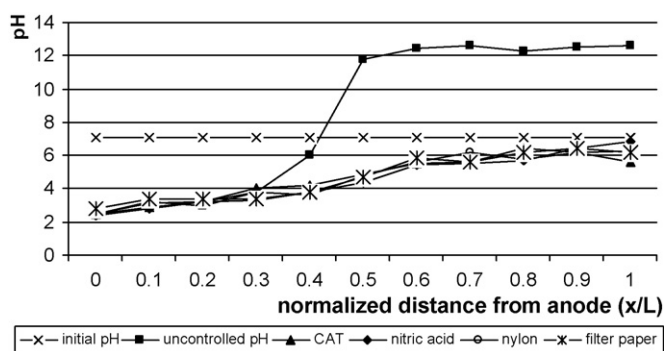


Fig. 2. Distribution of pH during the electrokinetic treatment, where x is a distance from anode and L is a length of sediment cake.

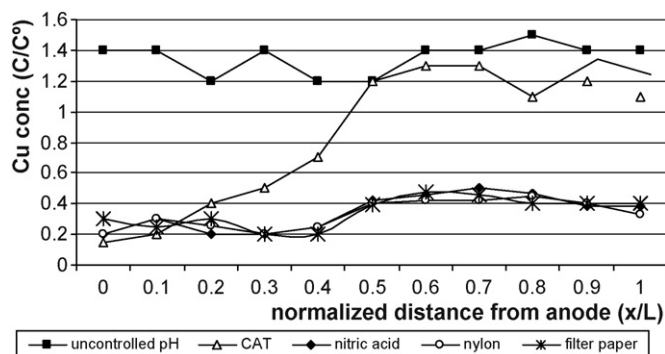


Fig. 3. Normalized Cu concentration profiles at the end of electrokinetic experiments.

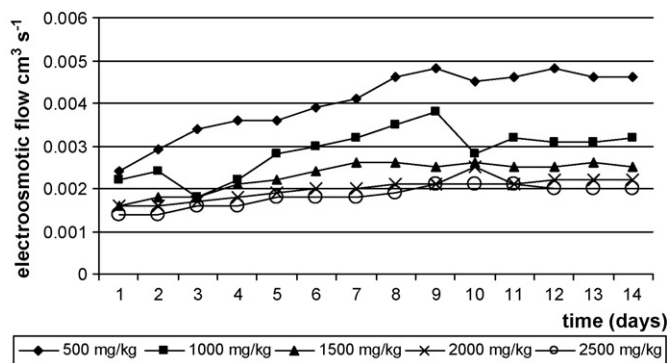


Fig. 4. Variation of the electroosmotic flow velocity during electrokinetic treatment.

the mobility of the cations and they associated with the soil as hydroxides.

There was no sudden pH shift observed when nylon and cation exchange membranes, 5 ml of 0.5 M HNO₃ at the cathode or filter paper barrier were introduced (Fig. 2) indicating that application of membranes and barriers stopped the alkaline front from penetration into the sediments. Similar findings were observed by Li et al. [29], where the employment of cation selective membrane for the diminishing of drastic pH changes and therefore increasing the efficiency of electrokinetic treatment of soils was discussed.

When the pH was controlled with nitric acid or barriers and/or membranes, Cu concentration found in the sediments after the electrokinetic treatment was in the range of 0.25–0.4 indicating that the 80–85% of Cu initially present in the sediments was removed from the matrix at the acidic (pH of 2.5–5.5) conditions (Figs. 2 and 3). This is in agreement with the findings of Suèr and Allard [27] where they observed pH influence on Cu, Ni and Zn electrokinetic migration in contaminated soils.

3.2. Electroosmotic transport

In all the tests the direction of electroosmotic flow was towards the cathode suggesting that lake sediments has net negative surface charge. The electroosmotic flow measured at different Cu concentrations is presented in Fig. 4.

