

ELECTROKINETIC COPPER AND IRON MIGRATION IN ANAEROBIC GRANULAR SLUDGE

JURATE VIRKUTYTE^{1,2}, MIKA SILLANPÄÄ² and PIET LENS^{1,*}

¹The sub-department of the Environmental Technology, University of Wageningen, Bomenweg 2, Wageningen, The Netherlands

²The department of Environmental Sciences, Laboratory of Applied Environmental Chemistry, University of Kuopio, FIN-50101 Mikkeli, Finland

(* author for correspondence, e-mail: piet.lens@wur.nl)

(Received 29 October 2005; accepted 2 March 2006)

Abstract. The application of low-level direct electric current (0.15 mA cm^{-2}) as an electrokinetic technique to treat copper-contaminated mesophilic anaerobic granular sludge was investigated. The sludge was obtained from a full scale UASB reactor treating paper-mill wastewater and was artificially contaminated by $\text{Cu}(\text{NO}_3)_2$ or CuEDTA^{2-} with initial copper concentrations of $1000 \text{ mg} \cdot \text{kg}^{-1}$ wet sludge. The effect of different electrokinetic cell layouts, pH and EDTA concentrations on the migration of copper and iron during electrokinetic treatment were evaluated. Both, the pH of the sludge cake or the copper complexation with EDTA significantly affected the migration direction of copper. In an 'open' cell (sludge cake in direct contact with air), the highest copper mobility was observed at pH 2.5 in both $\text{Cu}(\text{NO}_3)_2$ or CuEDTA^{2-} amended sludge. The highest copper accumulation was at the cathode ($22 \pm 2\%$) with CuEDTA^{2-} as contaminant. In a 'closed' cell (sludge cake not in contact with air), the highest accumulation was obtained for CuEDTA^{2-} at the anode and amounted to $4(\pm 0.5)\%$ and $2(\pm 0.05)\%$, respectively, at a final pH of 4.2 and 7.7 in the sludge cake.

Keywords: electromigration, copper, iron, granular sludge, pH

1. Introduction

It is well documented that contamination of the environment with heavy metals, radionuclides and hazardous organic compounds is growing every year, mainly due to inefficient waste handling techniques and incomplete treatment of domestic and industrial wastewater (Mulligan *et al.*, 2004), hazardous waste leakage from landfills (Hernandez *et al.*, 2003; Sheppard *et al.*, 2000; Dijkstra, 1998) and surface runoff. Due to increased environmental pollution, there is a continuous search for more efficient, sustainable and environmentally friendly techniques to remediate contaminated media. During the past decades, several new and innovative solutions for the clean-up of soils and sediments, solid waste, wastewater and sludge have been developed (Hashimoto *et al.*, 2004; Abramovitch *et al.*, 2003).

One of these emerging technologies are electrokinetic remediation techniques, which offer a great potential for the removal of charged contaminants from sludge (Kim *et al.*, 2002), soil (Virikutyte *et al.*, 2004; Ottosen *et al.*, 2002; Acar and Alshawabkeh, 1993) and timber waste (Velizarova *et al.*, 2002). The electrokinetic

process employs a low-level direct current across the contaminated medium, which induces the mobility of charged contaminants due to electromigration and electro-osmotic flow (Virkyte *et al.*, 2004; Haran *et al.*, 1996; Mattson and Lindgren, 1995). Electrokinetic techniques are beneficial technologies because they include low power consumption, control over the flow direction of both water and dissolved contaminants as well as confinement of contaminants in the electrode chambers that makes the subsequent treatment easier (Acar and Alshwabkeh, 1993).

As an essential element, copper is required by organisms for a wide range of metabolic processes (Fjällborg and Dave, 2003). Iron is an important nutrient too (Ito *et al.*, 2000). High levels of both metals are, however, hazardous for biota (Mulligan *et al.*, 2004). High concentrations of copper ($>26 \text{ mg} \cdot \text{L}^{-1}$) are toxic for e.g. the degradation of volatile fatty acids, acetate and propionate in particular (Lin and Chen, 1999). In addition, high concentrations of iron ($>300\text{--}500 \text{ mg} \cdot \text{kg}^{-1}$) may also be detrimental for humans and the environment (Dobermann and Fairhurst, 2000). Emery (1991) reported that iron toxicity is highly influenced by the copper levels. Hence, it is important to control the amount of copper and iron in the environment and thus to develop cost-effective techniques for their removal from contaminated media.

The aim of this study was to examine the electrokinetic mobility of copper and iron in anaerobic granular sludge – a porous medium consisting of anaerobic microbial consortia used in upflow anaerobic sludge bed (UASB) reactors for wastewater treatment (Hulshoff Pol *et al.*, 2004). The UASB granules were used as a model for anaerobic sludge. Laboratory scale experiments were conducted in two different electrokinetic cell layouts containing anaerobic granular sludge, artificially contaminated with copper. The effect of different pH, cell layout, draining and EDTA addition on the electromigration was examined.

2. Materials and Methods

2.1. SOURCE OF BIOMASS

Anaerobic granular sludge was obtained from a full-scale UASB reactor (Industriewater Eerbeek B.V., Eerbeek, The Netherlands) treating paper-mill wastewater (Lens *et al.*, 1999). Table I presents the main characteristics of the sludge used for the experiments. For electrokinetic experiments, anaerobic granular sludge was amended with 3.78 g of $\text{Cu}(\text{NO}_3)_2$, dissolved in 50 ml anaerobic demi-water ($T = 22 \pm 1^\circ\text{C}$, $\text{pH} = 7.1$), which resulted in a copper contamination of $1000 \text{ mg Cu kg}^{-1}$ (wet sludge). In CuEDTA^{2-} amended experiments, 3.78 g of $\text{Na}_2\text{H}_2\text{EDTA}$ (molar ratio of $\text{Cu}^{2+}:\text{EDTA}^{4-}$ was 1.2:1) was dissolved in 50 ml demi-water and added simultaneously with $\text{Cu}(\text{NO}_3)_2$. The added $\text{Cu}(\text{NO}_3)_2$ was assumed to adsorb onto the sludge granules or to form complexes mainly with organic matter, which are relatively mobile in the electric field.

TABLE I

Main characteristics of the experimental sludge (van Hullebusch *et al.*, 2005; Osuna *et al.*, 2004) (TSS – Total Suspended Solids, VSS – Volatile Suspended Solids)

Parameter	Unit	Amount
Mean density	kg · m ⁻³	1040
Water content	%	40
Background copper concentration	mg · kg ⁻¹ TSS	150 (± 5.6)
Background iron concentration	mg · kg ⁻¹ TSS	3880 (± 800)
TSS	%	22.6 (± 0.2)
VSS	%	73.9 (± 0.2)
pH		7.1
Carbonates	% of TSS	0.4 (± 0.2)
Total sulfur	mg · g ⁻¹ TSS	41.8 (± 1.0)
Total phosphorus	mg · g ⁻¹ TSS	6.6 (± 0.1)

TABLE II

Layout parameters of the laboratory scale electrokinetic cells used in this study

	Open cell layout	Closed cell layout
Distance between electrodes (cm)	22	17
Length of sludge cake (cm)	25	15
Membranes	–	Ion exchange
Current strenght (mA)	40	40
Duration (days)	14	14

The Cu(NO₃)₂ (and Na₂H₂EDTA) containing solution was in contact with the biomass for 48 h (Reddy *et al.*, 1997), during which it was thoroughly mixed. After the contamination procedure was over, this sludge, still suspended in the copper (EDTA) containing supernatant unless specified otherwise, was mounted in the electrokinetic set-up. Approx. 200 ml of demi-water was added to fully saturate the sludge cake. For experiments with drained sludge, the supernatant of the sludge was decanted, after which the drained copper loaded sludge was fully saturated in demi-water and mounted in the electrokinetic cell.

