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Performance of electroremediation in real contaminated sediments using a big cell, periodic voltage and innovative surfactants.

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Abstract

The present work focused on evaluating the electrokinetic (EK) treatment of real contaminated sediments with toxic metals and polycyclic aromatic hydrocarbons (PAHs), using a big laboratory EK cell, periodic voltage and recently tested non-ionic surfactants. The results indicated that the "day on-night off" application mode of voltage, in conjunction with the selected solubilising agents, favoured the overall EK process. Arsenic, nickel and chromium exhibited the highest removal percentages, obtaining 83%, 67% and 63%, respectively, while zinc and lead attained 54% and 41% at the maximum. Furthermore, in the experiments where the non-ionic surfactants were introduced in the electrolyte chambers, there was a major uniformly removal of PAHs from the entire sediment across the EK cell, indicating the high solubilisation capacity of the enhancing agents. Essentially, transport and in some cases removal of PAHs (particularly from sections adjacent to the electrolyte compartments) also occurred in the unenhanced EK run, mainly due their negative charge, their potential weak bonds to the soil matrix and to the periodic application of voltage. Maximum removal was obtained by the use of Nonidet P40 where app. 1/3 (ca. 6498 μg out of 20145 μg) of the total initial amount of PAHs were removed from the cell.

Keywords: electrokinetic remediation; sediments; PAHs; toxic metals; surfactants

1. Introduction

Electrokinetic (EK) remediation (also known as “electroremediation”) is one of the many techniques that can be employed for the decontamination of polluted sites (involving soils/sediments) from various inorganic (toxic metals) and/or organic (polycyclic aromatic hydrocarbons, PAHs) pollutants.

EK relies mainly on the application of direct electric current to a confined contaminated area by the simultaneous use of electrolyte solutions known as “anolyte” and “catholyte” (introduced in the anodic and cathodic chambers, respectively). The contaminants are, in turn, removed by a variety of electrochemically occurring phenomena (water oxidation and reduction, heat transfer) and transport mechanisms-processes (electromigration, electroosmosis, and electrophoresis) which act either individually or synergistically [1-3].

However, there are various other key points that have been reported to contribute in promoting and favouring the removal of the contaminants that are present in a soil/sediment sample, whether it is real or spiked. Electrodes material and configuration [4-8], use of solubilizing agents e.g. chelating agents, surfactants, cyclodextrins, co-solvents as well as granulometry of the soil/sediment sample [9-25], control and effect of operating parameters e.g. pH, electroosmotic flow (EOF), current density, voltage, etc. [26-31] are some of the most important factors affecting the overall efficiency of the EK process.

Considering its numerous applications both in the laboratory [32-36] as well as any attempt of pilot scale or scaling up [4, 5, 37-40], EK appears to be one of the most sufficient and cost-effective alternatives for treating, even, real sediments (dredged or surficial) which often come with the simultaneous presence of multiple contaminants which interact with the constituents of solid matrices, thereby creating other compounds that limit and/or incommode even more the EK process. However, when all contaminants and/or substances are dissolved, they are, then, easily transported (flushed) into the electrolyte chambers, thus obtaining their desirable removal from the polluted soil/sediment sample.

The majority of the EK remediation studies that exist in literature report, mostly, the remediation of surrogate spiked soil/sediment samples, by the use of small EK cells, with dimensions of sediment compartment Ø5 cm × L10 or L20 cm and of electrolyte chamber Ø5 cm × L5 cm, with the capacity of receiving approximately 250-500 g of soil/sediment (dry matter). In addition, most of the experiments reported in these studies are performed under the application of a constant voltage gradient, using ordinary and widely tested solubilizing agents, such as chelates (e.g. EDTA, EDDS, PDA, DTPA, LED3A, citric and acetic acid) [41, 42] as well as surfactants (e.g. Tween 80, Igepal CA-720, SDS, Triton X 100, APG, Calfax 16L-35) [11, 43-45] some of which are finally found inadequate of achieving a sufficient removal of contaminants.

The present work focused on the investigation of the overall performance of EK process in treating real surficial sediments, contaminated by toxic metals and PAHs. Specifications on the procedure included: (a) the use of an EK cell almost ten times bigger in capacity than the commonly used ones in laboratories, (b) periodic application of voltage (day on-night off mode), a tactic that has been implemented only a couple of times in the past, [27, 29] and (c) the use of newly introduced (in the EK technology) non-ionic surfactants (commercially known as Nonidet P40 and Poloxamer 407) that have successfully been implemented only in the previous works of the same team of authors [12, 13]; hence further investigation in a bigger scale and under the aforementioned experimental conditions is required. Furthermore, non-ionic surfactants are commonly used in electroremediation of soils/sediments due to their high solubilisation capacity, biodegradability and low potency to both terrestrial and aquatic organisms. In addition, these non-ionic surfactants achieved relatively high removal percentages of both organic (PAHs) and inorganic (toxic metals) contaminants, in comparison to previous EK studies and choices of solubilizing agents reported in literature. Nevertheless, EDTA was actually used in one of this work's experiments as one of the best chelating agents, so as to facilitate even more the metal extraction from the soil matrix and compare its effectiveness to the one of surfactants. Finally, acetic acid was introduced in the cathode chamber of the EK cell in all runs to depolarize the hydroxyl ions generated by various cathode electrolytic reduction processes. Further details on the experiments and on the advantages of using acetic acid are given in Section 2.2.

2. Materials and methods

2.1 Physicochemical properties of sediment samples and analytical methods used

Surficial sediments (n=4) were collected from four different, but adjacent, spots of Elefsis Bay, Athens, Greece, by the use of a Petersen zinc-plated grab sampler. They were, then, homogenized and stored at freezing conditions till the final sample reached the laboratories of Technical University of Crete (TUC). The homogenized sample was, in turn, air-dried for 72 h and sieved to remove the 2-mm oversize fraction. The dry matter was then chemically analysed for determining the total metal and PAH content. The physicochemical properties of the sediment are presented in Table 1.

Redox potential (ORP) and pH were calculated according to ASTM D4972, by the use of a Crison pH-meter. Moisture, organic matter and electrical conductivity (EC) were determined according to ASTM D2974, specific gravity using method ASTM D854-92 and cation exchange capacity (CEC) using EPA 9081. A refractometer (Siemens 5000) was used for X-ray diffraction to determine the main minerals in the sediment, while a grain size analysis was performed to classify it according to the Unified Soil Classification System (USCS). The sediment was, in turn, characterized according to ASTM D2488 as sand (S).

The content of six selected toxic metals was determined after acid digestion of the homogenized sediment sample according to EPA method 3051A and metal concentrations were measured in triplicate by the use of an ICP-MS (Agilent 7500-CX). The selection of the examined metals was based on their initial total concentrations and environmental significance.

On the other hand, the PAH content of the sediment was calculated according to DIN ISO 11465 for the dry matter and 18287 for SUM PAHs (equivalent to EPA 8072) using a Gas Chromatography Mass Spectrometry (GC-MS). Concentration values of the six metals, as well as the sixteen priority PAHs (also measured in triplicate), are also given in Table 1.

2.2 EK cell, set-up and experimental procedure

A schematic of the experimental EK set-up used is shown in Fig. 1. The cylindrical cell was made of Plexiglas, with dimensions of sediment compartment

Ø10cm x L30cm and of electrolyte chamber Ø10cm x L5cm. All chambers were provided with thread at their ends, for easily unscrewing and obtaining access to the sediment. High density circular perforated graphite electrodes (Ø10cm and 0.7cm thickness) and filter papers (Whatman) were placed at either end of the sediment compartment to prevent, as possible, the entry of fine sediment particles in the electrolyte chambers. The sediment was subjected to electric field under a periodic (day on-night off mode) voltage, which was generated by a DC power supply (Statron multimeter, 0-300V, 0-1.2A) and current changes were monitored and recorded throughout the experiment. Electrolyte solutions were circulated into their reservoirs via a multichannel peristaltic pump (Watson-Marlow, 205s) at a flow rate of 5 mL min^{-1} and electroosmotic flow (EOF) was measured on a daily basis through a calibrated bottle, connected to the cathode chamber.