It is documented that zeta potential influences the electroosmotic flow [22,30]. It seems that there is some controversy at which extent pH influences zeta potential and electroosmotic flow. For example, Reddy et al. [31] has stated that electroosmotic flow is directly proportional to soil zeta potential, e.g. when negativity of soil zeta potential increases, electroosmotic flow also increases. Certainly, the results in the current study show that at the beginning of the electrokinetic treatment when pH was acidic (pH 2.5–4) by the anode (Fig. 2), the electroosmotic flow started to increase from 0.0015–0.0025 cm³ s⁻¹ to 0.004–0.005 cm³ s⁻¹ with the change in time and pH (Fig. 4). At the end of experiments, when the pH was 4–6, the electroosmotic flow slightly decreased or remained constant. In addition, the same pattern in electroosmotic flow variation was observed in all the experiments (Fig. 4). However, this is in contrast to findings by Altin and Degirmenci [18], who stated that hydroxyl

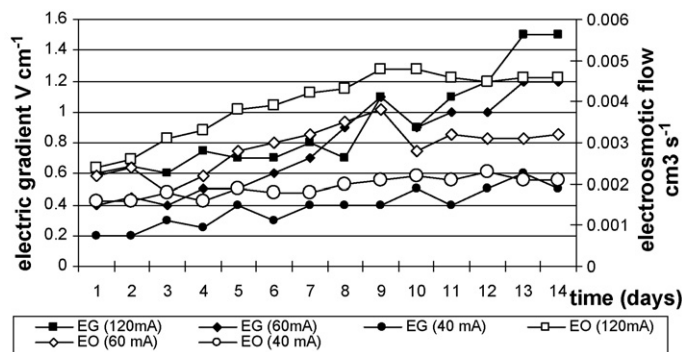


Fig. 5. Development of electroosmotic flow velocity and electric potential gradient profiles at various electric currents.

ions in the cathode compartment increase the pH of the system and therefore impairs the electroosmotic flow.

On the other hand, our observation is in good agreement with the finding that when H⁺ front, formed due to the electrolysis of water migrates through the soil, cationic concentrations in the pore water increases due to the desorption and/or dissolution of species [32]. Therefore, the decrease in pH and increase in the cations concentration in the pore water results in a reduction of zeta potential and the electroosmotic flow should decrease as well. Indeed, the overall electroosmotic flow was much higher (up to 0.005 cm³ s⁻¹) when pH was slightly acidic or circum neutral in comparison to extremely acidic conditions (pH 2.5–4) when the highest electroosmotic flow was 0.0035 cm³ s⁻¹ (Fig. 4).

The lowest electroosmotic flow (0.001–0.0015 cm³ s⁻¹ and 0.0015–0.002 cm³ s⁻¹) was observed with the highest Cu concentrations (2500 mg kg⁻¹ and 2000 mg kg⁻¹), respectively (Fig. 4). This is in accordance to Altin and Degirmenci [18], who argued that high metal concentration causes a decrease in soil's zeta potential, which also causes a decrease in electroosmotic flow as well. In addition to zeta potential, high copper concentration increases the conductivity in the bulk outside the electric double layer and electric field by-pass the double layer and thus no electroosmosis occur (Fig. 4).

To test the effect of electric current on the electroosmotic flow, several experiments were performed with different electric currents (Fig. 5). Results demonstrated that when the current was the highest (120 mA), the electroosmotic flow was also the highest (up to 0.005 cm³ s⁻¹), and with the decrease in current to 40 mA, the electroosmotic flow also decreased to as low as 0.0015 cm³ s⁻¹ (Fig. 5). This is consistent with the findings of Kim et al. [32], where electrokinetic heavy metal removal from tailing soils was tested. It was found that higher electroosmotic flow resulted from the higher voltage (electric field strength) applied. The increase in electroosmotic flow, with increase in current in the present study may also be associated with large voltage gradient, which occurs in the low conductivity region [33].

3.3. Electrical potential gradient

Fig. 5 presents variations in the electrical potential gradient across the sample when different electrical currents were applied

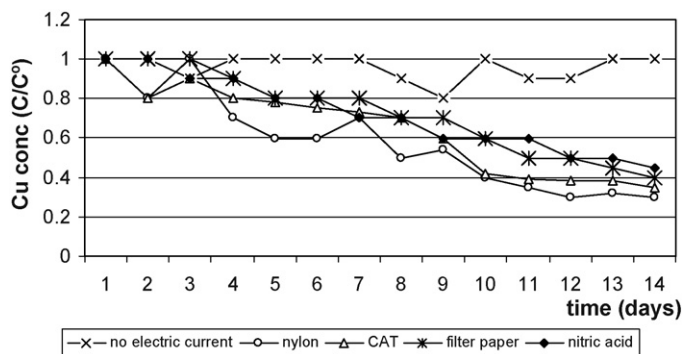


Fig. 6. Changes in Cu concentration in the sediments in time using various enhancement strategies.