2.2. ELECTROKINETIC SET-UP

Experiments were conducted in an ‘open’ and ‘closed’ electrokinetic set-up (Figure 1, Table I, II). In the ‘open’ cell, the granular sludge cake was continuously in contact with the air, whereas no air was in contact with the granular sludge cake mounted in the ‘closed’ set up. In the ‘open’ electrokinetic cell, the stainless steel (diameter 3 mm; length 5 cm) electrodes (supplied by Elektronika-WUR, the Netherlands) were immersed directly into the sludge cake (Figure 1a). There was 1.5 cm of the sludge behind each electrode and 22 cm in front of each electrode

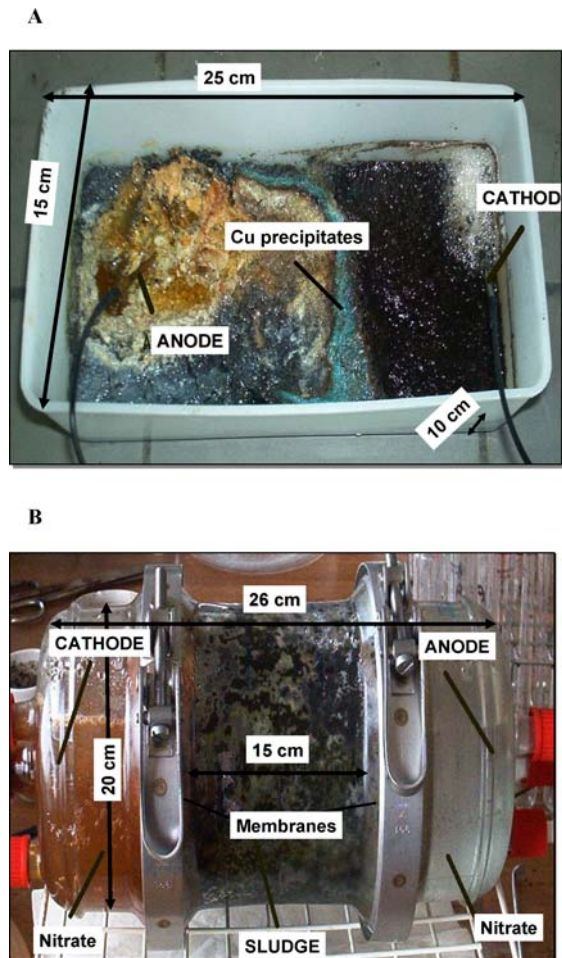


Figure 1. The (A) 'open' and (B) 'closed' electrokinetic set up used in this study.

in the 'open' electrokinetic cell. In the 'closed' (Figure 1b) electrokinetic cell (Ottosen and Hansen, 1992), the central compartment was separated from the anode and cathode compartments by, respectively, anion-exchange (IA1-204SXZL386) and cation-exchange (IC1-61CZL386) membranes (Ionics Inc, Watertown, Massachusetts, USA). The anode and cathode were immersed into a 0.05 M KNO_3 conductive solution (Figure 1b). The electrodes (diameter 3 mm, length 5 cm) were titanium bars (supplied by Elektronika-WUR, the Netherlands).

2.3. EXPERIMENTAL DESIGN

The amount of sludge placed in both the 'open' and 'closed' electrokinetic cells was 1000 g (wet sludge). The 'open' electrokinetic cell (length: 25 cm, width: 15 cm and

height: 15 cm) contained a sludge layer of 10 cm thick. The internal diameter of the 'closed' cell was 20 cm (Figure 1b). Variations in experimental conditions are presented in Table III. Electrokinetic remediation of the artificially contaminated sludge occurred at room temperature ($T = 22 \pm 1^\circ\text{C}$) for 14 days. In all experiments, the current strength in the sludge was 40 mA.

Throughout the treatment process, the voltage and the pH were monitored. The initial pH of the sludge cake was 6.9, which increased to 7.1 after Cu spiking. When the pH fluctuations were uncontrolled in the 'open' cell, the pH reached 12.5 at the cathode and 2.5 at the anode after electrokinetic treatment. To examine the effect of pH on the copper and iron migration, the pH was set manually to 2.5 or 7.7 in the sludge cake by 1 M HNO_3 addition at the cathode of the 'open' cell. When the pH fluctuations were uncontrolled in the electrolytes of the 'closed' cell, it reached 12.5 and 2.5 in the catholyte and anolyte, respectively. This gave a final average pH of 7.5–7.7 in the sludge cake upon termination of the electrokinetic treatment. When the pH in the catholyte was set to 2.5 by 1 M HNO_3 addition, the average pH in the sludge cake after the homogenization of the samples was 4.0–4.2 upon termination of the electrokinetic treatment.

At the end of the electrokinetic treatment, the power supplies were turned off, the electrode wires were disconnected and the electrokinetic cell was disassembled. Sludge samples were taken from the electrokinetic apparatus and sliced into five slices with a stainless steel serrated knife. The pH values and the copper and iron concentrations were determined in each slice.

2.4. ANALYSES

Each sludge slice was thoroughly homogenized prior to analysis. The pH of the sludge cake slices were measured as reported by Acar and Alshawabkeh (1996) by directly inserting a pH electrode into the sludge.

The total metal concentration in the homogenized anaerobic granular sludge samples (expressed as mg metal kg^{-1} dry weight) after electrokinetic treatment was determined after microwave destruction and aqua regia (HCl/HNO_3 , 3:1) digestion (Matthews CEM 2100, North Caroline, USA) as described by Virkutyte *et al.* (2005). 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, the concentrations of total metals were analyzed by flame Atomic Absorption Spectroscopy (AAS) (Perkin-Elmer 300, Shelton, USA). For the determination of Cu and Fe in the sludge solution, the liquid phase in the sludge was filtered through a $0.45 \mu\text{m}$ filter and the Cu and Fe content was measured using the Perkin-Elmer 300 Flame-AAS.

2.5. QUALITY ASSURANCE

The analysis of samples followed the standard quality assurance and control (QA/QC) procedures (Segura *et al.*, 2004). To ensure the accuracy of the

TABLE III
Experimental parameters of laboratory scale experiments

Set up	Open cell layout						Closed cell layout						
	A	B	C	D	E	F	A'	B'	C'	I	II	III	IV
Sludge	Drained fresh	Non- drained fresh	Drained fresh	Non- drained fresh	Drained fresh	Non- drained fresh	Non- drained fresh	Non- drained fresh	Non- drained fresh	Non- drained fresh	Non- drained fresh	Non- drained fresh	Non- drained fresh
Initial conc ($\text{mg} \cdot \text{kg}^{-1}$) in the sludge ^a	850 \pm (50)	1150 \pm (50)	850 \pm (50)	1150 \pm (50)	1150 \pm (50)	1150 \pm (50)	1150 \pm (50)	1150 \pm (50)	1150 \pm (50)	1150 \pm (50)	1150 \pm (50)	1150 \pm (50)	1150 \pm (50)
Contaminant	$\text{Cu}(\text{NO}_3)_2$	$\text{Cu}(\text{NO}_3)_2$	$\text{Cu}(\text{NO}_3)_2$	$\text{Cu}(\text{NO}_3)_2$	$\text{Cu}(\text{NO}_3)_2$	$\text{Cu}(\text{NO}_3)_2$	$\text{Cu}(\text{NO}_3)_2$	$\text{Cu}(\text{NO}_3)_2$	$\text{Cu}(\text{NO}_3)_2$	$\text{Cu}(\text{NO}_3)_2$	$\text{Cu}(\text{NO}_3)_2$	$\text{Cu}(\text{NO}_3)_2$	$\text{Cu}(\text{NO}_3)_2$
pH anode	12.5	12.5	7.7	7.7	2.5	2.5	12.5	7.7	2.5	12.5	2.5	12.5	2.5
Voltage (V)	10-30	12-28	10-28	12-30	10-30	10-30	12-28	12-30	10-30	10-28	10-30	10-30	12-30

^a Initial concentration of Cu is presented with the natural Cu content and without the Cu amount in the sludge liquid in experiments with sludge drainage.

experimental results, new ion exchange membranes and tubing were used for each experiment. After each experiment, the electrokinetic cells were immersed into a 0.05 M HCl solution for 24 h, soaked in a tap water container for 24 h and rinsed with deionized water to avoid cross contamination between experiments (Reddy and Chinthamreddy, 2003). The reliability of the chemical analysis was assessed using certified reference materials (CRM) by three replicate determinations of copper and iron and the range of recoveries was 95–106% (Segura *et al.*, 2004). The AAS calibration was checked after testing every five samples and a mass balance analysis was performed for each test. The distribution efficiencies of copper and iron were evaluated by calculating the difference between the initial and accumulated contaminant concentration at the electrodes.

