

Integration of electrokinetics and chemical oxidation for the remediation of creosote-contaminated clay

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Abstract

Remediation of clayey soils that are contaminated with polycyclic aromatic hydrocarbons (PAHs) is a challenging task that may require integration of several technologies. The benefits of integrating in situ electrokinetic remediation with chemical oxidation were evaluated in laboratory-scale experiments lasting for 8 weeks. A voltage gradient of 48 V/m of direct current and 4.7 V/m of alternating current and periodic additions of chemical oxidants were applied to creosote-contaminated soil. Electrokinetically enhanced oxidation with sodium persulphate resulted in better PAH removal (35%) than either electrokinetics (24%) or persulphate oxidation (12%) alone. However, the improvement was shown only within 1/3 (5 cm) of the soil compartment. Electrokinetics did not improve the performance of Fenton oxidation. Both chemical oxidants created more positive oxidation–reduction potential than electrokinetic treatment alone. On the other hand, persulphate treatment impaired the electroosmotic flow rate. Elemental analyses showed reduction in the natural Al and Ca concentrations, increase in Zn, Cu, P and S concentrations and transfer of several metal cations towards the cathode. In conclusion, the results encourage to further optimisation of an integrated remediation technology that combines the beneficial effects of electrokinetics, persulphate oxidation and Fenton oxidation.

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1. Introduction

Creosote is a distillate of coal tar of which more than 90% may comprise of polycyclic aromatic hydrocarbons (PAHs) and up to 20–40% of the 16 polycyclic aromatic hydrocarbons (PAHs) that have been defined as priority PAHs by the US EPA [1–3]. The International Agency for Research on Cancer (IARC) has classified creosote as a probable human carcinogen (group 2A carcinogen) and several of the individual PAHs as probable or possible human carcinogens (groups 2A and 2B) [4]. The content of benzo(a)pyrene in creosote has been restricted to $\leq 0.005\%$ in the European Union member states, and creosote impregnation

and the use of impregnated wood is only permitted by way of derogation for industrial applications [5].

Because creosote oil was used for a long time without any restrictions, the impacts of the long-term use can be found at several sites where elevated PAH concentrations have been determined from soils, sediments, groundwater and surface water [2]. In Finland, for example, wooden railway sleepers (cross ties) and other wood products have been impregnated with creosote since 1904 [1]. Over the years, creosote has leached deep into the ground and now it poses a threat to the groundwater quality. There is a great need for remediation technologies to clean up these contaminated sites in situ.

In situ remediation technologies in which electric current is led into soil have been extensively studied for several applications. The processes launched by the current and utilised for remediation purposes include enhanced flushing, transportation, volatilisation, oxidation and reduction. Electrokinetic remediation is a widely used term for these technologies, because contaminant movement is central to most applications.

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Electrokinetic removal of PAHs from soil can be accomplished by enhancing their dissolution with surfactants or cosolvents. PAHs do not carry an electric charge but they are transported with the electroosmotic flow of aqueous solutions. For example, Maini et al. [6] removed 90% of PAHs from 54 kg of soil from a former gasworks site in 22 days by using a non-ionic surfactant as an anolyte solution. The applied direct current (dc) voltage was 20 V (about 40 V/m) at the beginning of the treatment. Several experiments carried out on phenanthrene-spiked soil at laboratory scale suggest that the PAH removal efficiency is highly dependent on the type of soil and surfactant or cosolvent. By applying a voltage gradient of 100 V dc/m and surfactant or ethanol enhancements, significant removal of phenanthrene from clay after 229–236 days was established only within 6 cm distance from the anode [7,8]. Pulsed treatment with a higher voltage gradient significantly improved removal: at the end of the 275-day treatment, 90% of phenanthrene was recovered from the cathode effluent when a surfactant and a pulsed treatment with 200 V dc/m was used for 5 days, then followed by a break for 2 days [9]. An overall phenanthrene removal of 70–80% was obtained in 6 days in a 10 cm long kaolinite column with hydroxypropyl- β -cyclodextrin surfactant and voltage gradient of 140 V dc/m [10]. *N*-Butylamine solvent flushed 43% of phenanthrene out of glacial till clay in 127 days [11].

Instead of using surfactants or cosolvents to flush away the contaminants, removal of relatively nonpolar and sparingly soluble contaminants can be accomplished by electrochemical decomposition that takes place directly in soil. In ElectroChemical GeoOxidation (ECGO) technology, the so-called colloid conductor property of soil is exploited to carry dc and a weak alternating current (ac) and enhance natural reduction and oxidation (redox) processes on soil particles that act as microconductors [12,13]. In a field test with excavated soil and a small-scale in situ test, 95–96% of PAHs was decomposed in 70–75 days [14].

In situ oxidation can be enhanced by integrating electrokinetic and electrochemical processes with the use of chemical oxidants such as persulphates or hydrogen peroxide (H_2O_2) catalysed by ferrous (Fe^{2+}) or zero-valent iron (Fe^0) [15–17]. Fenton's reagent (H_2O_2 and Fe^{2+}) has been used to enhance bioremediation of PAHs in soil [18–20] and electrokinetic injection of Fenton's reagent, called EK-Fenton process, was recently demonstrated for the remediation of PAH and heavy metal contaminated soils [21,22]. In laboratory scale experiments with a 20 cm long electrokinetic cell, more than half of the spiked phenanthrene in kaolinite clay was removed in 13 days by applying a voltage gradient of 150 V dc/m and 7% H_2O_2 stabilised with sulphuric acid [22].

Sodium peroxodisulphate (sodium persulphate, $\text{Na}_2\text{S}_2\text{O}_8$) has been shown to be a more efficient for organic carbon removal and dissolve less minerals than H_2O_2 , when used for organic matter removal from clayey soils as a pretreatment for the determination of mineral phase properties [23,24]. The oxidation power of persulphate is strongest when the production of sulphate free radicals ($\text{SO}_4^{\bullet-}$) with a standard redox potential of 2.6 V is activated by Fe^{2+} [25,26], temperatures higher than 40 °C [26,27], reductants such as ascorbate [28] or γ -irradiation

[29]. Furthermore, electrolytic and photolytic generation of $\text{SO}_4^{\bullet-}$ from sulphates has been utilised in wastewater purification processes [26,30–32] but not in soil remediation.

Significant benefits could be obtained by integrating electrokinetic remediation with in situ chemical oxidation, because electrokinetic treatment can facilitate oxidant delivery and activation of oxidising radicals and simultaneously induce oxidative/reductive reactions directly in soil. The aim of this study was to find out whether the removal of PAHs from creosote-contaminated clay can be enhanced by integrating a low dc/ac voltage with the injection of Fenton's reagent or sodium persulphate. The influence of the treatment on the elemental composition of clay was also investigated.