A 1:3 liquid/solid ratio was deemed to be appropriate for rendering the sediment into the necessary saturated form, prior to gradually inserting it into the cell using a steel rod (app. 4100g of saturated soil were compacted into the EK cell). Graphite electrodes, filter papers and electrolyte compartments were then placed appropriately, filling the latter ones with the selected solutions. Finally, wires and tubes were connected and power supply was turned on.

All experiments were conducted at room temperature, without pH control, under an initial steady voltage gradient of ca. 0.7 V cm^{-1} (20 V, maintained only for a few hours, with the exception of 4EK experiment where the initial voltage lasted for app. 3 days) which was then reduced (mainly due to foaming phenomena created by the surfactants and/or due to electric current having peaked) and kept to 0.5 V cm^{-1} (15 V), without any further intervention. The duration of the experiments ranged between 18-21 days. Further detailed parameters associated with each experiment are presented in Table 2.

At the end of each experiment, the sediment was carefully extracted from the cell and divided equally into five slices (S1-S5, from anode to cathode). Each slice was analysed, in turn, in its toxic metal and PAH content to determine distribution of contaminants and assess their removal or accumulation. Measurements below detection limit were taken as half the limit. Sediment pH, ORP and EC values were also measured in each slice. Removal efficiency and energy consumption were calculated according to the following formulas:

$$\text{Removal efficiency} = \frac{C_o - C_i}{C_o} * 100\% \qquad (1)$$

and

$$E_u(t) = \frac{1}{u_s}\int_0^t VI(t)dt \qquad (2)$$

where C_i and C_o are the concentrations of each selected toxic metal or individual PAH (in mg kg^{-1} and ng g^{-1}, respectively) initially and after EK treatment in each of the five sediment slices, V the applied voltage, I(t) the electric current as a function of time and $E_u(t)$ the energy consumption per unit volume (u_s).

In all the experiments acetic acid was introduced in the cathodic chamber to neutralize the hydroxyl ions generated by electrolytic reduction of water. The choice of acetic acid was mainly based on the following reasons: a) most metal acetates are highly soluble, b) it is environmentally benign and biodegradable, c) acetate ions will prevent the formation of other insoluble salts in cathode, thereby preventing the development of a low EC zone and consequently the dissipation of excessive energy in the soil near the cathode [46].

1EK unenhanced experiment served as a control and reference test to examine removal contaminant only by the use of de-ionized water used as anolyte. 2EK and 4EK runs were conducted by applying 5% wt. Nonidet P40 and 3% wt. Poloxamer 407 in the anodic chamber, respectively, while maintaining acetic acid as catholyte for the whole duration of the experiment. Finally, in 3EK run, EDTA was introduced in the anodic chamber to compare results with the other experiments and evaluate its effectiveness in the removal of inorganic (metals) contaminants.

3. Results and discussion

3.1 Profiles of electric current, EOF and energy consumption in all EK experiments

3.1.1. Variation of electric current

In all EK experiments electric current initial values ranged between 450 mA (in 4EK run) and 530 mA (in 1EK run) to 540 mA (peak value in all EK experiments), as long as the voltage gradient was kept at ca. 0.7 V cm^{-1}. Under the appearance of foaming phenomena and/or the current peak, voltage gradient was manually reduced to 0.5 V cm^{-1}, causing an electric current decrease in all experiments till a final value of 10 mA. This decrease in current can be mainly attributed, apart from the voltage reduction, to precipitation of non-conductive sediment particles or depletion of mobile ions [47, 48]. The initial high current could also be attributed to the inflow of acidic solutions that lowered pH, thereby leading to additional mineral dissolution and consequently a higher current [2]. However, with increased elapsed time, ions are depleted and electromigrate to the electrodes, hence the decrease in current values.

Furthermore, the introduction of surfactants into the anodic chamber is also responsible for causing a decrease in the current drop rate, compared to the unenhanced run, where electric current drops much faster, as it is obvious from Fig. 2a. This delay in the current drop, which is particularly obvious in the 3EK run, where 0.1M EDTA in NaOH was used, can be most possibly attributed to the generation of OH^- from the dissociation of NaOH that neutralized H^+, and together with the electromigration of Na^+ towards the cathode helped in sustaining the current.

3.1.2. Variation of EOF

EOF was generated at relatively low levels, ranging from 100 mL (in the 1EK run) to 310 mL (in the 3EK run) with the unenhanced run obtaining the highest amount (see Fig. 2b). This phenomenon can be explained since the fraction of the sediment used (just < 2 mm) coupled with its classification (sand) are considered to be inhibitory factors in EOF, since silt and clayey sediments with percentages higher than 30% in the 45-μm undersize fraction are commonly used in literature to obtain higher amounts of EOF [9, 14]**.** Nevertheless, the sediment was deliberately used unaltered (no surrogate sample) so as to maintain its genuineness and provide, at the same time, a closer to reality approach.

Regarding the chelate enhanced experiment, EOF was measured at higher levels a fact that is directly related to the electric current sustained more in this EK run [28] . As it can be seen from Fig. 2b, generation of EOF was continued till the 18th day of treatment till it, inevitably, stopped as current values dropped to almost 30 mA and even below. This is an observation that can be directly related and justified by the decrease in current values [28]. In addition, EOF is strongly and directly dependent on the ζ potential, which drops with time due to depletion of solutes and thereby limited number of migrated protons, hence the decrease observed with time.

3.1.3. Energy consumption

Energy expenditure varied from approximately 546 kWh m^{-3} (in 2EK run) to 764 kWh m^{-3} (in 3EK run). The increased ionic strength of the circulating solution in 3EK run (0.1M EDTA in 1M NaOH) together with the release of Na^{+} ions resulting from the dissolution of Na_2–EDTA promoted the electrolysis reactions at the cathode by displacing OH^{-} ions from the electrode, in turn sustaining the current and thus producing the increased energy expenditure in this experiment. The rest of the EK experiments demonstrated similar values (ca. 568 kWh m^{-3} and 587 kWh m^{-3}, for 1EK and 4EK runs, respectively).

3.2 Profiles of pH, redox potential (ORP) and electrical conductivity (EC) in the sediment after all EK experiments

3.2.1. Sediment pH

Fig. 3a presents the sediment's pH profile after EK treatment in all experiments. The main trend of the pH (increasing from almost neutral to strongly basic in sections near the cathode) was maintained in all EK experiments, with slight variations depending on initial pH of the anodic solutions used. 1EK, 2EK and 4EK runs exhibited similar pH values for the respective sediment slices ranging from app. 6 to slightly above 11. This behaviour is commonly found in EK experiments and can be explained by the electrolysis of water, generating H^{+} and OH^{-} at the anode and cathode, respectively. H^{+} migrates, in turn, towards cathode and OH^{-} towards anode, resulting in low pH values in the anodic chamber and high pH values in the cathodic chamber.

In the experiment wherein EDTA was used as anolyte, pH values appeared elevated (even in the sediment slices close to anode) ranging from app. 8 (in the sediment sections near the anode) to app. 11 (x/L = 0.3, see. Fig. 3a). This is due to the initial pH value of the EDTA solution, combined with its solvent (1 M NaOH). The pH in the sections near the cathode fluctuated near 11 in all EK experiments.

It should also be noted that in all experiments the pH in the anodic chamber, eventually resulted in highly acid values (2-4) either within the first day of treatment (1EK, 2EK and 4EK) or in the middle of the duration of the experiment (3EK), maintaining a decreasing trend, at all times. This rate of the pH reduction is again strongly dependent on the initial pH of the anolytes used as well as their solvents (1 M NaOH, for the case of EDTA). On the other hand the pH of the acetic acid used in the cathodic chamber, increased rather quickly (after app. 2 days) to highly basic values, close to 12 or 13.

3.2.2. Sediment redox potential (ORP)

Fig. 3b depicts sediment's redox potential profile in all EK experiments. As it can be seen, ORP demonstrated positive values in sediment sections near the anode and negative values, moving towards the cathode. It is worth mentioned to refer to the high initial ORP values in the sediment sections close to the anode (x/L = 0.1, 105-145 mV). This has direct relevance to the non-renewal of the electrolytes, a tactic that was implemented in other studies of the authors [12, 13]. In the present study only a recirculation of the electrolytes occurred in all EK runs, thereby creating the prevalence of oxidizing conditions in half of the sediment bed (up to the middle) which turned into reducing only in the last section close to the cathode (x/L=0.9). The only exception was the 3EK run where the presence of EDTA in 0.1M NaOH didn't allow the creation of similar behaviour.