2.6. CALCULATIONS OF THE FATE OF COPPER AND IRON

The distribution of copper and iron among different compartments (liquid phase, granular phase and electrodes) was calculated for each final pH. The distribution was calculated from their concentrations in the liquid phase, in the sludge granules and the amount of metal deposited onto the electrodes. Data of total copper and iron concentrations were obtained from triplicates ($n = 3$).

3. Results

3.1. EVOLUTION OF OVERALL VOLTAGE

Upon introducing the low level current to a granular sludge cake in the ‘open’ cell, there was an increase in the voltage during the first days (from 17 V to 20 V). After approx. 6 days, the voltage drop to 18 V was followed by a constant increase in voltage to 30 V until it was stabilized at that value after 12–14 days of electrokinetic treatment. Then it decreased to 10 V (Figure 2). The evolution of the voltage gradient is demonstrated for a selected experiment. The changes in voltage gradient were similar in all the experiments in both the ‘open’ and ‘closed’ cell (Table III).

3.2. EFFECT OF SLUDGE LIQUID DRAINAGE ON THE COPPER AND IRON MIGRATION IN THE ‘OPEN’ CELL

The copper and iron concentration in the sludge solution was $190 \text{ mg} \cdot \text{L}^{-1}$ and $780 \text{ mg} \cdot \text{L}^{-1}$, respectively, prior to the electrokinetic treatment. Upon termination of the electrokinetic treatment in the ‘open’ cell (final pH of 4.2 in the sludge cake), the copper concentration in the sludge solution was $110 \text{ mg} \cdot \text{L}^{-1}$ and $200 \text{ mg} \cdot \text{L}^{-1}$, respectively, at the anode and cathode (Figure 3). The soluble iron concentrations amounted to $600 \text{ mg} \cdot \text{L}^{-1}$ and $760 \text{ mg} \cdot \text{L}^{-1}$, respectively, at the anode and cathode (Figure 3).

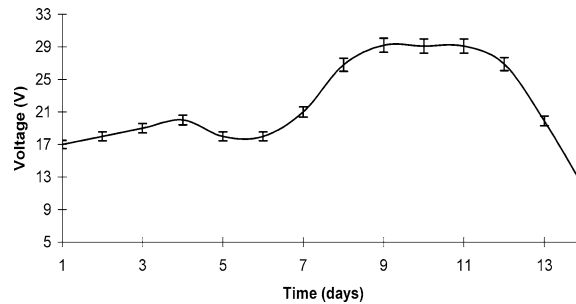


Figure 2. Example of typical evolution of voltage gradient during electrokinetic treatment of anaerobic granular sludge (experiment F).

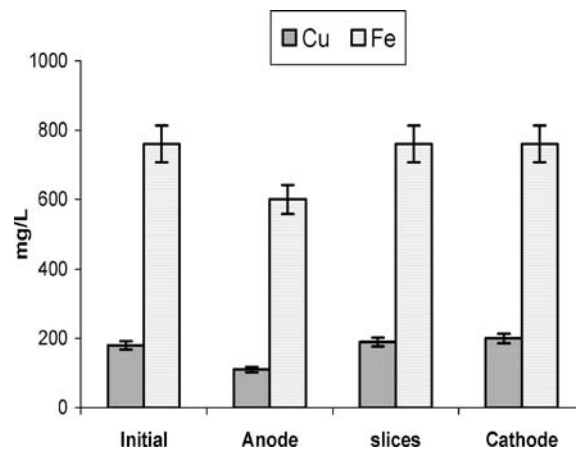


Figure 3. Initial amount of copper and iron in the sludge solution ('open' electrokinetic cell) prior to the electrokinetic treatment and the amount after the electrokinetic treatment (final pH 2.5 in the sludge cake).

When the copper contaminated solution was removed (drained sludge), the direction of the copper migration in the sludge cake was unclear and copper remained distributed throughout the matrix without a defined movement (Figure 4a–b). Also the iron distribution was undefined, i.e. it was either spread in the electrokinetic cell (Figure 4a and b) or slightly shifted towards the cathode (Figure 4c). This indicates that the stainless steel anodes did not release Fe into the granular sludge cake.

3.3. pH JUMP IN THE 'OPEN' AND 'CLOSED' ELECTROKINETIC CELLS

During the experiments in the 'open' cell, when the pH was extremely alkaline (10.5–12.5) or neutral (6.6–7.7) at the cathode side of an 'open' electrokinetic cell (with $\text{Cu}(\text{NO}_3)_2$ as contaminant), blue copper precipitates were observed upon termination of the experiments (Figure 1a). When the pH was adjusted to 2.5 at the

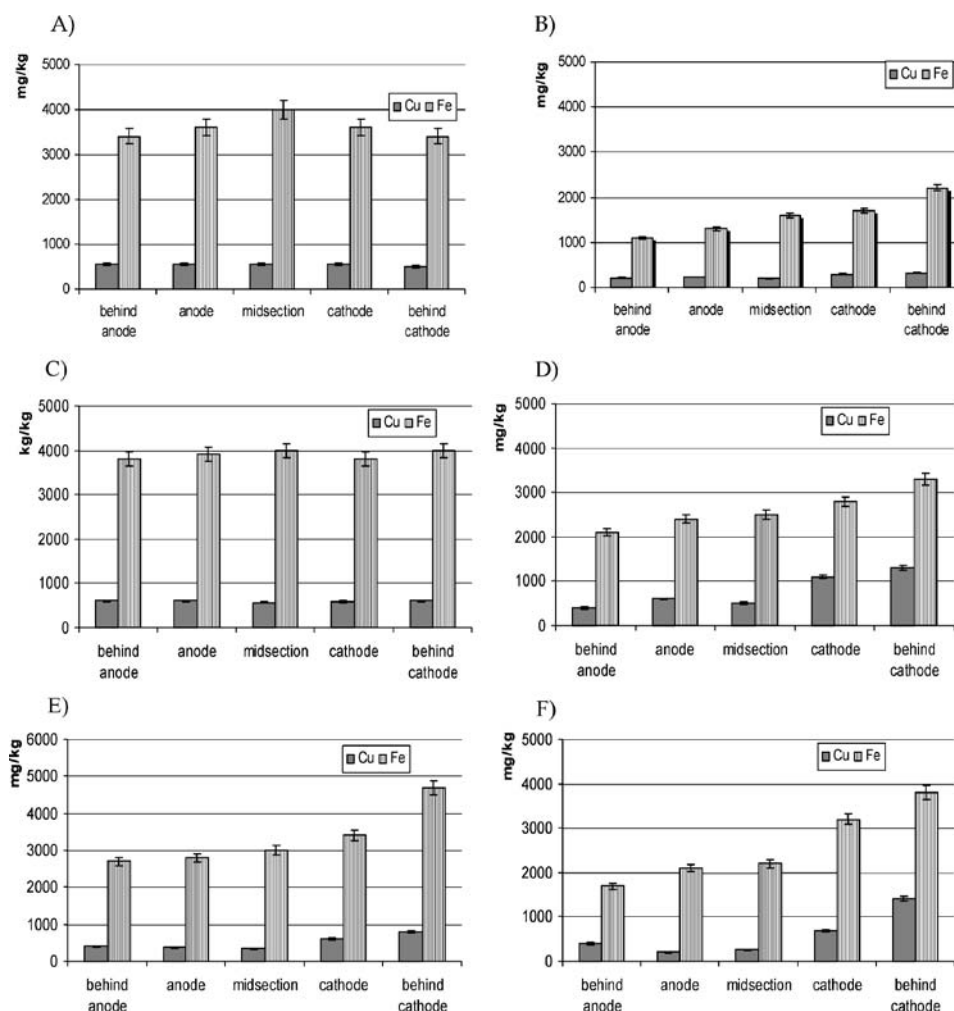


Figure 4. Effect of electrokinetic treatment in an ‘open’ cell on the copper and iron distribution in anaerobic granular sludge artificially contaminated with $\text{Cu}(\text{NO}_3)_2$: (A) Drained and (B) Non-drained fresh sludge with pH 12.5 at the cathode; (C) Drained and (D) Non-drained fresh sludge with pH 7.7 at the cathode; (E) Drained and (F) Non-drained fresh sludge with pH 2.5 at the cathode.