2. Materials and methods

2.1. Experiment configuration

Creosote-contaminated clay soil was obtained from a former impregnation site for wooden railway sleepers located in the city of Turku, south-western Finland. Clay was drilled from the depths of 1–5 m, homogenised thoroughly and stored in a closed container below 5 °C. Grain size analysis of the soil showed that 77 wt.% of the particles were smaller than 125 μm in diameter. Of those fine particles, 2.0 vol.% were >50 μm , 16% were 20–50 μm , 68% were 1–20 μm , and 24% were <1 μm in diameter. The initial water content was 31%, and organic matter content (LOI) was 2.2%.

The experiments on contaminated clay were carried out simultaneously in three electrokinetic test cells and in one reference cell without electric current (Fig. 1). The cells were made of 10-mm thick cast acryl. Between the electrolyte compartments there was cubic space (150 mm \times 150 mm \times 150 mm) filled with contaminated clay to the height of 10–11 cm (about 2.3 l) trying to avoid leaving any visible cavities or fractures in the clay matrix. The clay and electrolyte compartments were covered by acrylic lids and separated from the electrolytes with perforated acrylic baffle plates. Pore water monitoring and reagent injection wells were made of perforated polyvinyl chloride (PVC) tubes with an inner diameter of 23 mm, and attached to the bottom of the cell with duct tape. Polypropylene geotextile F-333 (Fibertex, Aalborg, Denmark) was used as a coating material for the perforated plates and wells. The electrokinetic cells were originally designed and used for the experiments of Ojala [33]. Before the new experiments, the acrylic parts were carefully cleaned and all the other parts were replaced.

A total voltage of 10 V (53 V/m), including an alternating current component of 10% (0.9 V, 4.7 V/m) at a frequency of 90 Hz, was led to plate electrodes that were located 19 cm away from each other. The plate electrodes (length 22 cm, width 4.8 cm) were made of stainless steel. The particular dc/ac combination was chosen with the aim of promoting redox reactions in soil, as in the ECGO technology that applies an ac component less than 10% of the dc voltage [12].

The electrolyte compartments were filled with 650 ml of 0.05 M $\text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$ buffer at pH 8.5 (anolyte) or pH 6.5 (catholyte). K_2HPO_4 and KH_2PO_4 were purchased from

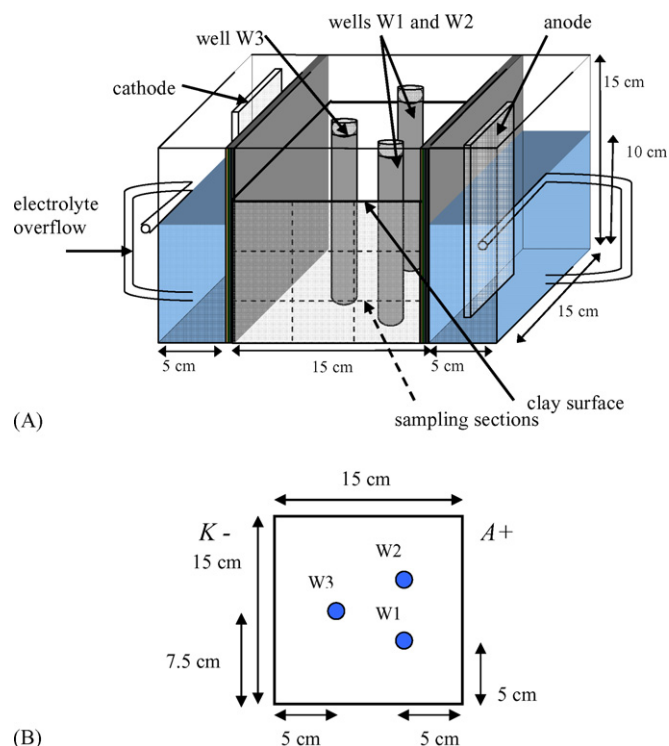


Fig. 1. Electrokinetic cell: (A) side view, (B) top view showing the locations of monitoring and injection wells W1, W2 and W3. All the three compartments were covered by acrylic lids during the experiments.

Sigma–Aldrich Laborchemikalien GmbH (Seelze, Germany) and their purity was $\geq 99\%$. During the experiments, fresh buffer solutions were pumped into the electrolyte compartments using peristaltic pumps that were programmed by means of LabVIEW 7.1 software (National Instruments, Austin, Texas) and an AD card. The buffer flow rate at anode was adjusted to 90–350 ml/day according to the electroosmotic flow in order to prevent depletion of the anolyte. The flow rate at the cathode was kept constant at 44 ml/day during the first 5 weeks, after which the flow rate was slowed down to 29 ml/day to correspond to the decrease in electroosmotic flow rate. The molarities of the added buffers were adjusted to either 0.025 or 0.05 M (pH 6.5 and 8.5), according to the buffer demand of the clay and electrolyte solutions. The total consumptions of K_2HPO_4 and KH_2PO_4 are given in Table 1.

During the experiments, LabVIEW 7.1 software and an AD card were used to collect data on the applied voltage, electric current and conductivity. Electroosmotic flow rate was calculated from the liquid volume collected from the

cathode compartment. Pore water pH and oxidation–reduction potential (redox-potential, E_h) were measured manually from the monitoring wells and electrolyte solutions, using ORION model 250A pH/ E_h meter with pH Triode and combination Pt redox electrodes.

2.2. Electrokinetic and (electro)chemical experiments

Chemical oxidants were used in two tests with an electric current and in two controls without current. The EK Fenton (electrokinetic Fenton) test included additions of 35 mM ferrous iron ($FeSO_4 \cdot 7H_2O$ from T.J. Baker, Deventer, Holland) every second week and fresh 3% (volume) hydrogen peroxide (H_2O_2 , Riedel-deHaën's pro analysis Perdrogen, distributed by Sigma–Aldrich Laborchemikalien GmbH, Seelze, Germany) twice a week into the anode compartment and into the monitoring and injection wells W1 and W2, so that the reagents would be effectively distributed in clay in the oxidising zone near the anode as they migrate towards the cathode. The total reagent volumes per injection time were 4.2 ml of ferrous iron and 34 ml of H_2O_2 . Fe^{2+} was allowed to migrate into the clay for 1–3 days before addition of H_2O_2 .