Near the anode, the ORP values were found positive, but with a slightly alkaline pH, but quickly turned into negative and remained in the entire cell, indicating the presence of reducing conditions (in combination with the high pH prevailing, particularly after x/L = 0.3 and moving towards the cathode).

3.2.3. Sediment electrical conductivity (EC)

The profile of sediment's EC is presented in Fig. 3c. EC is directly affected by changes in the pH as well as by the quantity of dissolved ionic species and tends to significantly decrease in the sediment sections where major pH changes occur. As it is shown in Fig. 3c, EC demonstrated similar behaviour in all EK experiments exhibiting relatively high values (app. 8-17 mS cm^{-1}) in sections near the anode, he lowest values in the middle of the cell and finally increasing trends towards the sediment slices close to the cathode. Such behaviour, that has also been reported in other studies [14, 49] can be attributed to the strong presence of ionic particles near the anode and to the absorption and/or precipitation of metals due to high pH near the cathode.

3.3 Contaminant removal profiles in all EK experiments

3.3.1 Distribution and removal of toxic metals in all EK experiments

Fig. 4 presents the effect of different anodic solutions on the mass distribution of the examined toxic metals after all EK experiments (see Figs. a, b, c, d, e and f) and on the maximum removal percentages obtained (see Fig. 6g).

It is noteworthy that there is a removal obtained in all measured metals (even the most difficulty mobilized) which, given the basic conditions that prevailed especially in the sections close to cathode (S3-S5) (see Fig. 3a), has been most possibly caused by the dissolution of their precipitated salts and their respective flushing to the electrolyte compartments. Arsenic displayed the highest removal percentages (app. 75%-83%, in sediment sections close to the anode), however, its removal was successfully attained along the whole EK cell. Zinc exhibited, also, removal tendencies (app. 41% and 54% in 2EK and 4EK runs) while Pb, which is one of the most immobile elements, obtained a 41% (in 3EK run). In addition, the accumulation of Zn, Ni and Pb that was observed in half of the experiments in section S1, could most possibly be attributed to migration of dissolved organic matter complexes, formed in cathode, to anode. Finally, Cr and Ni were removed in high percentages, as well, obtaining 63% and 67%, respectively in 2EK experiment. Finally, the “pseudo” increase (accumulation) in the content of Cu that appears in all EK experiments in the sections adjacent to the anode (at x/L=0.1) could be explained by the corrosion of copper wires which, due to the structural design of the cell, were passing through the electrolyte chambers. However, “real” Cu was actually removed from sediment slices near the cathode, as high as 57%.

Part of the explanation of the high removal of all the elements observed in all EK experiments (but mostly in 1EK run) lies in the periodic application of voltage. Schwarzenbach et al. [50] report that there is a stable “restrictive layer” of solution surrounding each soil particle that hinders the mass transfer of contaminants through that layer and into the bulk solution [50]. Under the “night off” voltage mode, both

EOF and turbulence of the bulk solution decreases, however, during this “down time” period, additional ions become solubilized and/or the diffuse double layer becomes less polarized [27]. When the voltage is switched on again, an EOF/electromigration “pulse” is created, increasing the solubilising action and/or movement of contaminants (both organic and inorganic) from the inside of the “restrictive layer” to the bulk solution. It is most likely that this phenomenon may be one of the main factors for the removal of the majority of the examined elements.

Of course, in the enhanced (with the surfactants) EK runs, the high solubilisation capacity of Nonidet P40 and Poloxamer 407 could be the primary reason for the removal of all contaminants. Since used in concentrations high above their CMC (critical micelle concentration) they formed numerous micelles which enhanced their solubility, despite the relatively low generation of EOF [12, 13]. On the other hand, EDTA assisted the removal of Cu and Pb

3.3.2 Distribution and removal of PAHs in all EK experiments

Figs 5a, 5b, 5c and 5d depict the distribution of PAHs along the treated sediment in all EK experiments, whereas Fig 6a presents the maximum removal percentages attained for each individual PAH. It is worth mentioned that in the present work PAHs removal was also studied in the unenhanced run to compare any results and conclusions with the enhanced runs. Thus, respective bar charts were prepared to depict the distribution of the remaining quantity of PAHs in each sediment slice after EK treatment (see Fig. 6b), as well as the total amount of PAHs removed from the sediment (see Fig. 6c).

Fig. 5a indicates a significant removal of all PAHs from sections near both ends of the EK cell. This removal has most possibly been derived from the washing of these sediment slices which are in direct contact with the electrolyte solutions (via the perforated graphite electrode and the filter papers). An additional observation which sustains the aforementioned explanation is the total removal of all PAHs (rather than a selective one from individual substances) a phenomenon which can only occur after dissolution and transport of these pollutants from the solid matrix to the liquid phase. Only acenaphthylene, acenaphthene and anthracene were not removed; but then again, these PAHs did not show any removal trend in all EK runs, whatsoever.

Another conclusion which follows this, as well as the rest of the EK experiments, is a transporting tendency of the majority of the PAHs in the second close to the anode (for 1EK run) sediment section. Essentially, these are PAHs which, being negatively charged, are moving towards the anode but failed to reach S1 section (the closest to the anode) so as to be flushed in the anodic chamber by the help of each individual electrolyte solution. It is quite impressive how the "black strip-ring", depicted in Fig. 7, moves as the experiment progresses and stops at S2. This “black ring” is mostly consisted of PAHs, TPHs, black carbon, as well as other non-measured and unidentified (in the present study) organic substances and oils which move towards the anode, mainly because of their negative charge.

The main reasons for the removal of PAHs taking place in this unenhanced run have been more analytically explained in Section 3.3.1 and can be mostly attributed to the periodic use of voltage, their charge, their weak bound to the soil matrix and finally to the diffusion and mass transfer of pollutants that occur even during the pause in the application of the voltage gradient (night off) [29, 50].

The results presented in Fig. 6c, where the total amount of PAHs removed from the cell and from each slice in all EK runs are shown, demonstrates the need of solubilising agents, even if the unenhanced run gave satisfying removal percentages, mostly due to the periodic application of voltage. As it can be seen, 2EK and 4EK runs demonstrated higher amounts of total PAHs removed from the sediment compared to 1EK. On the other hand in 3EK experiment, EDTA created various negatively charged metallic complexes and caused, also, precipitation phenomena both of which hindered the removal process of PAHs. This is quite obvious from Fig. 6c.

4. Conclusions

The main objective of this study was the performance evaluation of electroremediation in real contaminated sediments with toxic metals and PAHs, using a big laboratory EK cell, periodic voltage and newly tested surfactants. The main conclusions drawn from the present research are listed below:

1) The non-ionic surfactants (commercially known as Nonidet P40 and Poloxamer 407) displayed sufficient removal efficacy obtaining a 6498 μg and 5688 μg removal of SUM PAHs, respectively, from the EK cell. Individual PAHs were removed up to 69% (fluorene) in the aforementioned enhanced EK runs.

2) All EK runs exhibited a removal tendency for all selected elements, with percentages ranging from ca. 41% (for As) to almost 83% (for As). The periodic voltage and the solubilizing agents used are the main reasons for that.

3) The present study inferred that Nonidet P40 and Poloxamer 407 in conjunction with the application of periodic voltage gradient are capable of achieving sufficient removal of both toxic metals as well as PAHs from real contaminated sediments in a much higher degree than other already used non-ionic surfactants.

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List of Figures

Fig. 1 Schematic of the electrokinetic (EK) set-up.

Fig. 2 Profiles of (a) electric current (I) and (b) electroosmotic flow (EOF) with elapsed time.

Fig. 3 Profiles of (a) pH, (b) redox potential (ORP) and (c) electrical conductivity (EC) in the sediment after electrokinetic treatment.

Fig. 4 Effect of different anodic solutions on the mass distribution of the examined toxic metals after all EK experiments (a, b, c, d, e, f) and on the maximum removal percentages obtained (g).