cathode, no precipitates were observed. However, there were no visible precipitates when CuEDTA^{2-} was used as contaminant (data not shown). Also, no visible blue precipitates were observed in the sludge cake of the ‘closed’ electrokinetic cell at the different pH conditions tested.

Figure 5 presents variations in the pH of the sludge cake. The pH jump in the ‘open’ electrokinetic cell appeared at a normalized distance from the anode of 0.6–0.8 (Figure 5). However, no pH jump was observed in the experiments with the ‘closed’ electrokinetic cell, regardless the pH conditions (Figure 5).

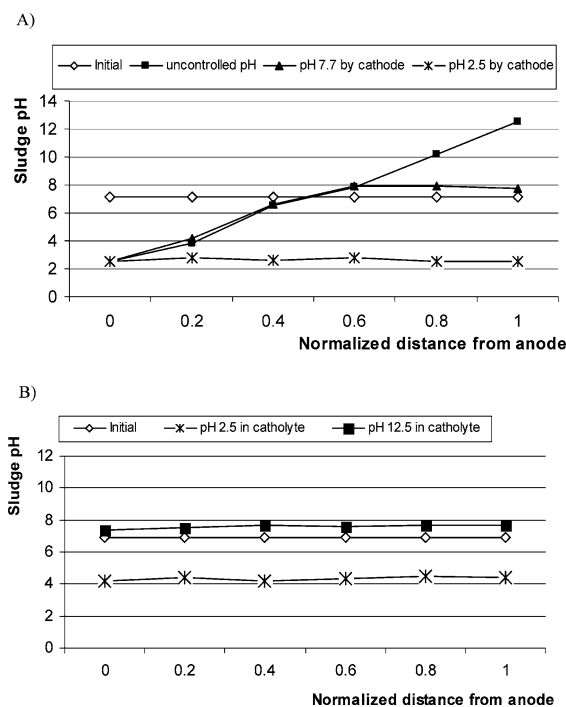


Figure 5. pH distribution in the sludge cake: (A) 'open' and (B) 'closed' electrokinetic cell. Normalized distance from anode is the ration between the actual distance between the electrodes and the actual sampling distance from the anode.

3.4. EFFECT OF pH ON THE COPPER AND IRON MIGRATION IN THE 'OPEN' CELL

When the pH was extremely alkaline (9.2–12.5), no mobility of copper or iron was observed (Figure 4a) in drained sludge. Interestingly, when the sludge solution was not drained, there was a pronounced movement of Fe towards the cathode (Figure 4b). The movement of copper was significant (Figure 4) in experiments with a final pH of 7.7 and 2.5 ($4(\pm 1)\%$ and $22(\pm 2)\%$ of Cu accumulation, respectively) of the sludge cake (Table IV A). The same pattern was observed for iron, where at a final pH of 2.5 in the sludge cake, the highest accumulation of iron at the cathode was $4(\pm 1)\%$ more than the initial concentration (Table IV A).

3.5. EFFECT OF EDTA ON COPPER AND IRON MIGRATION IN THE 'OPEN' CELL

The migration of the EDTA complexed copper ions was opposite to the migration when copper was added to the sludge as $\text{Cu}(\text{NO}_3)_2$. At pH 12.5, copper did not show the well-expressed migration just some fluctuation in the concentration (Figure 6a'), as it is known to form insoluble compounds at alkaline pH. At pH 7.7 ($900 \text{ mg} \cdot \text{kg}^{-1}$)

TABLE IV
Copper and iron concentrations ($\text{mg} \cdot \text{kg}^{-1}$) and distribution efficiencies in (A) 'open' and (B) 'closed' electrokinetic cell. The distribution efficiencies (%) are the value either $x\%$ less (depleted) or $x\%$ more (accumulated) than initially present in the sludge

Experiment	Contaminant	Initial concentration in sludge cake (Cu) ($\text{mg} \cdot \text{kg}^{-1}$)	pH in catholyte	Concentration at the anode (distribution efficiencies)	Concentration at the cathode (distribution efficiencies)
(A) 'Open' cell					
Fresh drained sludge					
A	Cu	850	12.5	600 (depletion: 30)	500 (depletion: 41)
A	Fe	3880	12.5	3200 (depletion: 18)	3000 (depletion: 23)
C	Cu	850	7.7	600 (depletion: 30)	650 (depletion: 24)
C	Fe	3880	7.7	3800 (depletion: 2)	4200 (accumulation: 8)
E	Cu	850	2.5	300 (depletion: 65)	800 (depletion: 6)
E	Fe	3880	2.5	2700 (depletion: 30)	4800 (accumulation: 24)
Fresh non-drained sludge					
B	Cu	1150	12.5	300 (depletion: 74)	400 (depletion: 65)
B	Fe	3880	12.5	1200 (depletion: 69)	2300 (depletion: 41)
A'	CuEDTA	1150	12.5	800 (depletion: 30)	700 (depletion: 39)
A'	FeEDTA	3880	12.5	1200 (depletion: 69)	2500 (depletion: 36)
D	Cu	1150	7.7	450 (depletion: 61)	1200 (accumulation: 4)
D	Fe	3880	7.7	2200 (depletion: 43)	3300 (depletion: 15)
B'	CuEDTA	1150	7.7	800 (depletion: 30)	600 (depletion: 48)
B'	FeEDTA	3880	7.7	3000 (depletion: 23)	2100 (depletion: 46)
F	Cu	1150	2.5	300 (depletion: 74)	1400 (accumulation: 22)
F'	Fe	3880	2.5	1400 (depletion: 64)	4000 (accumulation: 4)
C'	CuEDTA	1150	2.5	1250 (accumulation: 8)	300 (depletion: 74)
C'	FeEDTA	3880	2.5	1900 (depletion: 51)	4200 (accumulation: 8)

(Continued on next page)

TABLE IV
(Continued)

(B) 'Closed' cell		Initial concentration in sludge cake (Cu) (mg · kg ⁻¹)	pH in catholyte	pH in sludge cake	Concentration at the anode (distribution efficiencies)	Concentration at the cathode (distribution efficiencies)
Experiment	Contaminant		Fresh sludge			
I	Cu	1150	12.5	7.7	600 (depletion: 48)	800 (depletion: 30)
II	CuEDTA	1150	12.5	7.7	1100 (accumulation: 2)	900 (depletion: 22)
III	Cu	1150	2.5	4.2	700 (depletion: 39)	900 (depletion: 22)
IV	CuEDTA	1150	2.5	4.2	1200 (accumulation: 4)	400 (depletion: 65)