EK Persulphate test was an activated persulphate treatment with 35 mM ferrous iron addition every second week, and after 1–3 days of the injection, 1.7 M sodium peroxodisulphate (99% $Na_2S_2O_8$ by Riedel-deHaën, distributed by Sigma–Aldrich Laborchemikalien GmbH, Seelze, Germany) addition once a week into the monitoring and injection wells W1, W2 and W3. A total volume of 0.75 ml of ferrous iron and 7.5 ml of sodium peroxodisulphate was injected into the wells each time. The injection points compromised the different electromigration directions of Fe^{2+} and $S_2O_8^{2-}$ ions.

The test EK Only was conducted to investigate the effect of electrokinetic remediation (10 V dc/ac) on PAH concentrations without chemical oxidants. The same dc/ac combination and buffer solutions were used as in the EK Fenton and EK Persulphate experiments.

The experimental setups Fenton Only and Persulphate Only were carried out in the same experimental cell. To investigate the effects of the reagent additions on PAH concentrations without electric current, the same amount of Fenton's reagent as in EK Fenton test (4.2 ml Fe^{2+} , 32 ml H_2O_2) was periodically dosed to the one electrolyte compartment whereas persulphate (7.5 ml) and iron (0.75 ml) were dosed to the other electrolyte compartment. The 5-cm clay section located between Fenton Only and Persulphate Only sections was used as untreated Reference clay. Thus, the Reference clay was subjected to the same

Table 1
Total consumptions of the pH buffering and oxidising reagents

	$K_2HPO_4^a$	$KH_2PO_4^a$	Fe^{2+}	3% H_2O_2	$Na_2S_2O_8$
EK Fenton	87 g, 14.21	15 g, 2.51	36 mg (0.74 mmol)	510 ml (510 mmol)	
EK Persulphate	51 g, 8.31	14 g, 2.41	7.3 mg (0.13 mmol)		63 g (223 mmol)
EK Only	95 g, 15.61	16 g, 2.61			
Fenton Only	5.5 g, 0.61	0.1 g, 0.021	36 mg (0.74 mmol)	510 ml (510 mmol)	
Persulphate Only	0.2 g, 0.021	4.3 g, 0.61	7.3 mg (0.13 mmol)		63 g (223 mmol)

^a Consumption includes both 0.025 and 0.05 M solutions.

temperature and lightning conditions as the treatments, and it was assumed that the chemical oxidants did not penetrate into the Reference clay because there was no voltage gradient between the electrolyte compartments. The validity of this assumption is discussed in Section 3.3. Elemental composition of clay.

2.3. Chemical analyses

The initial PAH, metal and organic carbon concentrations were analysed from triplicate samples taken from homogenised clay immediately before the experiments and stored frozen at -20°C until analysis. At the end of the experiments, the test and reference batches of clay were divided into three horizontal sections (anode, central and cathode section) and three vertical sections (surface, middle and bottom layer) as shown in Fig. 1. Each of the nine sections was homogenised and analysed for PAH concentrations. For metal and organic matter analyses, the horizontal sections were combined so that only three samples (anode, central and cathode section) were analysed. At the end of the experiments, the electrolyte solutions of 500–600 ml were analysed for their PAH, elemental and total organic carbon contents.

Dry weight and organic carbon content as a loss on ignition (LOI, at 550°C) were determined from the soil samples according to the standard SFS 3008 [34]. The standard method SFS-EN 1484:1997 [35] was used to determine total organic carbon (TOC) content of the water samples. Acidified (0.5 ml HCl/100 ml sample, 36–38% J.T. Baker p.a. grade) sample was injected into a quartz column heated to 680°C . In the quartz column, carbon compounds were catalytically oxidized into carbon dioxide that was detected with IR-detector. Before measurement, inorganic carbon was removed from phosphoric acid (85% J.T. Baker p.a. grade) acidified solution by bubbling the sample solution with synthetic air. Measurement was made with Shimadzu TOC-V-CPN instrument. Standard used for quantitation was potassium hydrogen phthalate (KHP, Merck p.a.)

PAHs were extracted from the soil samples (8 g sample) by shaking them twice for one hour, using acetone (Rathburn, HPLC-grade) as an extraction solvent. The collected acetone phases were then combined. Then deionized water was added and the acetone–water solution was extracted with hexane (Rathburn, HPLC-grade). Water samples (35 ml sample) were directly shaken with hexane and the hexane phase was then concentrated to approximately 250 μl volume. For quantitation of the PAHs in hexane extract, an Agilent technologies gas chromatograph (GC) 6890 GC, equipped with HP-5MS column (J&W Scientific, USA) was connected to Agilent technologies 5973 mass selective detector (MSD). One microliter of hexane extract was injected in to the GC in pulsed splitless mode, and the PAHs were separated from each other using helium as carrier gas and by heating the GC oven gradually from starting temperature of 60°C to end temperature of 325°C . The eluted PAHs that reached MSD were ionized with electron ionization technique and quantitated with methodology based on selective-ion monitoring (SIM) and isotope dilution. Deuterated PAHs used as internal standards were naphthalene-d8 (Acros 98+%) and dibenzo(*a,h*)anthracene-d14 (Cambridge Isotope Laboratories, 97%). Unlabeled PAHs used for quantitation purposes were pur-

chased from Accustandard (Accustandard PAH mix Z-014G, 2.0 mg/ml).

Prior to the elemental analyses, clay samples were dried in room temperature over night and then ground and sieved to <2 mm fraction. Then the 1 g samples were digested with nitric acid (HNO_3 , J.T. Baker 65% p.a. grade) in a microwave oven (Milestone MLS-1200 MEGA or CEM MDS-81D) and after digestion filtrated through black ribbon filtration paper (Schleicher&Schuell Black ribbon 589/1) into 100 ml volumetric flask and diluted with water to 100 ml volume. For each set of digestions, blank sample was prepared from deionized water and reference sample was prepared from VKI QC Loam Soil certified reference material. Every fifth sample was prepared as duplicate. The analysed 26 elements were excited with inductively coupled plasma (ICP) method and detected with atomic-emission spectroscopy (AES). The instrument used for clay samples was Thermo Electron, IRIS Interpid II XDL DUO equipped with concentric nebuliser and cyclonic spray chamber. Both the radial and axial measurement modes were used, depending on the element measured. For correction of the spectral interferences inter-element correction method was used. Calibration solutions were made by dilution from custom made elemental solution (PrimAG-plus, Romil Ltd., England).