Fig. 5 Distribution of individual PAHs in sediment after EK treatment with anodic solutions (a) deionized water (DI) (b) Nonidet P40 (c) EDTA and (d) Poloxamer 407. Acetic acid 0.1M was used in the cathodic compartment of the cell in all EK runs.

Fig. 6 Effect of different anodic solutions on (a) PAHs maximum removal efficiency (b) distribution of PAHs in each slice after EK and (c) amount of PAHs removed per sediment slice and in total. Acetic acid 0.1M was used as catholyte in all EK runs.

*Acenaphthylene, Acenaphthene and Anthracene did not exhibit any removal in any of the EK experiments, mainly due to their low initial concentrations. However, it was deemed necessary to depict them in the diagram for comparison and consistency purposes.

Fig. 7 Depiction of the moving “black ring”, consisted of PAHs, TPHs, carbon black and other unidentified organic substances, during the (a) 4th (b) 8th (c) 14th and (d) 20th day of unenhanced treatment.

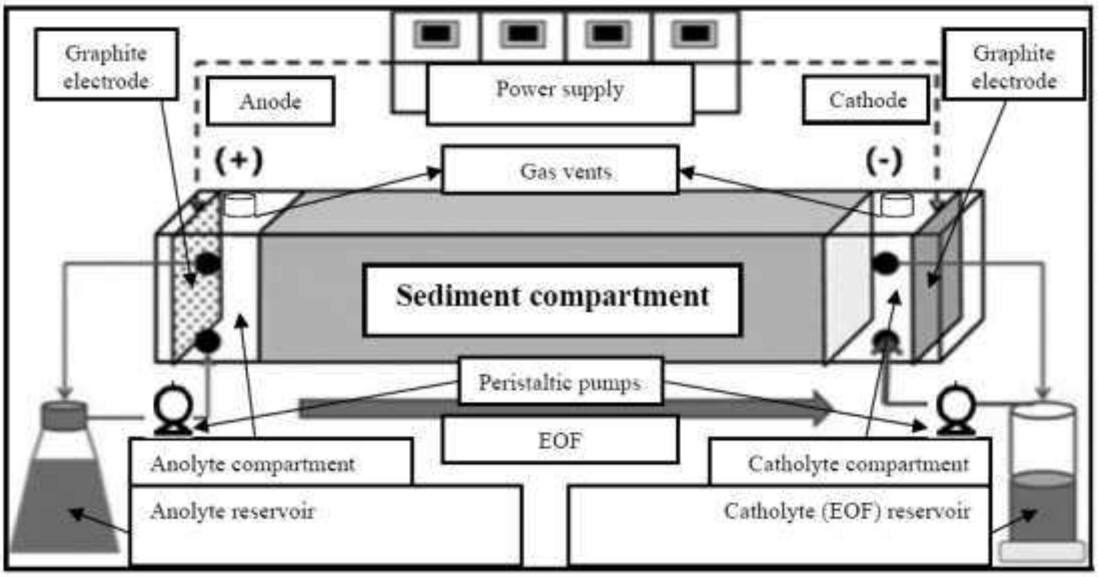
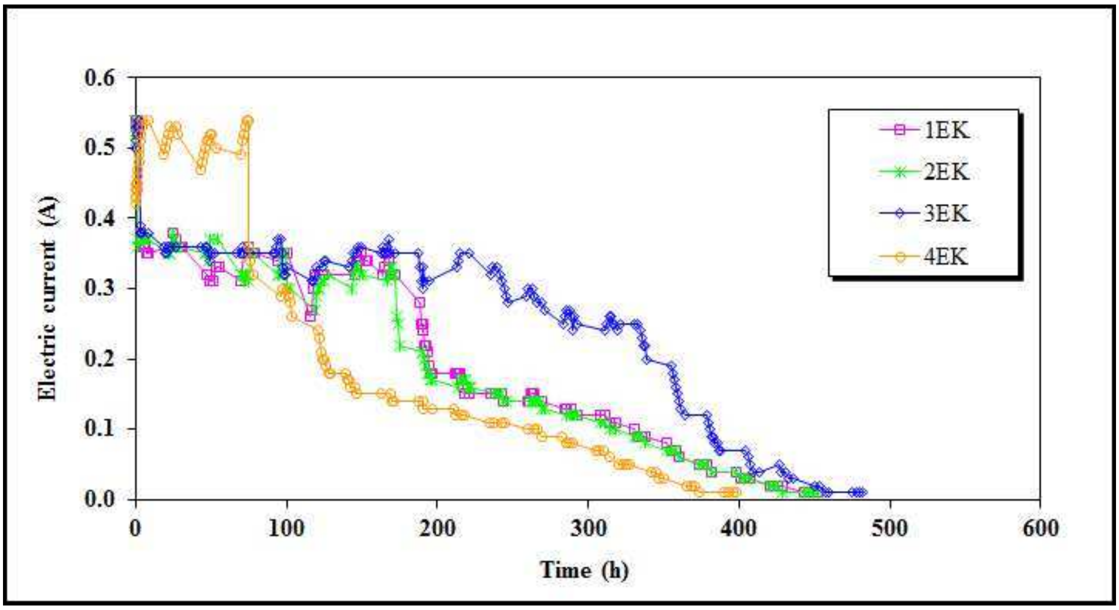
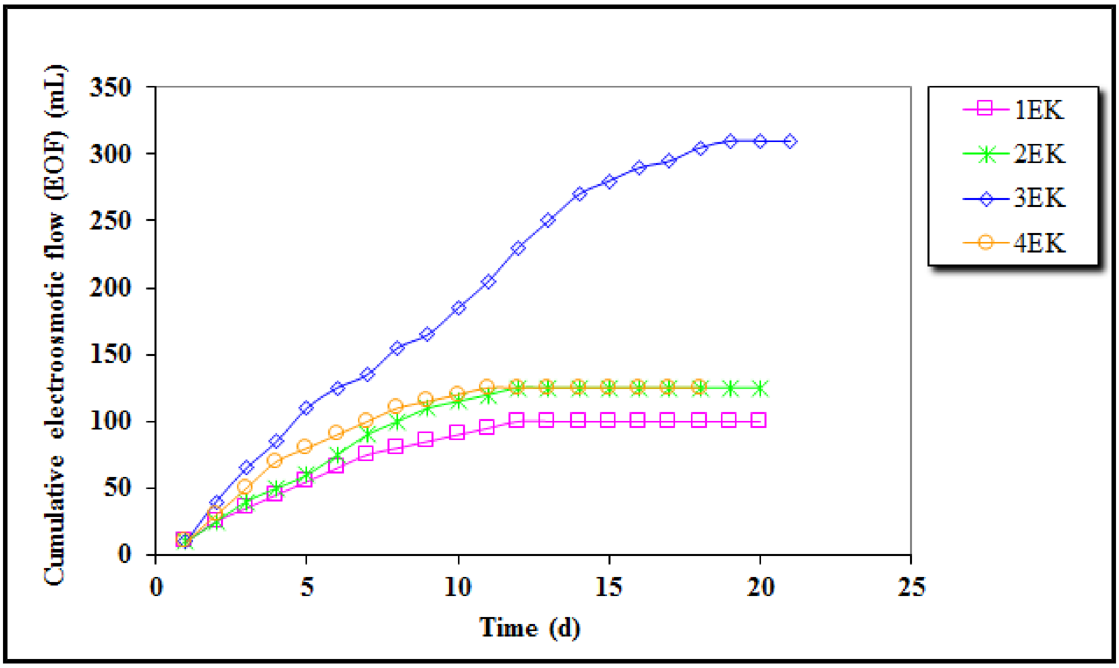

Graphite electrode
Power supply
Graphite electrode
Anode
Cathode
(+)
(-)
Gas vents
Sediment compartment
Peristaltic pumps
EOF
Anolyte compartment
Catholyte compartment
Anolyte reservoir
Catholyte (EOF) reservoir

Fig. 1



0.6
0.5
0.4
0.3
0.2
0.1
0.0
Electric current (A)
0
100
200
300
400
500
600
Time (h)
1EK
2EK
3EK
4EK