for 14 days to remove 1000 mg kg^{-1} of Cu from sediments. The final electrical potential gradient at 40 mA was 0.5 V cm^{-1} , at 60 mA it was 1.2 V cm^{-1} and 1.5 V cm^{-1} at an electric current of 120 mA (Fig. 5). It is evident that electrical potential gradient increased with an increase in the applied electrical current. This is consistent to the findings of Chung and Kang [25] where lead removal from contaminated marine clay by electrokinetics was investigated.

The increase in electric voltage gradient is related to the increase in the resistivity or current [34]. Therefore, the increase in resistance may be attributed to $\text{Cu}(\text{OH})_2$ precipitates in the high pH areas by build up of excess OH^- in the pore solution by the cathode. Moreover, Sah and Chen [35] argued that an increase in resistance and a subsequent increase in the electrical potential gradient might be due to the formation of non-conducting gaseous bubbles on the surface of electrodes due to the electrolysis of water when electricity is applied.

3.4. Different removal strategies of copper

After the experiments were completed, the total Cu concentrations were determined in each of the sediment slices. The normalized Cu concentration ratio across the specimens is presented as a function of time in Figs. 6 and 7. Fig. 6 shows Cu concentration development profiles in the sediments for the four experiments performed with several enhancement strategies. When there was no electricity, normalized concentration

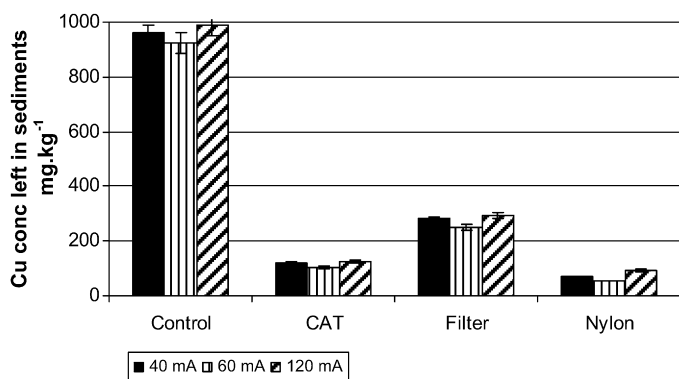


Fig. 7. Cu removal from lake sediments with various current strength (control experiment is performed without pH adjustment).

ratio of Cu in the sediments was $0.9\text{--}1 \text{ mg kg}^{-1}$ indicating that Cu migration did not occur (Fig. 6).

During experiments when nitric acid, nylon membrane, filter paper and cation selective membrane were used, a significant migration of Cu from sediments was observed over 14 days (Fig. 6). The migration Cu could be attributed to the desorption of contaminant ions into the pore solution by cation exchange of the hydrogen ions advancing across the matrix from the anode and its subsequent flushing towards the cathode by electromigration, electroosmosis and advection [25].

The most efficient Cu removal was achieved with nylon membranes when the normalized concentration decreased from 1 mg kg^{-1} to 0.25 mg kg^{-1} . Despite during 11 days of the experiments with cation exchange membrane, normalized Cu concentration in the sediments decreased from 1 mg kg^{-1} to 0.4 mg kg^{-1} in comparison to experiments with nylon membrane and filter paper (from 1 mg kg^{-1} to 0.45 mg kg^{-1} and from 1 mg kg^{-1} to 0.4 mg kg^{-1} , respectively), it remained constant afterwards and did not reach the values of nylon membranes (Fig. 6). Although there was significant Cu removal achieved when filter paper was used as a barrier (from 1 mg kg^{-1} to 0.4 mg kg^{-1}), the removal was at a lesser extend than with nylon membrane or cation exchange membrane.

However, major disadvantage of filter paper as a barrier is that trapped particles cannot be regenerated. On the contrary, membranes usually have pores too small for particles to enter so the bulk occurs at the membrane surface. Therefore, the membrane can be reused after appropriate cleaning or flushing. Inevitably, membranes or barriers will show losses in flux because of increased contaminant concentrations, precipitations and fouling. Further research is warranted to evaluate the extent of concentration polarization and other phenomena that causes the loss in flux.