Water samples were passed through a 0.45 μm filter (Milliex-MCE 25 mm 0.45 μm syringe filter) and stabilised with nitric acid (0.5 ml/100 ml sample, Merck, 65%, Suprapure). They were excited or ionised with inductively coupled plasma (ICP) and analysed with AES (Thermo Jarrell Ash Corp. ICP-AES dual detector system, IRIS Advantage) or mass spectrometry (MS) (Perkin-Elmer PE-SCIEX ICP-MS system, ELAN 6000). The ICP-AES instrument was equipped with Meinhardt nebulizer. The instrument was calibrated using custom made calibration solutions at concentrations 0.1–1.0 mg/ml, purchased from Inorganic Ventures. At least one background correction was used for each emission line, and emission spectra were measured when needed. In the ICP-MS instrument, cross-flow nebulizer and Scott double-pass spray chamber were used. Calibration solutions were prepared from multiple element solutions Merck (ICP-IV) and Spectrascan (Spex QC-21, Spex LCMS-2) and single element solutions from Spectrascan. Ruthenium was used as an internal standard.

The analyses were carried out using accredited methods. The analytical laboratory is accredited by the Finnish Accreditation Service, FINAS, according to the standard EN ISO/IEC 17025. For each set of samples or between every 20 samples, one blank sample and one reference sample with duplicate was prepared. Reference sample results were monitored using Average- (X-chart) and Range-control charts (R-chart) and if results were out of control limits samples were reanalyzed, until acceptable quality was achieved.

3. Results and discussion

3.1. Physical parameters

The changes in electric current in EK Fenton test were similar to those in EK Only test but the current was systematically

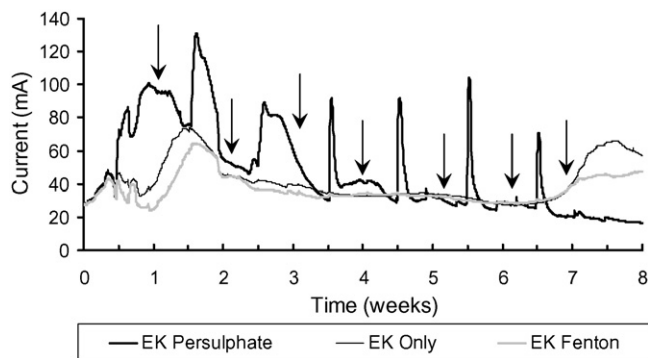


Fig. 2. Electric currents in the tests EK Fenton, EK Persulphate and EK Only during the 8-week treatment. The arrows indicate the injections of persulphate. Hydrogen peroxide was injected twice as often.

2–15 mA lower in EK Fenton (Fig. 2). Additions of Fe^{2+} or H_2O_2 had no influence on the electric current. Each persulphate addition, which was equivalent to about 0.6 M of sodium and persulphate ions, significantly increased the current by increasing the ion concentration. However, after the first three persulphate additions (after 3 weeks), current peaks did not last longer than 1 day after the addition. This might be due to the precipitation of metal sulphates, phosphates and hydroxides which prevented electromigration of ions. In particular, Suer et al. [36] have observed precipitation of calcium sulphate during electrokinetic remediation of soils with high sulphur content. The unexpected increase in current observed during the last week of EK Fenton and EK Only treatments might indicate dissolution of minerals and swelling of clay that released more ions from the clay. Reddy and Saichek [7] and Grundl and Michalski [37] have observed fluctuating or even constantly increasing electric currents under electrokinetic remediation of natural soils and sediments.

Most of the time, the electric current was between 20 and 40 mA ($0.38\text{--}0.76\text{ mA/cm}^2$ of electrode surface). The high ion concentrations due to the buffer and persulphate additions led to current peaks of up to 130 mA (2.46 mA/cm^2). Soil temperature might have increased due to these high currents, though occasional monitoring of temperature did not track any changes. Similar peak values were observed during pulsed surfactant-enhanced electrokinetic remediation [38]. Ideal current density over longer-term treatments may be case-sensitive: current densities of $0.1\text{--}0.2\text{ mA/cm}^2$ [40] and $0.1\text{--}1\text{ mA/cm}^2$ [41] have been recommended to optimise electromigration, electroosmosis and energy consumption.

The electroosmotic flow rates were at their highest during the second week of the treatment (Fig. 3). Up to 500 ml/day of the buffer solution passed through the clay in all the electrokinetic tests, corresponding to a flow rate of 2.20 cm/day and electroosmotic conductivity of $6.67 \times 10^{-5}\text{ cm}^2/(\text{s V})$. However, electroosmotic flow decreased with time. In EK Only and EK Fenton, the flow rates between days 14 and 56 ranged from 200 to 320 ml/day. As compared with EK Only, EK Fenton decreased the electroosmotic flow rate by 50–100 ml/day during the second week of treatment. With EK Persulphate, a continuing decrease to a final rate of only 20–40 ml/day was observed after the peak value.

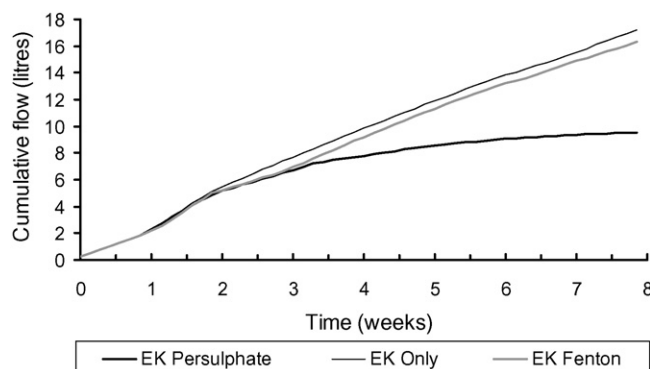


Fig. 3. Cumulative electroosmotic flow rates.

Previous studies of Reddy and Saichek [7] with kaolin clay and deionised water showed that it is possible to maintain a nearly constant electroosmotic conductivity of $2.46 \times 10^{-6}\text{ cm}^2/(\text{s V})$ for 230 days if the applied voltage gradient and electric current are low, 100 V/m and $<1\text{ mA}$. Even higher, constant electroosmotic flow was obtained with dilute sodium hydroxide (NaOH), which also increased the current [8]. Electroosmotic flow of pure deionised water rapidly ceased at higher voltages (200 V/m, pulsed) and currents (5–10 mA). After all, phenanthrene removal with deionised water as an electrolyte was only obtained in the above mentioned experiments when the higher voltage, current and NaOH addition were combined [38]. This illustrates the complexity of optimising electroosmotic flushing.