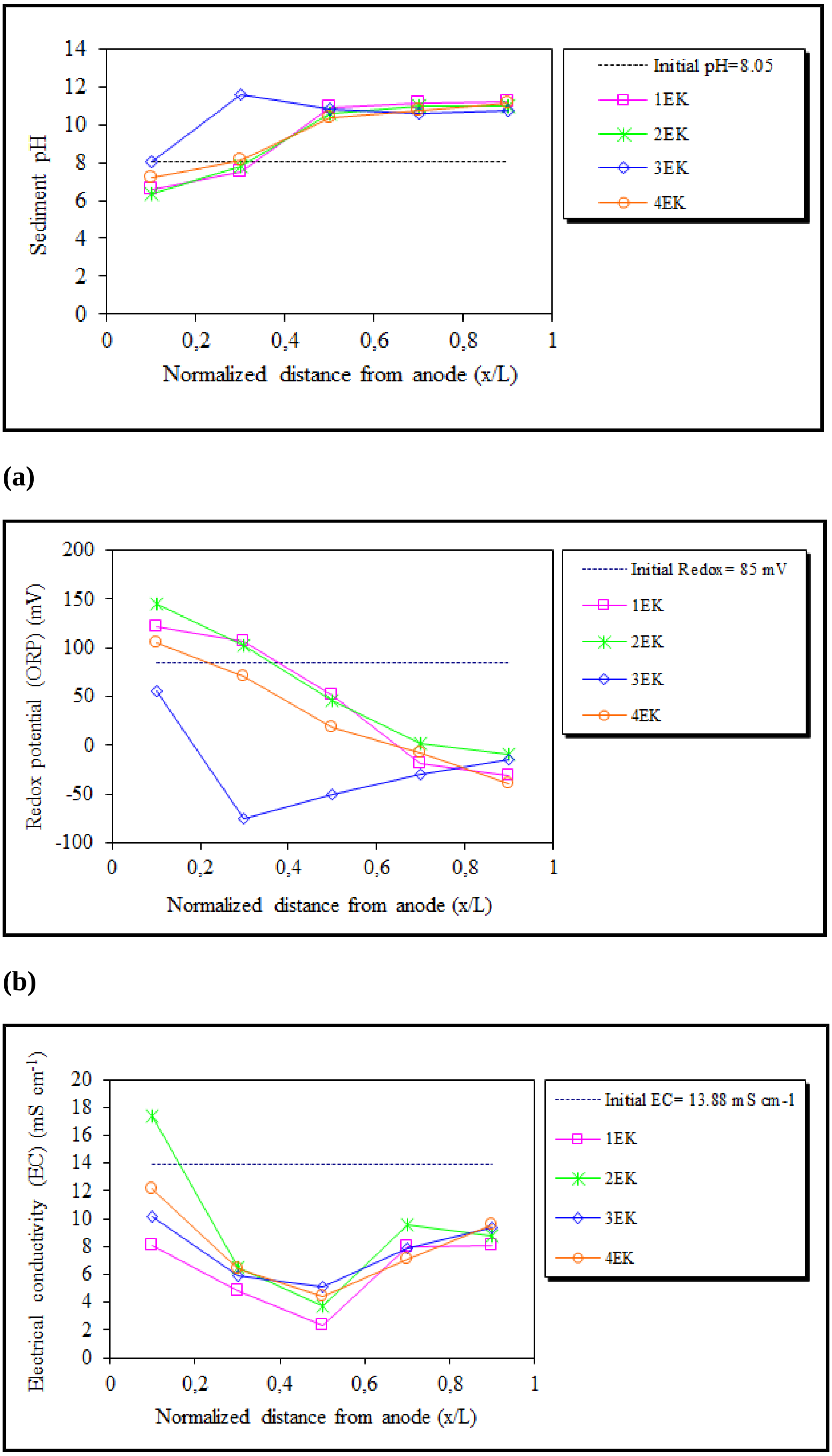
(a)



350
300
250
200
150
100
50
0
Cumulative electroosmotic flow (EOF) (mL)
0
5
10
15
20
25
Time (d)
1EK
2EK
3EK
4EK

(b)

Fig. 2


Sediment pH
14
12
10
8
6
4
2
0
0
0,2
0,4
0,6
0,8
1
Normalized distance from anode (x/L)
Initial pH=8.05
1EK
2EK
3EK
4EK
Redox potential (ORP) (mV)
200
150
100
50
0
-50
-100
0
0,2
0,4
0,6
0,8
1
Normalized distance from anode (x/L)
Initial Redox= 85 mV
1EK
2EK
3EK
4EK
Electrical conductivity (EC) (mS cm-1)
20
18
16
14
12
10
8
6
4
2
0
0
0,2
0,4
0,6
0,8
1
Normalized distance from anode (x/L)
Initial EC= 13.88 mS cm-1
1EK
2EK
3EK
4EK

(a)

(b)

(c)

Fig. 3

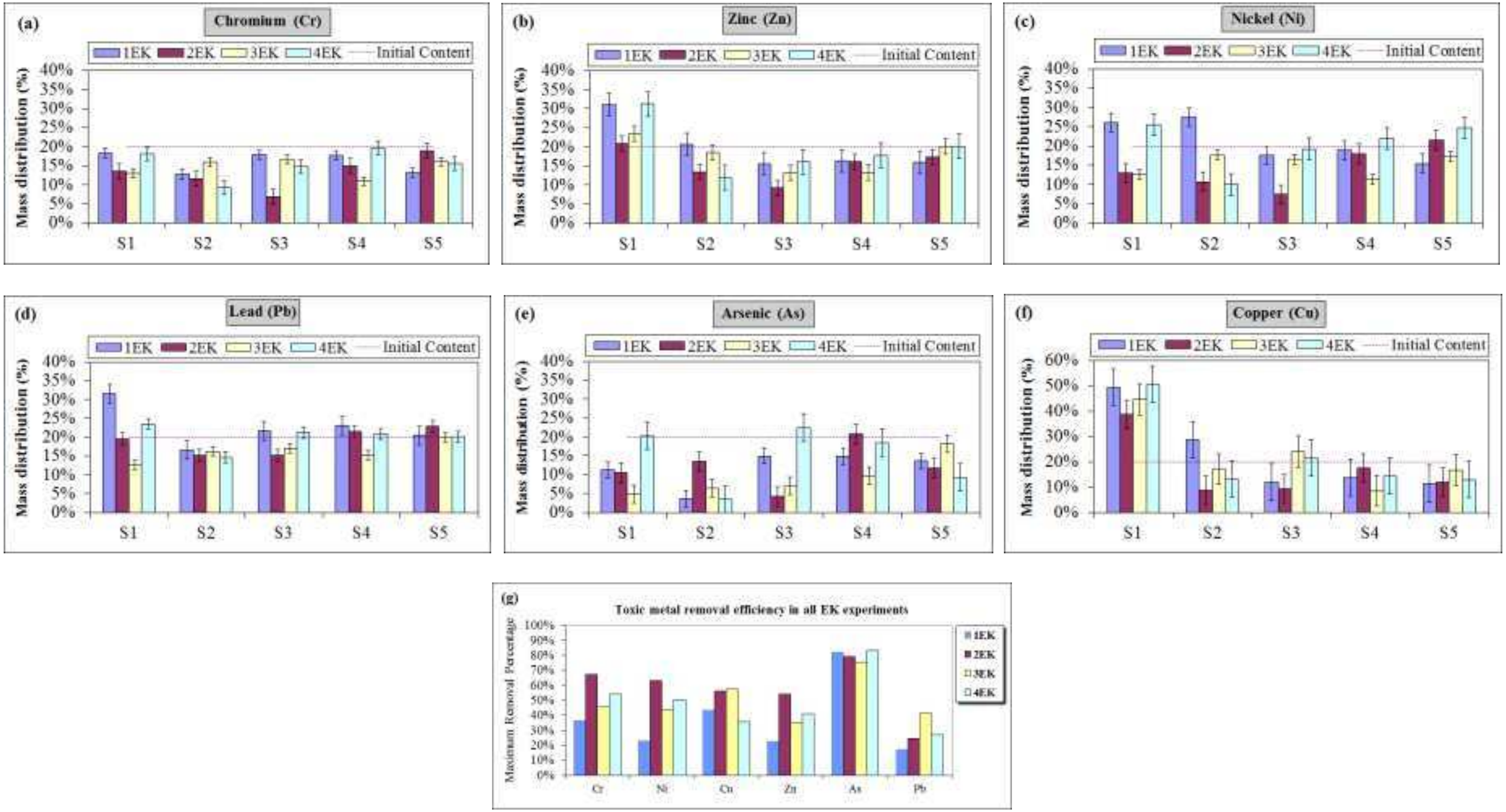

(a)
Chromium (Cr)
(b)
Zinc (Zn)
(c)
Nickel (Ni)
(d)
Lead (Pb)
(e)
Arsenic (As)
(f)
Copper (Cu)
1EK
2EK
3EK
4EK
Initial Content
Mass distribution (%)
0%
5%
10%
15%
20%
25%
30%
35%
40%
50%
60%
S1
S2
S3
S4
S5
(g)
Toxic metal removal efficiency in all EK experiments
Maximum Removal Percentage
0%
10%
20%
30%
40%
50%
60%
70%
80%
90%
100%
Cr
Ni
Cu
Zn
As
Pb