3.4.1. Nylon membrane

Nylon is a manufactured fiber in which the fiber forming substance is a long-chain synthetic polyamide in which less than 85% of the amide-linkages ($-\text{CO}-\text{NH}-$) are attached directly to two aromatic rings [36]. The nylon material is hydrophilic. The permeability of the nylon membrane is much higher than that of for example porous ceramic of similar characteristics, which is due to its much lower thickness [37]. Moreover, experiments conducted using nylon membranes have a potential to be time and cost efficient in comparison to other high quality porous membranes.

Usually high quality polyamide barriers have uniform pore sizes. Several advantages are reported by Risbud and Bhone [38], which are flexibility and easy-to-handle structure, instant and complete wetting, in-flammability, and resistance to alkaline products, oils, neutral salts and organic solvents. Due to membrane's high surface area and high binding capacity, ions may successfully immobilize within the membrane. Pores are able to retain OH^- ions, however, the exact mechanism should be researched further. The results obtained in the current study showed that the high efficiency of nylon (polyamide) membrane may be attributed to its structure as it is capable to prevent OH^- formed by the cathode from penetration into the anodic com-

partment and sediments and therefore impairing the remediation process.

However, it is reported by Goodfellow Cambridge Ltd., nylon membrane manufacturer that barriers have intolerance to very low pH environments (pH 1.5–2.5). However, experimental conditions in the current study allowed application of this barrier as the pH environment has not reached critical pH values (Fig. 2).

3.4.2. Filter paper barrier

Filter paper barrier is a deep-bed filter made of randomly arranged fibers. It has been reported by Yang and Chen [39] that the efficiency of filter papers to perform as membranes highly depends among other parameters on polarity and size of the fibers, the thickness, the charge and density of the particles passing through it. Experimental results showed that filter paper could be used as an efficient barrier to stop OH^- ions in the electrokinetic experiments. Apparently, as filter paper is chemically non-reactive, the main ion retention mechanism is size exclusion as pore size of a filter is smaller than OH^- ions, they remain physically trapped within the barrier.

Therefore, the normalized Cu concentration reached 0.35 mg kg^{-1} in the sediments after the electrokinetic treatment, in comparison to 0.9 mg kg^{-1} when no barrier or membranes were used (Fig. 6). The advantages of filter paper barrier can be attributed to its resistivity to acid and alkali influence, efficient performance time and low replacement costs [40].

3.4.3. Cation selective membrane

Cation selective membranes usually consist of polystyrene with negatively charged anionic groups like SO_3^{2-} attached to phenol rings [41]. These negatively charged groups are balanced by positively charged cations, like Na^+ . During experiments strongly acidic cation permeable membrane, which is sometimes called Na type membrane was selected. The physicochemical characteristics of this membrane include relatively small thickness of 0.13–0.15 mm, strong resistivity to acids and bases, long lasting performance and minor maintenance activity. However, the cost efficiency is lower in comparison to nylon or filter paper barriers. Ion exchange membranes have a charged surface and it attracts dissolved ions, with appropriate charge. Oppositely charged ions are transported through the membrane but ions with the same charge are rejected.

3.5. Removal of Cu with varying EK strategies and different current strength

Fig. 7 presents Cu concentration in the sediments after the control experiment without the application of the current and the electrokinetic experiments with different current strength and various remediation strategies. The amount of Cu found in the sediments after the electrokinetic treatment was always lower than after the control experiment, performed without the electrical current or employment of membranes and barriers.

According to Fig. 7, the amount of Cu found in sediments was lower with the increase of current strength from 40 mA to 60 mA. However, then 120 mA current was applied, the amount of Cu found in the sediments was the highest (up to 300 mg kg^{-1}),

regardless the remediation strategy. Similar observations were made by Nystroem et al. [2], when harbor sediments were electrodiagnostically treated to remove Cu, Zn, Pb and Cd. Therefore, the optimum current strength should always be found for the efficient treatment as it is obvious that higher current does not always guarantee the highest removal efficiency. When 120 mA was applied, there was some foaming observed by the anode in the sediments. However, authors state that the development of the foam did not significantly affect the Cu concentration changes in the sediments.