Theoretically, electroosmotic flow rate is directly proportional to the applied voltage gradient, zeta potential of soil particles and dielectric constant of the fluid and inversely proportional to the fluid viscosity [39]. In practice, it is important to supply charge-carrying ions and control the pH of the system [22,39–42]. The high ionic strength in EK Persulphate test should have promoted electroosmosis, but the charge-carrying ions were probably eliminated as they formed precipitations at the high pH region near the cathode [42]. At regions with low pH, the zeta potential decreases (turns more positive), which may have created zones of low electroosmotic conductivity [41,42].

Despite the use of pH buffers, the pH of the catholyte solution increased to 12–13 in a few days and remained at this level during the treatment whereas the pH of the anolyte was around 2 in all the electrokinetic tests. Consequently, pH values measured from the monitoring wells indicated that pH fronts were also formed in clay. At the beginning, clay buffered the pH drop at the monitoring well W1 located 5 cm away from anode compartment. The buffering effect lasted longer in EK Fenton test than in EK Persulphate and EK Only tests: the pH remained above 4 for 2.5 weeks in EK Fenton test, then dropping to 2–3 for the rest of the experiment. Furthermore, Fenton's reagent acted as a buffer at the monitoring well W3, 5 cm away from cathode compartment. At W3, the pH ranged between 6 and 8 in EK Fenton with the final pH of 6, whereas the final pH was 4 (range 4–12) in EK Persulphate and 12 (range 6–12) in EK Only.

Oxidation–reduction potential (E_h) followed the trends in pH: positive E_h values (oxidative conditions) occurred at acidic pH values and negative E_h values (reductive conditions) occurred

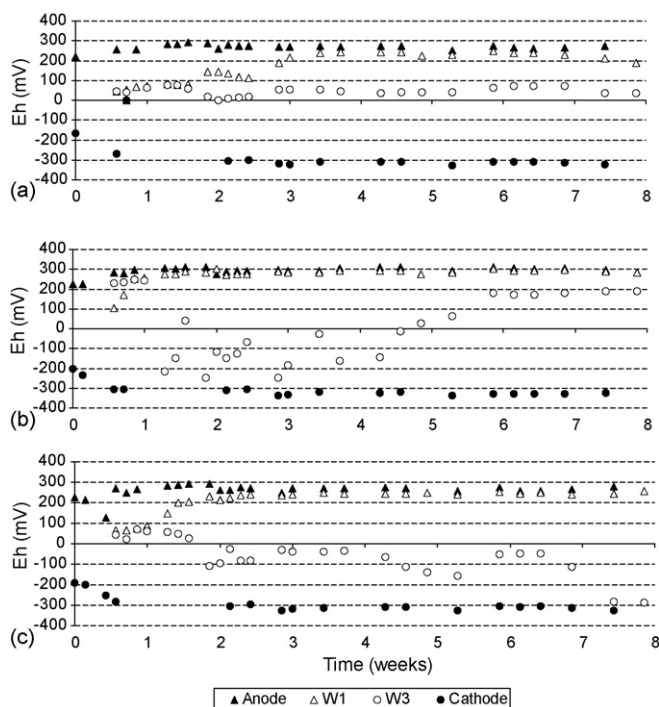


Fig. 4. Redox potentials (E_h) measured from the anode and cathode solutions and from the injection and monitoring wells W1 (5 cm away from anode) and W3 (5 cm away from cathode) in tests (a) EK Fenton, (b) EK Persulphate and (c) EK Only.

at basic pH values (Fig. 4). Without added oxidants, the E_h at the anode compartment and at monitoring well W1 was between +200 and +300 mV, but mostly negative at the catholyte compartment and W3. However, addition of chemicals created oxidative conditions in clay even near the cathode: the E_h at W3 remained positive all the time in EK Fenton test and during weeks 6–8 in EK Persulphate test.

Changes in the physical structure of the clay were observed after the experiments. The clay was slightly compacted near the anode due to all the treatments with an electric current. However, the clay had not dried out: the water content ranged from 29 to 32% in all the treated as well as untreated clay samples. As an indication of sulphide reduction, a dark and bad-smelling stripe extended to a distance of 2–3 cm away from the cathodes in the electrokinetic tests. White precipitations, obviously sulphates or phosphates, were formed in the clay and catholyte solution of EK Fenton and EK Persulphate tests. Oxidation of iron was observed near the anode. Iron and probably other metals, too, caused some clogging of the textile filters around the acrylic plates and injection wells.

No reduction in organic matter content of the clay was observed. The organic matter content (LOI) of the soil was 1.8–2.2% in all the other treated and untreated samples but 2.4–2.6% in those treated with persulphate. It is possible that there were some organic impurities in the reagent.

3.2. PAH removal efficiency

After 8 weeks at the ambient laboratory temperature, the total PAH concentration in the untreated Reference clay was

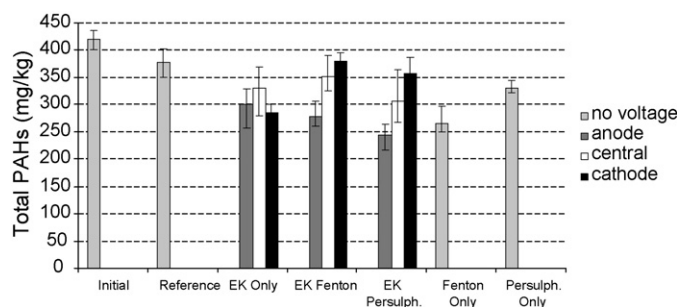


Fig. 5. The average PAH concentrations ($\sum 16$ PAHs) and ranges initially, in Reference clay and in the anode, central and cathode sections of the electrokinetically (EK) treated clays. The average concentrations are calculated from concentrations in surface, middle and bottom layers ($n = 3$).

380 mg/kg in the bottom, 403 mg/kg in the central and 350 mg/kg in the surface layer (Table 2). The loss of PAHs, as compared to the clay samples that were stored frozen, was 4–17%. This loss could be due to volatilisation, biodegradation or leaching of PAHs.

The oxidants were found to remove PAHs both as such and in combination with electrokinetics, when the PAH concentrations in the treated clays were compared with the concentrations at the same depths in the Reference clay. The ranges of residual PAHs (Fig. 5) demonstrate that all the treated clays within 5 cm of the injection points of the chemical oxidants and the cathode and anode sections of EK Only contained significantly less PAHs than the Reference clay. The influence of the electrochemical treatment on PAHs was the strongest in the vicinity of anode in EK Fenton and EK Persulphate, because a majority of the reagents were applied to anolyte solution or injection wells W1 and W2. The highest PAH removal efficiencies were achieved in the anode section of EK Persulphate (35%), in Fenton Only (30%), anode section of EK Fenton (26%), cathode section of EK Only (24%) and in Persulphate Only (12%). There were no significant differences in the removal efficiencies of EK Fenton, EK Persulphate, EK Only and Fenton Only, however, the removal of PAHs in Persulphate Only was lower than in the other treatments. Electrokinetics improved the performance of persulphate as compared with Persulphate Only.