Fig. 4

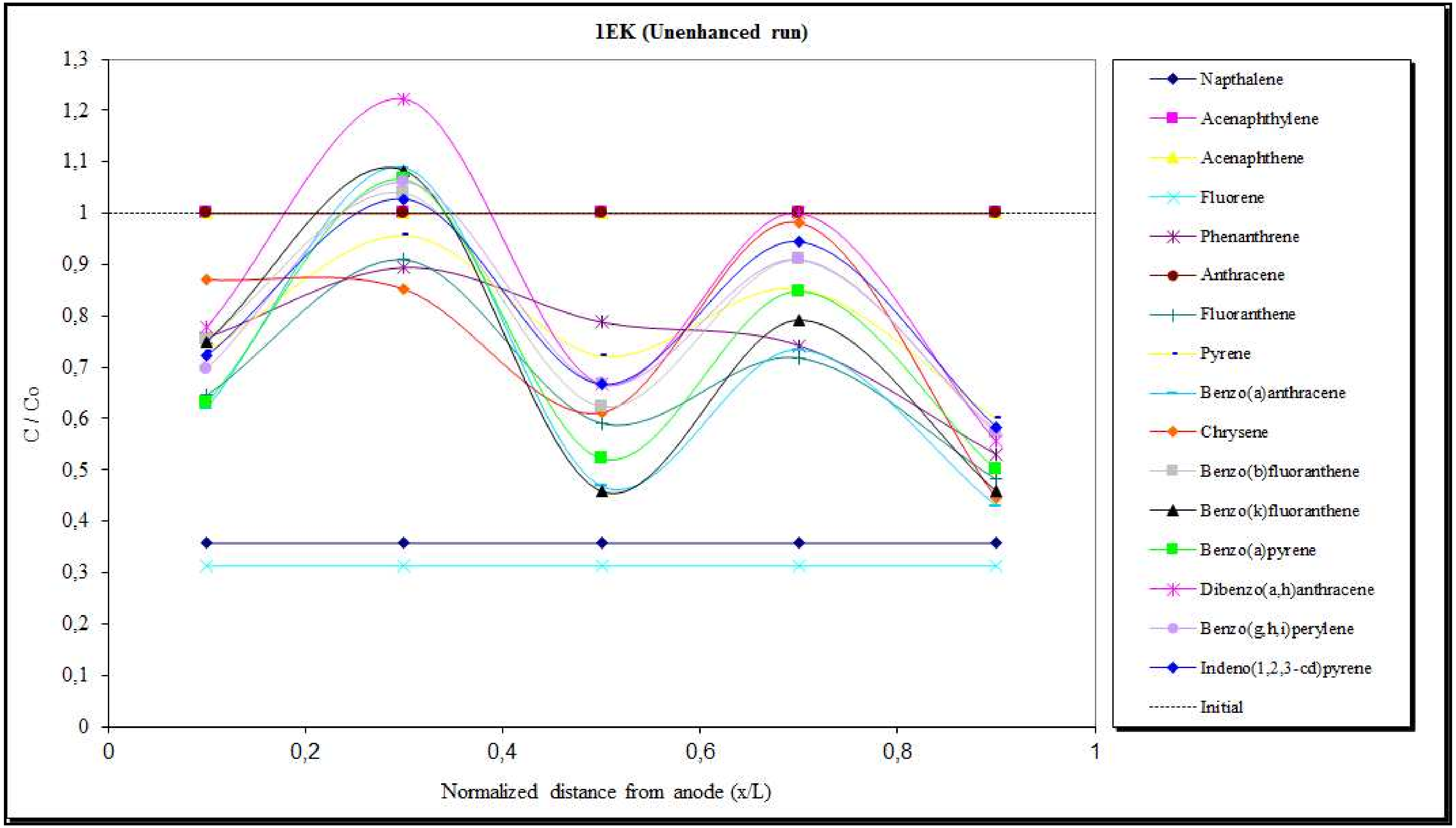

1EK (Unenhanced run)
C / Co
1,3
1,2
1,1
1
0,9
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0
0
0,2
0,4
0,6
0,8
1
Normalized distance from anode (x/L)
Napthalene
Acenaphthylene
Acenaphthene
Fluorene
Phenanthrene
Anthracene
Fluoranthene
Pyrene
Benzo(a)anthracene
Chrysene
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(a)pyrene
Dibenzo(a,h)anthracene
Benzo(g,h,i)perylene
Indeno(1,2,3-cd)pyrene
Initial