The removal efficiencies were 85% when using nylon membrane, 80% with cation exchange membrane and 70% when filter paper was used (Fig. 7). There was no complete Cu removal from lake sediments achieved, which maybe be attributed to the water splitting at the membranes or barriers, among other factors such as optimum current strength and treatment enhancement strategy. As discussed by Ottosen et al. [41], water splitting by the cation exchange membrane at very high current densities is observed in the experiments with soil. Therefore, alkaline front produced from water splitting at the cation exchange membrane may hinder the migration of Cu. Indeed, the Cu concentration left in the sediments after the electrokinetic treatment with cation exchange membrane was lower in comparison to nylon membrane (Fig. 7).

3.6. Mass balance

After the electrokinetic treatment for 14 days at 40 mA, an approximate mass balance was calculated for Cu in the electrokinetic system in comparison to Cu in the spiked sediments. The recovery of Cu from the sediments was 95–105% (Table 4). As it is suggested by Saichek and Reddy [33], several discrepancies in the mass balance may be attributed to the detection limits in the chemical analyses, contaminant adsorption to the electrokinetic cell walls, tubing and sample bottles.

Cathode and catholyte compartments contained 22–25 times more Cu than anode and catholyte I regardless the initial concentrations used (Table 4). In addition, there is a significant amount of Cu retained by the membrane or barrier indicating that when remediation conditions are optimized it may be possible to retain more Cu or any other target metal in the membrane or barrier itself, hence diminishing the necessity for the pumping out contaminants from cathode compartment after the electrokinetic treatment is over.

4. Conclusions

Laboratory scale experiments demonstrated that efficiently utilized barriers and membranes coupled with experimental strategies can hinder alkaline front and thus enhance migration of Cu in artificially contaminated lake sediments.

The electroosmotic flow was always directed from the anode to the cathode and was the highest with the lowest (500 mg kg^{-1}) Cu concentration.

The electroosmotic flow and electrical gradient increased with the increase in electric current and was the highest at 120 mA.

Employment of membranes and barrier was found to be efficient in removing Cu from sediments achieving 85%, 80% and 70% removal efficiencies with nylon membrane, cation exchange membrane and filter paper, respectively, with different electric currents. However, for the cost efficiency it is important to calculate the limiting current density and apply density, which is less than limiting current density.