In EK Fenton and EK Persulphate, PAH concentrations increased from the anode towards the cathode section. When compared to the Reference clay, no enrichment of PAHs was observed in any section. Since the improvement in PAH removal efficiency was observed within a limited distance from the injection points of the chemical oxidants, the average removal efficiencies in the entire cell ($n = 9$) were lower: 11% in EK Fenton, 19% in EK Persulphate and 19% in EK Only. However, a homogeneous decline in PAH concentration was obtained throughout the electrokinetic cell in EK Only test.

It does not seem to be possible to obtain a uniform PAH destruction in soil treated with EK Fenton or EK Persulphate, owing to the heterogeneous physico-chemical conditions between the electrodes. Thus, the primary target is to clean up the zone close to the anode properly, then expand the treatment zone with the help of injection wells or relocation of the electrodes.

Table 2
Individual PAH characteristics, initial concentrations (in dry weight) and average removals in 5-cm clay sections taken from the vicinity of the anode and cathode and middle of the soil compartment, after the 8-week treatment

Number of rings	IARC class ^a		Concentration (S.D.) (mg/kg)			Average removal ^b (%)					
			Initial ^c	Reference ^d			EK Fenton Anode	EK Persulphate Anode	EK Only Cathode	Fenton Only	Persulphate Only
				Surface	Middle	Bottom					
2	2B	Naphthalene	126 (9.5)	71	101	103	67	36	51	60	7.5
3		Acenaphthylene	22 (1.1)	17	20	18	40	78	18	31	54
3		Acenaphthene	6.4 (0.3)	5.2	5.8	5.5	26	58	17	31	19
3		Fluorene	21 (0.7)	17	20	19	19	35	18	33	13
3		Phenanthrene	87 (2.2)	80	89	82	8.9	15	15	26	1.4
3		Anthracene	21 (0.7)	19	21	19	29	79	15	27	47
4		Fluoranthene	23 (0.9)	22	23	21	8.0	13	15	13	1.6
4		Pyrene	48 (1.2)	46	48	44	11	47	15	12	11
4	2A	Benzo(a)anthracene	14 (0.5)	15	16	15	8.1	47	20	13	9.0
4		Chrysene	16 (0.4)	16	17	15	1.0	9.4	12	12	0.4
5	2B	Benzo(b)fluoranthene	4.5 (<0.0)	6.7	7.6	6.8	19	22	28	17	7.2
5	2B	Benzo(k)fluoranthene	6.0 (0.3)	6.2	6.6	5.7	-1.6	6.8	6.1	4.2	-7.2
5	2A	Benzo(a)pyrene	11 (0.3)	15	15	14	12	73	17	12	47
5	2A	Dibenzo(a,h)anthracene	1.2 (0.1)	1.1	1.1	1.0	-4.2	12	6.4	5.5	4.3
6	2B	Indeno(1,2,3-cd) pyrene	5.2 (0.5)	5.0	5.3	4.6	5.0	15	4.4	5.6	1.7
6		Benzo(g,h,i)perylene	7.5 (0.4)	7.0	7.3	6.2	6.4	37	3.5	3.3	16
		Total (\sum 16) PAHs	420 (18)	350	403	380	26	35	24	30	12

^a International Agency for Research on Cancer (IARC) classification: 2A = probable human carcinogen, 2B = possible human carcinogen [4].

^b $n = 3$ (bottom, middle and surface section).

^c Stored frozen during the experiments. $n = 3$.

^d Stored under ambient laboratory conditions during the experiments.

The removal of PAHs with 2–3 fused rings (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene) was found to be significantly better than the removal of 4–6-ring PAHs (Table 3) when the means were compared with two-tailed Student's *t*-test (SPSS Inc., Chicago, IL, USA). Removal efficiency generally improved stepwise with each additional ring but the differences between each ring number were not statistically significant. Physical/chemical properties of PAHs are related to the molecular size, for example, water solubility usually decreases and vapour pressure increases with increasing size, although the trends are not always consistent and differences exist in the methodologies used to determine these parameters [43]. The major component in creosote, naphthalene, is rather volatile and water-soluble two-ringed molecule and it was thus easily removed in most tests. Naphthalene is also a possible human carcinogen. The other possible and prob-

able human carcinogens contained four to six rings. However, the removal of the five-ringed carcinogen benzo(a)pyrene in EK Persulphate test, 73%, was surprisingly high. This might indicate the prevalence of oxidative mechanisms that were not controlled by the molecular size. Previous experiments on electrochemical oxidation have resulted in almost similar degradation efficiency for all the investigated PAHs [14]. In Fenton oxidation, benzo(a)pyrene is more easily oxidised than fluorene and fluoranthene that contain ring structures with five carbons [44,45]. PAH amenability to persulphate oxidation has not been examined.

The most effective of the treatments tested in this study, EK Persulphate, had an advantage of creating highly oxidative conditions. However, it also caused clogging of clay and the power of electroosmotic flushing was therefore lost by the end of the treatment. The high reagent consumption might also impair the

Table 3
Average removal (%) of individual 2–3- and 4–6-ring PAHs from clay and the statistical difference (*p*) between these PAH groups

	Soil section ^a	2–3 ring PAHs (%) ($n = 18$)	4–6 ring PAHs (%) ($n = 30$)	Significance, p^b
Reference		13	-6.3	0.00013
EK Fenton	Anode	32	6.4	0.00007
EK Persulphate	Anode	50	28	0.008
EK Only	Cathode	22	13	0.007
Fenton Only		35	9.8	0.0000013
Persulphate Only		24	9.1	0.013

^a The data set includes results from bottom, middle and surface samples taken from the vicinity (5 cm) of anode or cathode or from the middle of the soil compartment.

^b Two-tailed Student's *t*-test.

feasibility of EK Persulphate treatment for in situ remediation. The dosage of persulphate was 18 g/kg of soil, and the weight ratio of persulphate to soil organic matter was about 1:1. In a field study, 1.7 g of persulphate was used per kilogram of BTEX-contaminated soil, which was, however, said to be a relatively low dosage [46]. On the other hand, the dosage of persulphate has been several folds higher than the amount of organic matter when persulphate oxidation has been used to determine the bioavailable fraction of PAHs [47] or to decompose organic matter in soil [23,24]. So far, there is no sufficient information available on the efficacy and optimal dosages of persulphate in connection with electrokinetics. EK Fenton, however, was recently used for the cleanup of phenanthrene-spiked soil and the removal was up to 42%, suggesting higher remediation potential for EK Fenton than what was demonstrated in this study with 8.9% removal for phenanthrene [48].