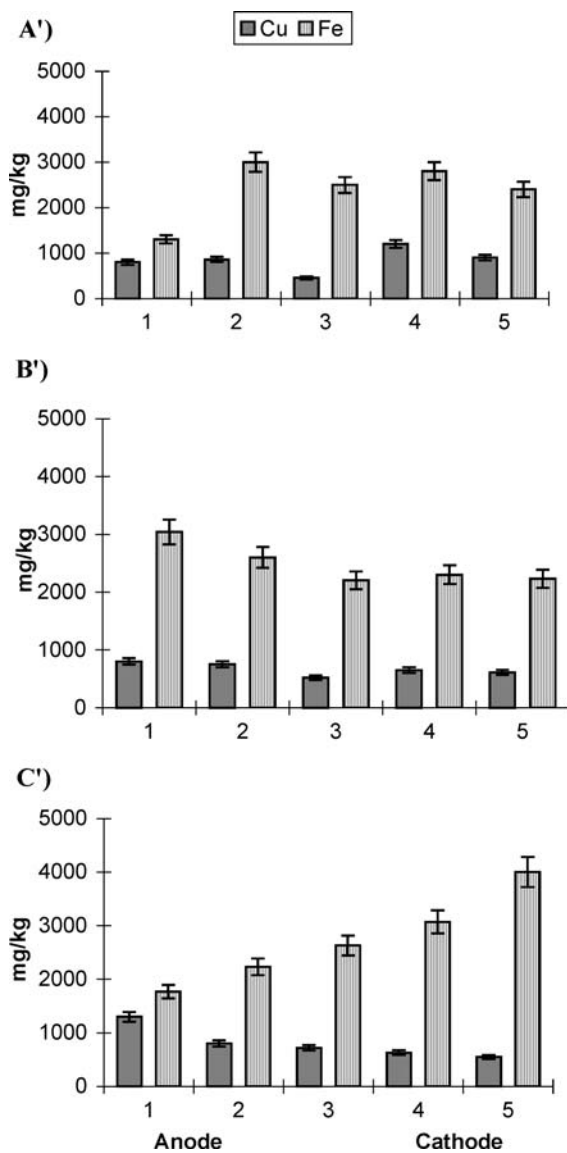


Figure 6. Effect of electrokinetic treatment in an 'open' cell on the copper and iron distribution in the anaerobic granular sludge artificially contaminated with CuEDTA. (A') Fresh sludge with pH 12.5 at the cathode; (B') Fresh sludge with pH 7.7 at the cathode and (C') Fresh sludge with pH 2.5 at the cathode.

and 2.5 ($1300 \text{ mg} \cdot \text{kg}^{-1}$), copper, in the presence of EDTA, migrated towards the anode (Figure 6b' and c'). Iron (Figure 6b') also migrated towards the anode in the presence of EDTA at pH 7.7 ($3000 \text{ mg} \cdot \text{kg}^{-1}$). Interestingly, iron migrated towards the cathode ($3880 \text{ mg} \cdot \text{kg}^{-1}$) at pH 2.5 when complexed with EDTA (Figure 6c').

When copper was complexed with EDTA, the copper distribution towards the cathode was considerably lower than towards the anode (Table IV A). The highest Cu accumulation was found at the anode at a final pH of 2.5 in the sludge cake ($8 \pm 1\%$ more than initially present). The migration of iron was also directed more towards the anode than to the cathode (Table IV A). The highest efficiency was when the final pH of the sludge cake was 2.5 and the accumulation of iron at the cathode reached $8 (\pm 1)\%$ more than initially present in the sludge. Interestingly, the EDTA addition did not significantly enhance the Cu removal from the spiked anaerobic granular sludge as the highest accumulation obtained in the absence of EDTA was $22 (\pm 2)\%$ (Table IV A), whereas in the presence of EDTA, the accumulation reached only $8 (\pm 1)\%$.

3.6. COPPER TRANSPORT IN THE 'CLOSED' ELECTROKINETIC CELL

Copper depletion amounted to $48 (\pm 2)\%$ and $30 (\pm 2)\%$ at, respectively, the anode and the cathode in the 'closed' cell at a final pH of 7.7 in the sludge cake (experiment I, pH 12.5 in the catholyte). When the pH was lowered to 2.5 in the catholyte (experiment II, final pH of 4.2 in the sludge cake), copper migrated from the anode ($39 (\pm 2)\%$ depleted) to the cathode ($22 (\pm 2)\%$ enriched) (Table IV B).

When the sludge was amended with CuEDTA^{2-} (experiment III, final pH of 7.7 in the sludge cake), copper accumulated ($2 \pm 0.5\%$) at the anode and depleted ($22 \pm 2\%$) at the cathode (Table IV B). Moreover, in the 'closed' cell (experiment IV, final pH 4.2 in the sludge cake), copper accumulated ($4 \pm 2\%$ more than initially present) at the anode and depleted ($65 \pm 2\%$ less than initially present) at the cathode (Table IV B).

3.7. COPPER AND IRON DISTRIBUTION IN THE 'OPEN' ELECTROKINETIC CELL

Figure 7 presents the average amount of copper and iron in the liquid phase, in the granules and deposited onto the electrodes. The pH has a significant influence on the copper and iron distribution in the sludge liquid and granules (Figure 7). Copper and iron were found to be significantly deposited onto the electrodes when the pH of the system was kept acidic and slightly alkaline. When the pH was acidic, there was also a significant amount of copper and iron that remained associated with the sludge granules. In contrast, when the pH increased to a final pH of 12.5 in the sludge cake after the electrokinetic treatment, a considerable portion of copper and iron was found in the liquid phase (Figure 7).

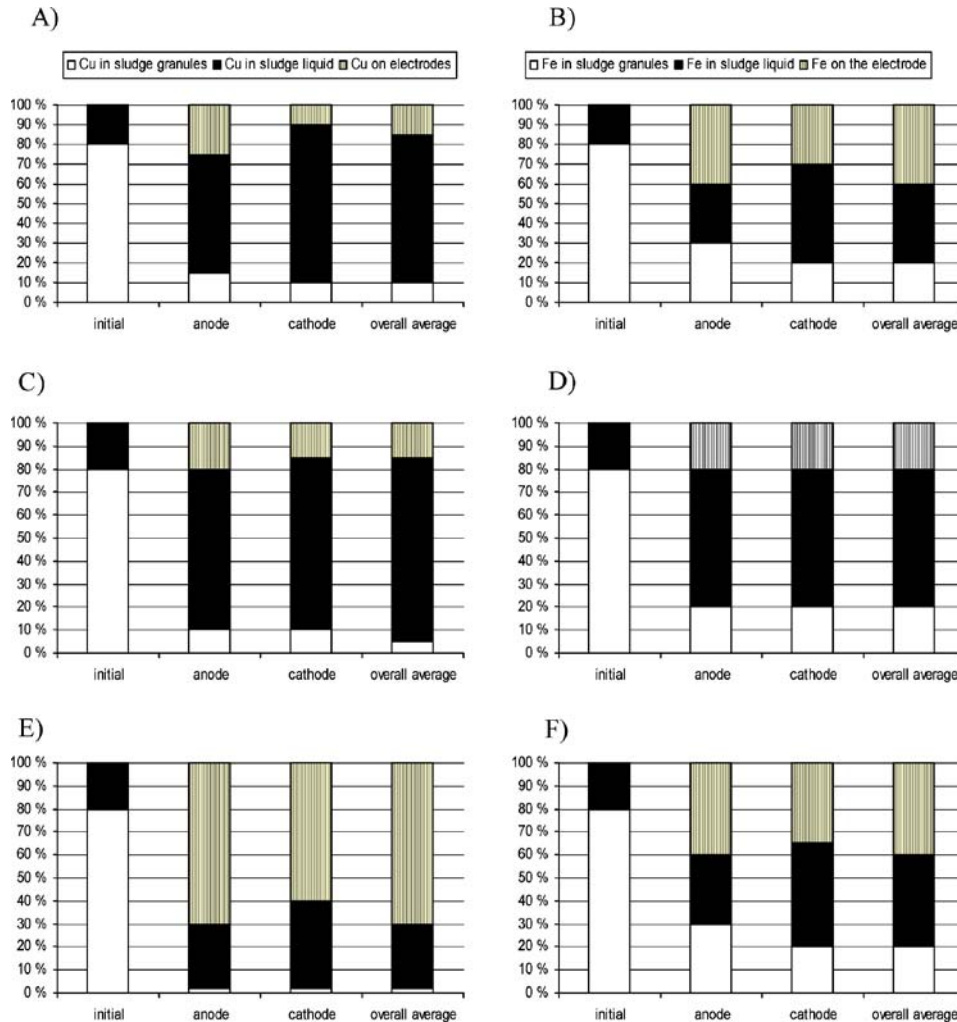


Figure 7. Distribution of Cu (A, C, E) and Fe (B, D, F) among selected experimental fractions in the 'open' cell. (A) and (B) final sludge pH 2.5; (C) and (D) final sludge pH 7.7; (E) and (F) final sludge pH 12.5.