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References

- [1] S. Raicevic, T. Kaludjerovic-Radoicic, A.I. Zouboulis, In situ stabilization of toxic metals in polluted soils using phosphates: theoretical prediction and experimental verification, *J. Hazard. Mater.* 117 (2005) 41–53.
- [2] G.M. Nystroem, L.M. Ottosen, A. Villumsen, Electrolytic removal of Cu, Zn, Pb and Cd from harbor sediment: influence of changing experimental conditions, *Environ. Sci. Technol.* 39 (2005) 2906–2911.
- [3] C.C. Lin, H.L. Lin, Remediation of soil contaminated with the heavy metal (Cd^{2+}), *J. Hazard. Mater.* 122 (2005) 7–15.
- [4] J. Virkutyte, E. van Hullebuch, M. Sillanpää, P. Lens, Copper and trace element fractionation in electrokinetically treated methanogenic anaerobic granular sludge, *Environ. Pollut.* 138 (2005) 518–529.
- [5] S.O. Kim, S.H. Moon, K.W. Kim, S.T. Yun, Pilot scale study on the ex situ electrokinetic removal of heavy metals from municipal wastewater sludges, *Water Res.* 36 (2002) 4765–4774.
- [6] D.B. Gent, R.M. Bricka, A.N. Alshwabkeh, S.L. Larson, G. Fabian, S. Granade, Bench- and field-scale evaluation of chromium and cadmium extraction by electrokinetics, *J. Hazard. Mater.* 110 (2004) 53–62.
- [7] J. Virkutyte, E. Velizarova, A.B. Ribeiro, M. Sillanpää, Copper and chromium electrokinetic migration in CCA-treated timber waste, *Water Air Soil Pollut.* 160 (2005) 27–39.
- [8] E. Velizarova, A.B. Ribeiro, L.M. Ottosen, A comparative study on Cu, Cr and As removal from CCA-treated wood waste by dialytic and electrokinetic processes, *J. Hazard. Mater.* B94 (2002) 147–160.
- [9] J. Virkutyte, M. Sillanpää, P. Latostenmaa, J. Martisius, Electrokinetic copper removal from lake sand: the process design and kinetics, *Int. J. Surf. Min. Reclam. Environ.* 18 (2004) 220–231.
- [10] S.-H. Liu, H.P. Wang, M.Y. Yu, Y.-J. Huang, H.-C. Wang, Speciation of copper in a contaminated soil during H_3PO_4 -assisted EKR, *J. Electron Spectrosc. Relat. Phenom.* 144–147 (2005) 311–314.
- [11] L.M. Ottosen, A.J. Pedersen, A.B. Ribeiro, H.K. Hansen, Case study on the strategy and application of enhancement solutions to improve remediation of soils contaminated with Cu, Pb and Zn by means of electrokinetics, *Eng. Geol.* 77 (2005) 317–329.
- [12] S. Amrate, D.E. Akretche, C. Innocent, P. Seta, Removal of Pb from a calcareous soil during EDTA-enhanced electrokinetic extraction, *Sci. Tot. Environ.* 349 (2005) 56–66.
- [13] K. Popov, A. Kolosov, Y. Ermakov, V. Yachmenev, A. Yusupovich, N. Shabanova, B. Kogut, A. Frid, Enhancement of clay zeta-potential by chelating agents, *Colloids Surf. A: Physicochem. Eng. Aspects* 244 (2004) 25–29.
- [14] W.S. Kim, S.O. Kim, K.W. Kim, Enhanced electrokinetic extraction of heavy metals from soils assisted by ion exchange membranes, *J. Hazard. Mater.* 118 (2005) 93–102.
- [15] D.M. Zhou, C.F. Deng, L. Cang, Electrokinetic remediation of a Cu contaminated red soil by conditioning catholyte pH with different enhancing chemical reagents, *Chemosphere* 56 (2004) 265–273.
- [16] G. Maini, A.K. Sharman, G. Sunderland, C.J. Knowles, S.A. Jackman, An integrated method incorporating sulfur-oxidizing bacteria and electrokinetics to enhance the removal of copper from contaminated soils, *Environ. Sci. Technol.* 34 (2000) 1081–1087.
- [17] D. Turer, A. Genc, Assessing effect of electrode configuration on the efficiency of electrokinetic remediation by sequential extraction analysis, *J. Hazard. Mater.* B119 (2005) 167–174.
- [18] A. Altin, M. Degirmenci, Lead(II) removal from natural soils by enhanced electrokinetic remediation, *Sci. Tot. Environ.* 337 (2005) 1–10.
- [19] K.R. Reddy, U.S. Parupudi, S.N. Devulapalli, C.Y. Xu, Effect of soil composition on the removal of chromium by electrokinetics, *J. Hazard. Mater.* 55 (1997) 135–158.
- [20] A.N. Alshwabkeh, H. Sarahney, Effect of current density on enhanced transformation of naphthalene, *Environ. Sci. Technol.* 39 (2005) 5837–5843.
- [21] R.H. Loeppert, D.I. Suarez, Methods of soil analysis. Part 3, in: J.M. Bingham (Ed.), *Chemical Methods—SSSA Book Series No. 5*, American Society of Agronomy, Madison, WI, 1996, pp. 451–455.
- [22] L.Y. Wick, P.A. Mattle, P. Wattiau, H. Harms, Electrokinetic transport of PAH-degrading bacteria in model aquifers and soil, *Environ. Sci. Technol.* 38 (2004) 4596–4602.