Precipitation of sulphates and rapid conversion of Fe^{2+} to Fe^{3+} may have limited the oxidising capability of persulphate in this study. The dosage of persulphate should be lower, or the pH better controlled. In addition to the precipitate formation, there are several other problems associated with integrated use of electrokinetics and persulphate oxidation. If persulphate dissociates rapidly in the anode compartment, the negative ions will not be carried into the soil against their electrokinetic flow directions. In order to expand the treatment zone, persulphate and iron were injected into all the three wells, too. However, these injections did not lead to anticipated results, probably because persulphate, iron and creosote failed to come into sufficient, right-time contact to be able to react with each other. Electrolysis of water also led to reductive conditions deeper in soil. EK Fenton is more convenient to perform, because both hydrogen peroxide and iron can be dosed to the anode compartment and they move into the same direction.

The dosage of hydrogen peroxide per soil weight in EK Fenton and Fenton Only was as high as the higher dose used by Piskonen and Itävaara [20] that was shown to enhance the mineralization of phenanthrene and pyrene but not to affect the biodegradation of benzo(a)pyrene. Therefore, the oxidation power of Fenton's reagent alone was not high and the applied voltage did not improve its efficiency as expected. The dosage of Fe^{2+} was much smaller in the present study. However, the larger reservoir of iron that was present in natural iron-containing minerals was supposed to play a bigger role in the Fenton-type oxidation than the added iron that easily oxidised near the anode.

The observations during the experiments suggest that a higher dosage of hydrogen peroxide could be used to increase the in situ oxidation power of the EK Fenton treatment without severely affecting the electroosmotic flow rate. Buffers such as KH_2PO_4 are known to stabilise H_2O_2 [49], so that the treatment should have theoretically worked deeper in the clay. The positive E_h at W3 did indicate transportation of H_2O_2 towards the cathode. However, the E_h of 300 mV in EK Fenton and EK Persulphate was probably not high enough for rapid PAH oxidation. Alshawabkeh and Sarahney [50] reported 88% decomposition of naphthalene in 8 h in sodium chloride solution by using current densities of 9–18 mA/l which produced E_h as high as 1380 mV,

whereas no decomposition was observed in a control with E_h of 350 mV.

Taking the low applied voltage and short treatment time into account, EK Only resulted in surprisingly high reduction in PAH concentration throughout the creosote-contaminated clay, as compared with previous experiments on spiked kaolin with buffered or unbuffered water as electrolytes [7,8,38]. The possibly favourable effect of the ac component on PAH removal should be therefore investigated in more detail. Furthermore, integrated processes should be optimised to ensure more complete cleanup, which requires clarification of the roles of in situ flushing and oxidation processes.

3.3. Elemental composition of clay

After the electrokinetic treatments, the concentrations of metals that typically occur as cations, such as Ca, Cu, K, Mg, Mn and Zn, were found to increase in the direction from the anode section towards the cathode section (Table 4). Precipitation at the high pH zone probably prevented the metals from leaching into the catholyte. The treatments led to an increase in Cu, Zn, K and P concentrations in soil. Zn and Cu were obviously released from the brass valves, as indicated by turquoise precipitations found in the tubing. The concentrations of Cr, Ni and Mo that were present in the stainless steel electrodes were not markedly elevated in clay. The buffer solutions acted as a source of K and P. Furthermore, elevated concentrations of S were found in EK Persulphate and Persulphate Only tests. No release of As was observed. Elevated As concentrations during electrokinetic remediation, as reported by Maini et al. [6], could be due to the dissolution of As-bearing minerals [51].

The amount of Fe^{2+} added to the Fenton and persulphate treated clays, 7.3 or 36 mg/kg, was negligible as compared to the natural Fe (total) content of the clay, 37,700 mg/kg. Corrosion of the plate electrodes could have acted as an additional source of Fe. However, no elevated concentrations of Fe in the treated clays was observed.

The elemental composition of the Reference clay was slightly different from the initial composition. For example, the Al and Ca concentrations had decreased during the storage in the untreated experimental cell by 20% and 17%, respectively, possibly due to their leakage into the anolyte and catholyte solutions. During the 8-week experiments, about 1/3 of the anolyte and catholyte of the Reference test cell were displaced by fresh solutions. Furthermore, it can be seen that the addition of $\text{Na}_2\text{S}_8\text{O}_8$ to the catholyte resulted in some advection or diffusion of Na and S into the Reference clay section in the centre of the test cell. Therefore, it cannot be ruled out that some of the observed PAH loss from the Reference clay during the 8-week experiments was due to the chemical oxidants.

3.4. PAHs, organic matter and metals in electrolyte solutions

Concentrations of PAHs and total organic carbon (TOC) were analysed from the electrolyte solutions at the end of the experiments. Based on the liquid flow rates, the samples represented

Table 4
Concentrations of elements (mg/kg dry weight) in clay samples initially and at the end of the 8-week treatment^a

	Initial (range)	Reference	EK Fenton			EK Persulphate			EK Only			Fenton Only	Persulphate Only
			Anode	Middle	Cathode	Anode	Middle	Cathode	Anode	Middle	Cathode		
Al	24,900 (20,800–28,800)	19,800	19,400	21,400	20,000	13,400	20,800	24,900	23,800	26,900	25,500	20,600	26,400
As	7.3 (7.0–8.0)	7.0	7	7	7	7	8	7	8	8	8	7	8
B	7.7 (4.0–10)	<4	<4	5	<4	<4	6	4	6	7	7	4	9
Ba	160 (140–180)	140	120	100	190	130	130	150	150	140	200	140	160
Be	1.0 (1.0–1.0)	1	0.8	0.9	1	<0.6	0.7	1	0.9	1	1	1	1
Ca	3850 (3370–4160)	3200	1950	2160	3580	1290	2140	4270	2500	2740	4240	3420	3510
Co	14 (13–15)	13	8	10	21	7	11	20	8	11	21	14	12
Cr	46 (41–51)	40	60	47	40	60	56	54	51	53	45	41	46
Cu	32 (31–33)	40	99	190	220	110	120	200	110	200	110	32	77
Fe	37,700 (35,900–39,300)	34,300	30,900	32,400	38,700	29,000	33,800	37,800	32,300	35,600	44,300	35,200	37,000
K	6640 (5570–7720)	5890	7580	7660	9690	6700	7160	7380	9000	8900	11,300	7520	8190
Mg	10,300 (9660–10,900)	9330	6500	8660	12,000	5440	8400	12,400	6760	9160	13,200	9400	9790
Mn	437 (410–470)	380	220	300	620	190	300	590	230	320	640	390	370
Mo	<1.0	<1	2	<1	<1	4	<1	<1	<1	<1	<1	<1	<1
Na	440 (340–520)	810	260	280	280	270	440	660	370	390	470	490	1760
Ni	32 (30–33)	29	20	27	61	22	29	59	19	27	50	30	28
P	540 (530–550)	570	9930	3590	1200	5070	2950	2590	11,100	5860	1490	1340	1920
Pb	14 (13–14)	12	16	12	13	21	12	12	21	13	13	13	13
S	113 (110–120)	780	110	160	110	2690	2980	1040	120	120	130	370	1810
Ti	1150 (1100–1180)	990	870	950	1020	940	1040	1110	1160	1340	1330	1060	1360
V	58 (53–62)	50	45	55	53	41	54	56	53	67	62	52	62
Zn	87 (82–90)	84	69	100	330	90	100	210	67	120	230	84	100