4. Discussion

4.1. VARIATION OF THE OVERALL VOLTAGE

Voltage fluctuations during electrokinetic treatment are related to the changing resistivity between the anode and cathode (Ottosen *et al.*, 2002). According to Ohm's law ($V = I \times R$, where I is current and R is resistivity), the voltage increases when the resistivity or current increases. Due to the electrolysis of water, the sludge cake

gradually acidifies and the electrical resistance decreases due to electrochemical exchange reactions on the surface of the granules.

The increase in voltage (Figure 2) means that the H^+ front formed at the anode migrates through the sludge (Ottosen *et al.*, 2002, Velizarova *et al.*, 2002). Therefore, the increase in the resistance may be attributed to copper and iron precipitates in high pH areas. Also, the increase in the resistance may be due to the formation of non-conducting gaseous bubbles on the surface of electrodes due to the electrolysis of water reactions (Sah and Chen, 1998).

The small decrease of the voltage after 4 days of operation might be due to a lack of charged particles at the beginning of electrokinetic experiments, as proposed by Velizarova *et al.* (2004). Lee and Yang (2000) showed similar voltage fluctuations in the electrokinetic Pb removal from contaminated soils. The voltage increased due to an increase in $Pb(OH)_2$ concentration by build-up of excess OH^- in the pore fluid near the cathode.

Voltage fluctuations were similar in experiments with and without drainage of the sludge solution in the 'open' cell. It was expected that there will be no initial voltage drop in the experiments with the non-drained sludge because of the significant amount of ions in the sludge solution, which kept the conductivity high. However, the voltage drop was still observed (data not shown). This decrease could be attributed to the rapid complexation of the produced H^+ and OH^- by the sludge matrix and the copper or iron ions. This rapid initial complexation removed ions that transport charge, thus leading to a drop in voltage.

4.2. THE pH JUMPS IN THE 'OPEN' AND 'CLOSED' ELECTROKINETIC CELLS

It has been widely reported in the literature that the transport rate of hydrogen ions is almost twice the mobility of hydroxyl ions (Acar and Alshawabkeh, 1993). Therefore, the position of a pH jump, an area where a drastic change in pH occurs, is always close to the cathode (Figure 5). During the electrokinetic treatment process, due to the electrolysis of water, the pH in the close vicinity of the cathode increases significantly (pH = 12.0–12.5) due to the transport of hydroxyl ions from the cathode. The formed hydroxyl ions migrate through the granular sludge cake and this alkaline front may have detrimental effects on the electrokinetic treatment efficiency. There was no pH jump observed in the 'closed' electrokinetic cell (Figure 3b), which can be attributed to the conditioning of the cathode with the HNO_3 solution.

Kim *et al.* (2005) discovered that the decrease of the electrokinetic treatment effectiveness may be attributed to the possible formation of metal precipitates (Cu, Fe, Zn, Ni, Co, Cd in particular) and increase of adsorbed and immobile metal species. The location of the pH jump may also be influenced by the concentration and mobility of ions present in the matrix through affecting the distribution of electric fields and formation of hydroxide complexes (Li *et al.*, 1997).

Blue precipitates were observed in the experiments without drainage of the sludge solution of the 'open' electrokinetic cell at pH 12.5 (Figure 1). Due to the contact with air in that cell, most of the copper present in the solution precipitates as hydroxides when the pH gets extremely alkaline.

4.3. COPPER AND IRON MIGRATION AT HIGH CATHODE pH IN THE 'OPEN' CELL

The observed migration of copper in the electrokinetic cells is a net movement of copper species present in both the sludge solution and the sludge granules. The amount of copper found in the sludge solution after the spiking was only 17 (\pm 2)% higher than the initial copper concentration in the sludge (Figure 7), which suggests that a considerable amount of copper remained in a free ionic state or was bound to the soluble fractions in the sludge. This contrasts the findings of Kim *et al.* (2002), who determined that Cu has an extremely strong affinity to organic matter present in digested municipal wastewater sludge, with which it forms relatively insoluble Cu-organic complexes. These differences in findings might be attributed to the types of sludges, e.g. the sludge used in the current study mainly contained intact microorganisms, whereas cells are disintegrated in anaerobically digested municipal sludge.

The mobility of copper and iron in the 'open' (pH 12.5 and 7.7) and 'closed' (pH 12.5 in the catholyte attributing to a final pH of 7.7 in the sludge cake) electrokinetic cells and the efficiency of the electrokinetic distribution of copper and iron in the sludge were low (Table IV A) compared to the migration of the contaminants at acidic pH (final pH 2.5 in the sludge cake, 'open' cell). This is most probably due to the formation of insoluble and hence immobile species. Indeed, due to the electrolysis of water, the OH⁻ ions formed at the cathode significantly raise the pH of the system (Figures 4 and 6). If the pH in the sludge cake is kept at neutral and/or alkaline conditions, copper will precipitate in the form of hydroxides and oxy-hydroxides (Cu(OH)₂⁰), sulfides and carbonates (Hernandez *et al.*, 2003). Additionally, iron also tends to precipitate as hydroxides and oxy-hydroxides, which are barely soluble when the pH of the system is higher than 7 (Mercer, 2001; Straub *et al.*, 2001; Alloway, 1995).

4.4. COPPER AND IRON MIGRATION AT LOW CATHODE pH

When the pH was adjusted to 2.5 in the 'open' electrokinetic cell (Figure 4), copper as well as iron was transported towards the cathode with final copper and iron concentrations of, respectively, 20 (\pm 2)% and 5 (\pm 2)% higher than the initial concentration (Table IV A). This movement was most probably due to the electromigration of copper species. It is well documented that when the pH is acidic, copper is solubilized from the soil (Yeung *et al.*, 1997; van Cauwenberghe, 1997) and sludge (Kim *et al.*, 2002) matrices, forming positively charged species, which

migrate to the negatively charged cathode (Table IV A). The transport behavior of Cu and Fe is more pronounced at low pH as there are positively charged species such as Cu^{2+} or $\text{Cu}(\text{OH})^+$ and $\text{Fe}^{2+}/\text{Fe}^{3+}$, which, under the applied electric field, moved through the sludge cake (Table IV A) according to their charges. Therefore in order to solubilize Cu and Fe species and initiate their migration in the sludge matrix, it is necessary to adjust the pH at the cathode to a low pH.

4.5. EFFECT OF pH ON THE MIGRATION OF COPPER AND IRON EDTA IN THE 'OPEN' CELL

Chelating agents such as EDTA have proved to be the most efficient extractants, which form negatively charged compounds with heavy metals (Yeung *et al.*, 1997). When the pH in the sludge was maintained at 12.5, EDTA addition did not induce the movement of either copper or iron species (Figure 6a'). This is due to the formation of insoluble complexes, as reported by Popov *et al.* (1999). On the contrary, at the final pH of 7.7 in the sludge, copper migration towards the anode occurred, which can be attributed to the formation of CuEDTA^{2-} complexes (Nowack, 2002; Sillanpää *et al.*, 2001). Iron showed migration towards the anode at the final pH of 7.7, which could be attributed to the favourable formation of Fe(III)EDTA^- complexes (Kari and Gigger, 1996).