Fig. 5a

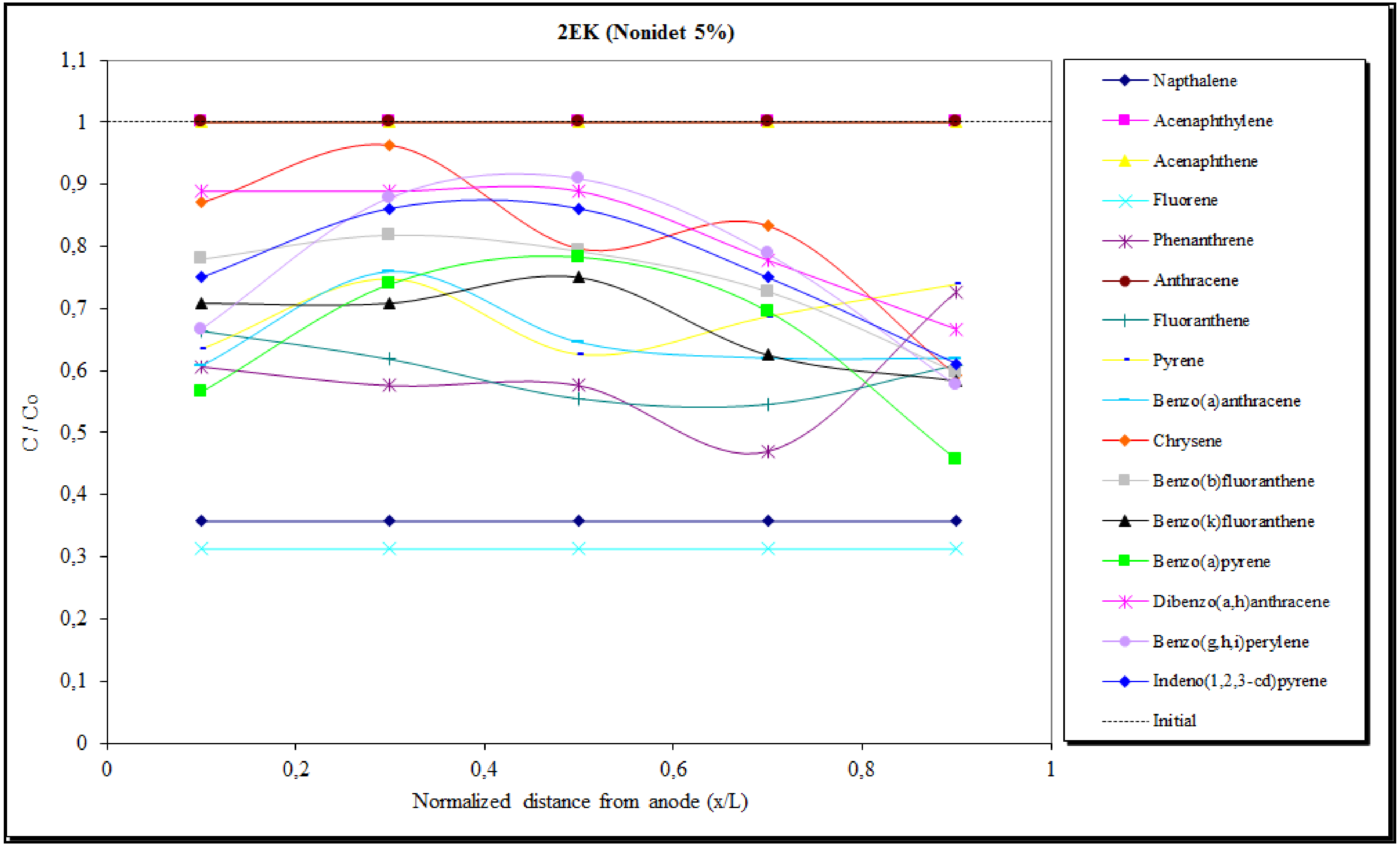

2EK (Nonidet 5%)
C / Co
1,1
1
0,9
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0
0
0,2
0,4
0,6
0,8
1
Normalized distance from anode (x/L)
Napthalene
Acenaphthylene
Acenaphthene
Fluorene
Phenanthrene
Anthracene
Fluoranthene
Pyrene
Benzo(a)anthracene
Chrysene
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(a)pyrene
Dibenzo(a,h)anthracene
Benzo(g,h,i)perylene
Indeno(1,2,3-cd)pyrene
Initial

Fig. 5b

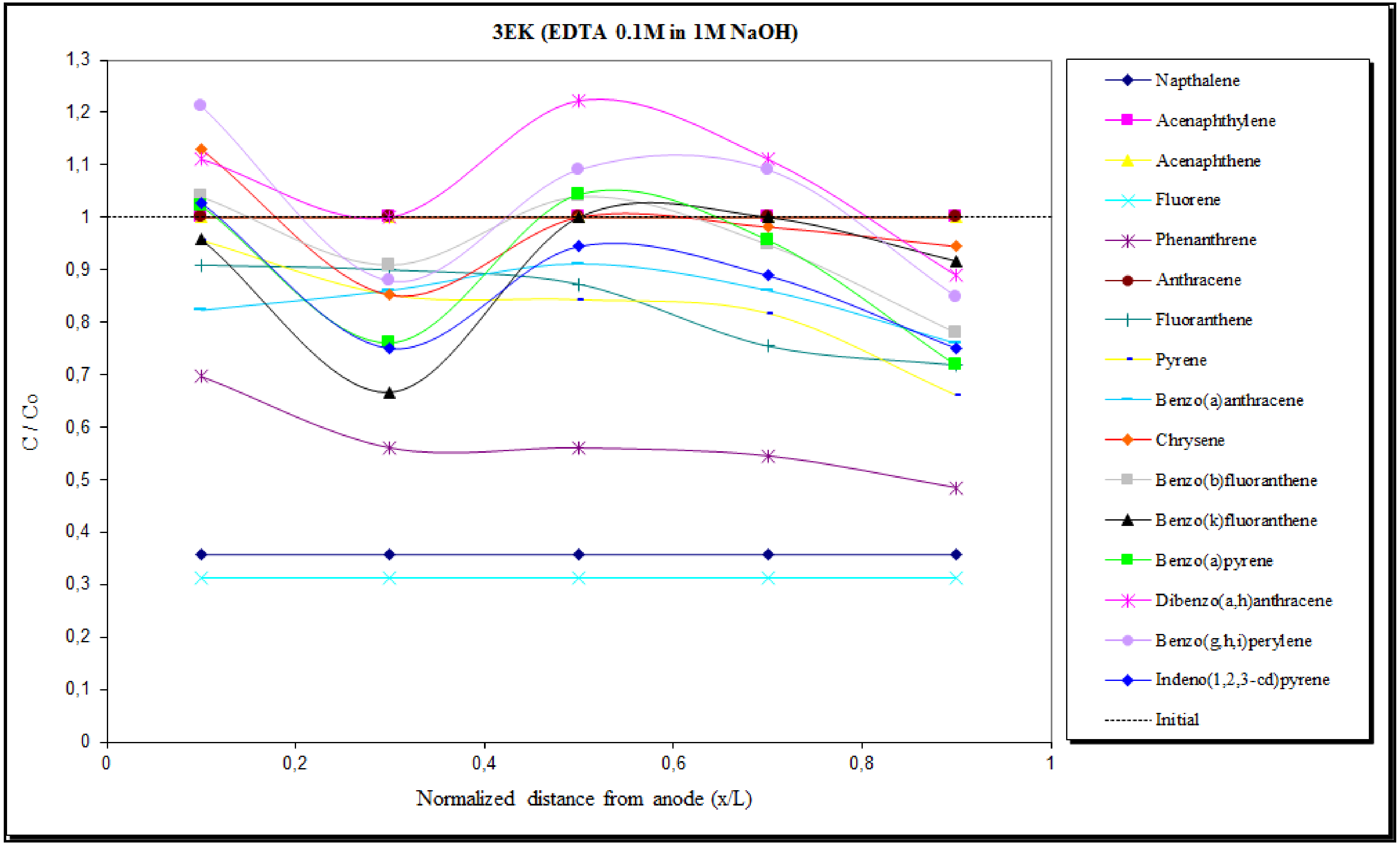

3EK (EDTA 0.1M in 1M NaOH)
C / Co
1,3
1,2
1,1
1
0,9
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0
0
0,2
0,4
0,6
0,8
1
Normalized distance from anode (x/L)
Napthalene
Acenaphthylene
Acenaphthene
Fluorene
Phenanthrene
Anthracene
Fluoranthene
Pyrene
Benzo(a)anthracene
Chrysene
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(a)pyrene
Dibenzo(a,h)anthracene
Benzo(g,h,i)perylene
Indeno(1,2,3-cd)pyrene
Initial