- [23] M. Segura, C. Cámara, Y. Madrid, C. Rebollo, J. Azcárate, G.N. Kramer, B.M. Gawlik, A. Lamberty, Ph. Quevauville, Certified reference materials (CRMs) for quality control of trace-element determinations in wastewater, *TrAC Trends Anal. Chem.* 23 (2004) 194–202.
- [24] K.R. Reddy, S. Chinthamreddy, Effects of initial form of chromium on electrokinetic remediation in clays, *Adv. Environ. Res.* 7 (2003) 353–365.
- [25] H.I. Chung, B.H. Kang, Lead removal from contaminated marine clay by electrokinetic soil decontamination, *Eng. Geol.* 53 (1999) 139–150.
- [26] K.R. Reddy, S. Chinthamreddy, Enhanced electrokinetic remediation of heavy metals in glacial till soils using different electrolyte solutions, *J. Environ. Eng.* 130 (2004) 442–455.
- [27] P. Suèr, B. Allard, Mercury transport and speciation during electrokinetic soil remediation, *Water Air Soil Pollut.* 143 (2003) 99–109.
- [28] P. Suèr, K. Gitye, B. Allard, Speciation and transport of heavy metals and macroelements during electroremediation, *Environ. Sci. Technol.* 37 (2003) 177–181.
- [29] Z. Li, J.W. Yu, I. Neretnieks, Removal of Pb(II), Cd(II) and Cr(III) from sand by electromigration, *J. Hazard. Mater.* 55 (1997) 295–304.
- [30] L.J. West, D.I. Stewart, Effect of zeta potential on soil electrokinetics, *Geoenvironment* 2000 (1996) 1535–1549.
- [31] K.R. Reddy, C.Y. Xu, S. Chinthamreddy, Assessment of electrokinetic removal of heavy metals from soils by sequential extraction analysis, *J. Hazard. Mater.* B84 (2001) 279–296.
- [32] S.O. Kim, K.W. Kim, D. Stüben, Evaluation of electrokinetic removal of heavy metals from tailing soils, *J. Environ. Eng.* 128 (2002) 705–715.
- [33] R. Saichek, K.R. Reddy, Effect of pH control at the anode for the electrokinetic removal of phenanthrene from kaolin soil, *Chemosphere* 51 (2003) 273–287.
- [34] L.M. Ottosen, T. Eriksson, H.K. Hansen, A.B. Ribeiro, Effects from different types of construction refuse in the soil on electrokinetic remediation, *J. Hazard. Mater.* 91 (2002) 205–219.
- [35] J.G. Sah, J.Y. Chen, Study of the electrokinetic process on Cd and Pb spiked soils, *J. Hazard. Mater.* 58 (1998) 301–315.
- [36] G. McCrum, C.P. Buckley, C.B. Bucknall, *Principles of Polymer Engineering*, Oxford University Press, Oxford, UK, 1997.
- [37] D.J. Upadhyay, N.Y. Cui, C.A. Anderson, N.M.D. Brown, A comparative study of the surface activation of polyamides using an air dielectric barrier discharge, *Colloids Surf. A: Physicochem. Eng. Aspects* 248 (2004) 47–56.
- [38] M.V. Risbud, R.R. Bhonde, Polyamide 6 composite membranes: properties and in vitro biocompatibility evaluation, *J. Biomater. Sci. Polym. Ed.* 12 (2001) 125–136.
- [39] L. Yang, P. Chen, Chitosan/coarse filter paper composite membrane for fast purification of IgG from human serum, *J. Membr. Sci.* 205 (2002) 141–153.
- [40] A.M. Dessouki, M. El-Tahawy, H. El-Boohy, S.A. El-Mongy, S.M. Badawy, Chemical reactive filter paper prepared by radiation-induced graft polymerization. I, *Radiat. Phys. Chem.* 54 (1999) 627–635.
- [41] L.M. Ottosen, H.K. Hansen, C. Hansen, Water splitting at ion-exchange membranes and potential difference in soil during electrokinetic remediation, *J. Appl. Electrochem.* 30 (2000) 1199–1207.

Glossary

Cation exchange membrane (CAT): membrane containing fixed anionic charges and mobile cations which can be exchanged with other cations present in an external fluid in contact with the membrane

Concentration (C): concentration of any compound (in mg kg^{-1} or mg l^{-1})

Current density: determines the deviation of the electrode potential from its equilibrium value when an external current is passed

DC: direct current

Electromigration: movement of ionic species in the media–water solution

Electroosmosis: bulk flow of moisture present in the contaminated media from the anode to the cathode

Limiting current density: current density at which dramatic increases in resistance are observed in an ion exchange membrane system under the influence of an applied electric field between the upstream and downstream

Membrane: structure, having lateral dimensions much greater than its thickness, through which mass transfer may occur under a variety of driving forces