When the pH is neutral and slightly acidic, copper forms negative compounds with EDTA (CuEDTA^{2-} , CuHEDTA^- , CuOHEDTA^-) and carbonates ($\text{Cu}(\text{CO}_3)_2^{2-}$) (Osuna *et al.*, 2004; Bolan *et al.*, 2003). Yuan and Weng (2003) argued that complexes as FeOOH-EDTA-Cu^- can also contribute to the copper transport towards the anode. According to their charges, negative compounds move towards the anode under the influence of an electric field, as also observed in this study (Figure 6c'). Interestingly, iron migrated towards the cathode at the final pH of 2.5 at the cathode suggesting that positive complexes or compounds prevailed, instead of forming negatively charged EDTA complexes. Indeed, as observed by Kari and Giger (1996), who investigated speciation and fate of EDTA in municipal wastewater treatment, if pH falls below 6, Fe(III)EDTA^- is the dominant species. However, when increased concentrations of Cu, Ni and Zn are present, Cu(II)EDTA^{2-} , Ni(II)EDTA^{2-} and Zn(II)EDTA^{2-} are the dominating species. Therefore, at the final pH 2.5 and $1150 \text{ mg} \cdot \text{kg}^{-1}$ of Cu present in the sludge cake, $\text{Fe}^{3+}/\text{Fe}^{2+}$ should have been formed, which migrated towards the negatively charged cathode.

4.6. PRACTICAL APPLICATION OF ELECTROKINETICS FOR SLUDGE CLEAN-UP

The main difference between both electrokinetic setups is the positioning of the electrodes and the exposure to air. In the 'open' cell, electrodes are inserted directly into the sludge cake and in the 'closed' cell, electrodes are immersed into the electrolyte solution (Figure 1). The more practical solution is to position electrodes

straight into the contaminated medium and/or to position them using different electrode wells or trenches. However, Alshwabkeh *et al.* (1999) observed that this configuration may develop inactive electric fields between electrodes of the same polarity. Additionally, one of the reasons why the copper and iron migration efficiency was higher in the 'open' cell could be attributed to some inactive electric field areas present in the soil when using the 'closed' cell layout (Table IV). This was also observed by Turer and Genc (2005), who tested the Cu, Zn and Pb removal efficiency using rectangular and circular electrokinetic units.

When electrodes are positioned directly into the sludge or any other contaminated medium, several questions arise, e.g. how to remove contaminants upon termination of the remediation process and how to prevent electrodes from drying, while maintaining for example unsaturated conditions in the medium. Wiczorek *et al.* (2005) reported that a special electrode system is necessary to prevent electrodes from drying, thus avoiding the spreading of acid and base fronts and maintaining unsaturated conditions in the medium. Alshwabkeh *et al.* (1999) suggested that electrodes used in electrokinetic experiments should be chemically inert, electrically conductive and hollow. The lumen of the hollow electrode can facilitate removal of the contaminants via the extraction solution. Also, hollow electrodes allow the injection of the purging solution into the subsurface, if necessary.

The 'open' and 'closed' electrokinetic set-ups used in this study (Figure 1) do not allow to calculate net removal efficiencies of copper and iron from the sludge cake. Hence, the accumulation and distribution are presented as the major electrokinetic treatment assessment tool (Table IV). The highest accumulation values for copper and iron at a final pH of 7.7 and 2.5 in the sludge cake corresponded to the abundance of soluble and mobile species at these pH values (Table IV) as also observed by Kim *et al.* (2002), Velizarova *et al.* (2002) and Acar *et al.* (1993). The latter indicates that future optimization of the migration of charged contaminants out of sludge matrixes need to improve their solubility. Besides EDTA⁴⁻ addition (Table IV), this could be also achieved by variations in temperature (Mohammadi *et al.*, 2005), as increasing temperatures may increase the transport rate of heavy metals towards the appropriate electrodes. Alternatively, the pH of the sludge cake could be reduced and, therefore solubilization of contaminants could be achieved, by the addition of sulfur-oxidizing bacteria and subsequent aeration of the sludge cake, as these bacteria produce sulfuric acid from the reduced sulfur compounds present in anaerobic sludge (Maini *et al.*, 2000).

5. Conclusions

Application of low-level electric current to anaerobic granular sludge in both 'open' and 'closed' cell layouts significantly induced the mobility of contaminants towards the electrodes. The pH is an important factor in the mobility of copper under an externally applied electric field (40 mA). At pH 12.5, there is no movement of

copper ions in the sludge. At pH 2.5, copper and iron significantly move towards the cathode.

The addition of chelating agents may direct contaminants exclusively towards the anode. This may be further used as an advantage in optimization of the overall electrokinetic process, for example to combine the sludge consolidation with simultaneous removal of organic contaminants and heavy metals. Moreover, during the consolidation, pore water moves exclusively towards the cathode and contaminants move towards the anode, where they can be extracted or removed using conventional physicochemical methods. The addition of EDTA at pH 2.5 failed to significantly induce the mobility of both copper and iron. However, it facilitated copper and iron migration towards the anode. The 'open' cell layout yields higher copper and iron transport under the applied electric field than the 'closed' cell, therefore the 'open' cell layout may be more efficiently applied *in situ*.

Acknowledgments

This research was supported through the European Community Marie Curie training site "Sulfur and Metals" (HPMF-CT-2002-01899) via the programme "Improving the Human Research Potential and the Socio-economic Knowledge Base". The Academy of Finland is also thanked for the research funding (decision number 200759).

References

- Abramovitch, R.A., Qing, L.C., Hicks, E., & Sinard, J. (2003). In situ remediation of soils contaminated with toxic metal ions using microwave energy. *Chemosphere*, 53, 1077–1085.
- Acar, Y.B., & Alshawabkeh, A.N. (1996). Electrokinetic remediation: I. Pilot Scale Tests with Lead-spiked Kaolinite. *Journal of Geotechnical Engineering*, 122, 173–185.
- Acar, Y.B., & Alshawabkeh, A.N. (1993). Principles of electrokinetic remediation. *Environmental Science and Technology*, 27, 2638–2647.
- Alloway, B.J. (1995). *Heavy metals in soils* (2nd ed.). London, England: Chapman and Hall.
- Alshawabkeh, A.N., Yeung, A.T., & Bricka, R.M. (1999). Practical aspects of In situ Electrokinetic Extraction. *Journal of Environmental Engineering*, 125, 27–35.
- Bolan, N.S., Khan, M.A., Donaldson, J., Adriano, D.C., & Matthew, C. (2003). 'Distribution and bioavailability of copper in farm effluent. *Science of Total Environment*, 309, 225–236.
- Dijkstra, E. (1998). A morphological study on the development of humus profiles in heavy metal polluted and non-polluted forest soils under Scots pine. *Geoderma*, 61, 4495–4505.
- Dobermann, A., & Fairhurst, T. (2000). Rice. Nutrient disorders & nutrient management. Potash & Phosphate Institute (PPI), Potash & Phosphate Institute of Canada (PPIC) and International Rice Research Institute.
- Emery, T. (1991). *Iron and your health: Facts and fallacies*. CRC Press Inc.
- Fjällborg, B., & Dave, G. (2003). Toxicity of copper in sewage sludge. *Environment International*, 28, 761–769.