^a The concentrations of the following metals were below detection limits in all samples: Cd (<0.4 mg/kg), Sb (<4 mg/kg), Se (<2 mg/kg) and Sn (<2 mg/kg).

Table 5
Concentrations of PAHs, total organic carbon (TOC) and elements in water samples after the 8-week treatments

Collection time ^a	EK Fenton		EK Persulphate		EK Only		Fenton Only (37 days)	Persulphate Only (37 days)
	Anolyte (2.3 days)	Catholyte (2.3 days)	Anolyte (6.5 days)	Catholyte (10 days)	Anolyte (2.3 days)	Catholyte (2.1 days)		
Total PAHs (µg/l)	3.12	542	29.0	226	9.94	433	<1.0	<1.0
TOC (mg/l)	7.83	94.3	23.4	203	13.1	102	15.5	22.5
Ag (µg/l)	0.25	<0.2	20.0	<0.2	0.28	<0.2	<0.2	0.29
Al (mg/l)	0.69	0.27	128	1.16	0.84	0.35	<0.05	7.04
As (µg/l)	68.9	19.2	246	11.9	113	15.7	38.3	88.0
B (µg/l)	<50	122	<50	60.9	<50	152	<50	<50
Ba (µg/l)	2.99	2.73	57.6	<1	3.37	<1	<1	30.7
Ca (µg/l)	0.35	0.43	10.3	0.49	0.23	0.10	13.3	230
Cd (µg/l)	1.26	<0.3	3.58	<0.3	0.91	<0.3	<0.3	9.24
Cr (mg/l)	3.19	<0.01	17.1	<0.01	3.03	<0.01	<0.01	0.02
Cu (mg/l)	8.64	0.18	121	0.07	14.5	0.12	0.02	86.5
Fe (µg/l)	14.6	0.17	61.4	0.24	11.1	0.10	0.83	1.75
K (mg/l)	1 780	4 020	2 710	3 100	1 380	5 370	820	1 010
Mg (µg/l)	0.23	0.73	67.3	0.49	0.22	0.13	42.1	251
Mn (µg/l)	175	12.2	2 980	7.84	139	10.2	88.0	17 200
Mo (µg/l)	652	19.2	663	9.24	309	6.28	11.7	2.98
Na (µg/l)	11.0	21.0	20.6	1 490	8.80	25.4	54.4	3 770
Ni (µg/l)	1 270	8.58	11 100	<2	893	3.37	11.2	962
Pb (µg/l)	388	4.91	2 090	0.72	753	<0.5	<0.5	100
S (µg/l)	88.3	1.78	1 680	4.29	85.2	0.42	70.3	5 300
Sb (µg/l)	4.49	<1	7.28	1.88	6.75	<1	<1	<1
Se (µg/l)	<50	<50	<50	<50	<50	<50	<50	<50
Si (µg/l)	7.42	15.5	65.1	12.2	14.2	11.1	11.8	130
U (µg/l)	0.10	0.14	25.9	0.19	0.66	0.38	<0.1	0.30
Zn (mg/l)	4.08	0.07	68.7	0.16	8.40	0.10	0.02	56.5

^a Collection time of the sample was estimated based on liquid flow rate.

periods of 2–10 days, but precipitated and adsorbed material probably stayed in the electrolyte compartments longer because no proper mixing was used. Transportation of PAHs and organic matter to the catholytes was observed (Table 5). Estimation with the average catholyte overflow rates yielded cumulative PAH recoveries of 8.8 mg for EK Fenton, 2.2 mg for EK Persulphate and 7.8 mg for EK Only test, which was about 1–4% of the removed PAHs. The low PAH recovery from the effluent might suggest that a larger proportion of PAHs was removed via oxidation than electroosmotic flushing. The importance of direct oxidation mechanism is also supported by the findings of Reddy and Karri [48] and the fact that the high electroosmotic flow in EK Fenton did not yield better results than EK Persulphate. However, adsorption of some PAHs to the apparatus cannot be ruled out. Maini et al. [6] recovered only 0.1% of the removed phenanthrene from a granular activated carbon (GAC) column, while other authors have presented total mass balances within ± 6 to $\pm 21\%$ of the initial concentration [7,9].

With the exception of K and Na, anolytes contained higher concentrations of metals than catholytes. Thus, it seems that the concentration gradient that was observed in soil was created by both electromigration of metals towards the cathode and leaching from soil under the low pH regime. Persulphate leached Cu, Ni, Zn, Ca, Mg, Mn and Si from soil even without applied voltage. Cu and Zn concentrations that were elevated especially in the cathode section of clay were highest in the anolyte solution. This finding supports the hypothesis that they entered the system from the corroding electrodes and valves, mainly from the anode compartment, and migrated towards the cathode.

4. Conclusions

Electrokinetic soil remediation is a potential *in situ* remediation technology. In EK Only test, 19% of PAHs were removed from the entire clay compartment of the electrokinetic cell. However, *in situ* chemical oxidation suffers from poor delivery of oxidants deep into the soil, and significant benefits by integrating these processes were observed only in the vicinity of oxidant injection point.

In 8 weeks, up to 35% of the total PAHs were removed from the clay section near the anode by integrating electrokinetic treatment with persulphate oxidation. Combination of electrokinetics with Fenton oxidation was not better than electrokinetic treatment alone. However, these preliminary experiments showed an apparent need to optimise the reagent dosages, applied voltage gradient and ratio of dc and ac voltages, and possibly to lengthen the treatment time.

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