- Haran, B.S., Popov, B.N., Zheng, G., & White, R.E. (1996). Development of a new electrokinetic technique for decontamination of hexavalent chromium from low surface charged soils. *Environmental Progress*, 15, 166–172.
- Hashimoto, S., Watanabe, K., Nose, K., & Morita, M. (2004). Remediation of soil contaminated with dioxins by subcritical water extraction. *Chemosphere*, 54, 89–96.
- Hernandez, L., Probst, A., Probst, J.L., & Ulrich, E. (2003). Heavy metal distribution in some French forest soils: evidence for atmospheric contamination. *Science of Total Environment*, 312, 195–219.
- Hulshoff Pol, L.W., de Castro Lopes, S.I., Lettinga, G., & Lens, P.N.L. (2004). Anaerobic sludge granulation. *Water Research*, 38, 1376–1389.
- Ito, A., Umita, T., Aizawa, J., Takachi, T., & Morinaga, K. (2000). Removal of heavy metals from anaerobically digested sewage sludge by a new chemical method using ferric sulfate. *Water Research*, 34, 751–758.
- Kari, F.G., Giger, W. (1996). Speciation and fate of ethylenediaminetetraacetate (EDTA) in municipal wastewater treatment. *Water Research*, 30, 122–134.
- Kim, W.S., Kim S.O., & Kim K.W. (2005). Enhanced electrokinetic extraction of heavy metals from soils assisted by ion exchange membranes. *Journal of Hazardous Materials*, B118, 93–102.
- Kim, S.-O., Moon, S.-H., Kim, K.-W., & Yun, S.-T. (2002). Pilot scale study on the ex situ electrokinetic removal of heavy metals from municipal wastewater sludges. *Water Research*, 36, 4765–4774.
- Lee, H.H., & Yang, J.W. (2000). A new method to control electrolytes by pH by circulation system in electrokinetic soil remediation. *Journal of Hazardous Materials*, B77, 227–240.
- Lens, P., Vergeldt, F., Lettinga, G., & van As, H. (1999). ¹H-NMR study of the diffusional properties of methanogenic aggregates. *Water Science and Technology*, 39, 187–194.
- Li, Z., Yu, J.W., & Neretnieks I. (1997). Removal of Pb(II), Cd(II) and Cr(III) from sand by electromigration. *Journal of Hazardous Materials*, 55, 295–304.
- Lin, C.Y., & Chen, C.C. (1999). Effect of heavy metals on the methanogenic UASB granule. *Water Research*, 33, 409–416.
- Maini, G., Sharman, A.K., Sunderland, G., Knowles, C.J., & Jackman, S. (2000). An integrated method incorporating Sulfur-oxidizing bacteria and electrokinetics to enhance removal of copper from contaminated soil. *Environmental Science and Technology*, 34, 1081–1087.
- Mercer, J.F.B. (2001). The molecular basis of copper-transport diseases. *Trends in Molecular Medicine*, 7, 64–69.
- Mattson, E.D., & Lindgren, E.R. (1995). Electrokinetic Extraction of Chromate from Unsaturated Soils. *American Chemical Society*, 11–20.
- Mohammadi, T., Moheb, A., Sadrzadeh, M., & Razmi, A. (2005). Modelling of metal ion removal from wastewater by electrodialysis. *Separation and Purification Technology*, 41, 73–82.
- Mulligan, C.N., & Yong, N. (2004). Natural attenuation of contaminated soils. *Environment International*, 30, 587–601.
- Nowack B. (2002). Environmental chemistry of Aminopolycarboxylate chelating agents. *Environmental Science and Technology*, 36, 4009–4016.
- Osuna, M.B., Zandvoort, M.H., Iza, J., & Lens, P.N.L. (2004). Effect of cobalt sorption on metal speciation in anaerobic granular sludge. *Journal of Environmental Quality*, 33, 1256–1270.
- Ottosen, L.M., Eriksson, T., Hansen, H.K., & Ribeiro, A.B. (2002). Effects from different types of construction refuse in the soil on electrokinetic remediation. *J. Haz. Mater.*, 91, 205–219.
- Ottosen, L.M., & Hansen, H.K. (1992). Electrokinetic cleaning of heavy metal polluted soil. *Internal report, Fysisk-Kemisk Institut and Institut for Geologi og Geoteknik*. Denmark: Technical University of Denmark, (in English).
- Popov, K., Yachmenev, V., Kolosov, A., & Shabanova, N. (1999). Effect of soil electroosmotic flow enhancement by chelating reagents. *Colloids and Surfaces. A: Physicochem. Engineering Aspects*, 160, 135–140.

- Reddy, K.R., & Chinthamreddy, S. (2003). Effects of initial form of chromium on electrokinetic remediation in clays. *Adv. Environ. Res.*, 7, 353–365.
- Reddy, K.R., Parupudi, U.S., Devulapalli, S.N., & Xu, Y. (1997). Effect of soil composition on the removal of chromium by electrokinetics. *Journal of Hazardous Materials*, 55, 135–158.
- Sah, J.G., & Chen J.Y. (1998). Study of the electrokinetic process on Cd and Pb spiked soils. *Journal of Hazardous Materials*, 58, 301–315.
- Segura, M., Cámara, C., Madrid, Y., Rebollo, C., Azcárate, J., Kramer, G.N., Gawlik, B.M., Lambert, A., & Quevauville, Ph. (2004). Certified reference materials (CRMs) for quality control of trace-element determinations in wastewater. *TrAC Trends in Analytical Chemistry*, 23, 194–202.
- Sillanpää, M., Orama, M., Rämö, J., & Oikari, A. (2001). The importance of ligand speciation in environmental research: a case study. *Science of Total Environment*, 267, 23–31.
- Sheppard, D.S., Claridge, G.G.C., & Campbell, I.B. (2000). Metal contamination of soils at Scott base, Antarctica. *Applied Geochemistry*, 15, 513–530.
- Straub, K.L., Benz, M., & Schink, B. (2001). Iron metabolism in anoxic environments at near neutral pH. Mini review. *FEMS Microbiology Ecology*, 34, 181–186.
- Turer, D., & Genc A. (2005). Assessing effect of electrode configuration on the efficiency of electrokinetic remediation by sequential extraction analysis. *Journal of Hazardous Materials*, B119, 167–174.
- Van Cauwenberghe, L. (1997). Electrokinetics: Technology Overview Report. Groundwater Remediation Technologies Analysis Centre, 1–17.
- van Hullebusch, E.D., Utomo, S., Zandvoort, M.H., & Lens, P.N.L. (2005). Comparison of three sequential extraction procedures to describe metal fractionation in anaerobic granular sludges. *Talanta*, 65, 549–558.
- Velizarova, E., Ribeiro, A.B., Mateus, E., & Ottosen, L.M. (2004). Effect of different extracting solutions on the electrokinetic remediation of CCA-treated wood waste Part I. Behaviour of Cu and Cr. *Journal of Hazardous Materials*, B107, 103–113.
- Velizarova, E., Ribeiro, A.B., & Ottosen, L.M. (2002). A comparative study on Cu, Cr and As removal from CCA-treated wood waste by dialytic and electrokinetic processes. *Journal of Hazardous Materials*, 94, 147–160.
- Virkutyte J., Sillanpää, M., Latostenmaa, P., & Martiusius, J. (2004). Electrokinetic copper removal from lake sand: the process design and kinetics. *International Journal of Surf. Mining, Reclam. Environ.*, 18, 220–231.
- Virkutyte, J., van Hullebusch E., Sillanpää, M., & Lens, P. (2005). Copper and trace element fractionation in electrokinetically treated methanogenic anaerobic granular sludge. *Environmental Pollution*, 138, 518–529.
- Wieczorek, S., Weigand H., Schmid M., & Marb C. (2005). Electrokinetic remediation of an electroplating site: design and scale-up for an in-situ application in the unsaturated zone. *Engineering Geologists*, 77, 203–215.
- Yeung, A., Hsiu, C., & Menon, R.M. (1997). Physicochemical soil—contaminant interactions during electrokinetic extraction. *Journal of Hazardous Materials*, 55, 221–237.
- Yuan, C., & Weng, C.-H. (2003). Sludge dewatering by electrokinetic technique: effect of processing time and potential gradient. *Advances in Environmental Research*, 7, 727–732.