Fig. 5c

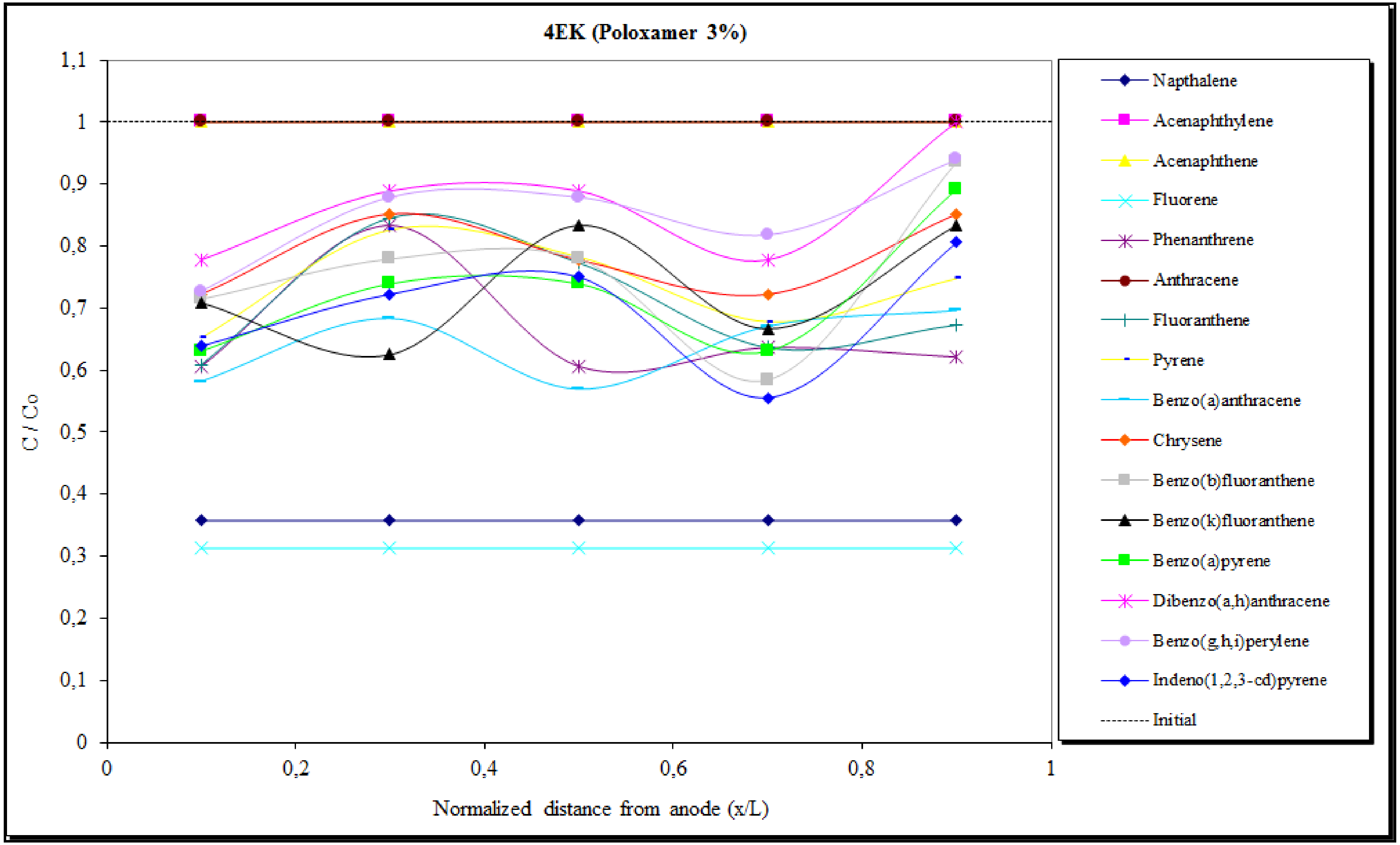

4EK (Poloxamer 3%)
C / Co
1,1
1
0,9
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0
0
0,2
0,4
0,6
0,8
1
Normalized distance from anode (x/L)
Napthalene
Acenaphthylene
Acenaphthene
Fluorene
Phenanthrene
Anthracene
Fluoranthene
Pyrene
Benzo(a)anthracene
Chrysene
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(a)pyrene
Dibenzo(a,h)anthracene
Benzo(g,h,i)perylene
Indeno(1,2,3-cd)pyrene
Initial

Fig. 5d

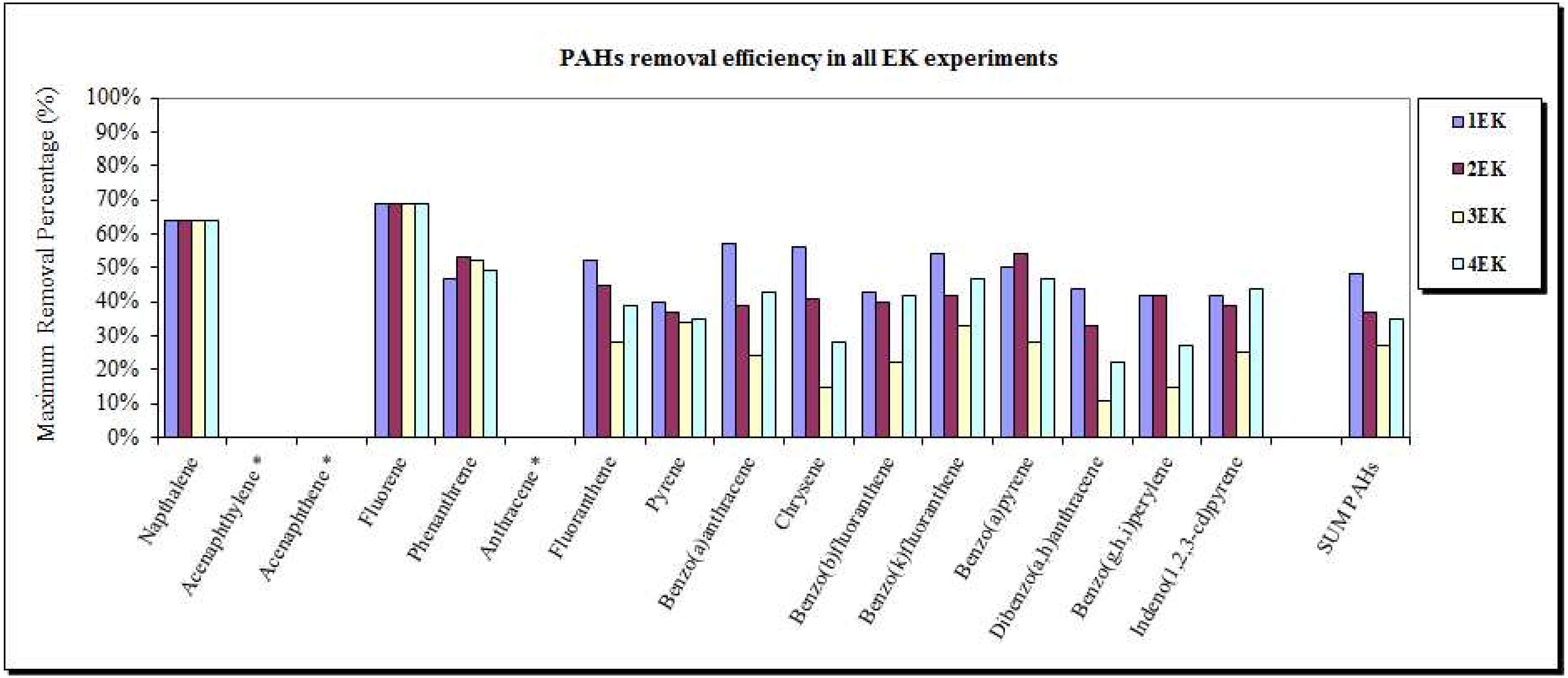

PAHs removal efficiency in all EK experiments
Maximum Removal Percentage (%)
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
Napthalene
Acenaphthylene *
Acenaphthene *
Fluorene
Phenanthrene
Anthracene *
Fluoranthene
Pyrene
Benzo(a)anthracene
Chrysene
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(a)pyrene
Dibenzo(a,h)anthracene
Benzo(g,h,i)perylene
Indeno(1,2,3-cd)pyrene
SUM PAHs
1EK
2EK
3EK
4EK

Fig. 6a

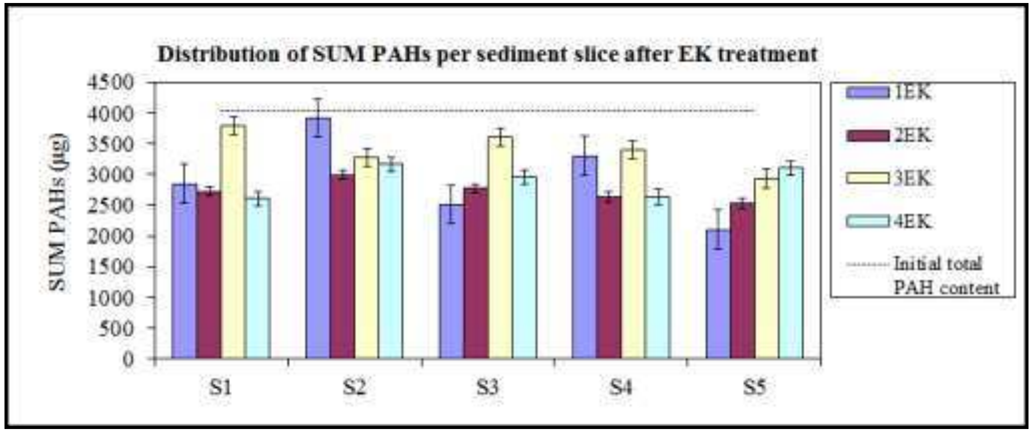

Distribution of SUM PAHs per sediment slice after EK treatment
SUM PAHs (µg)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
S1
S2
S3
S4
S5
1EK
2EK
3EK
4EK
Initial total PAH content

Fig. 6b

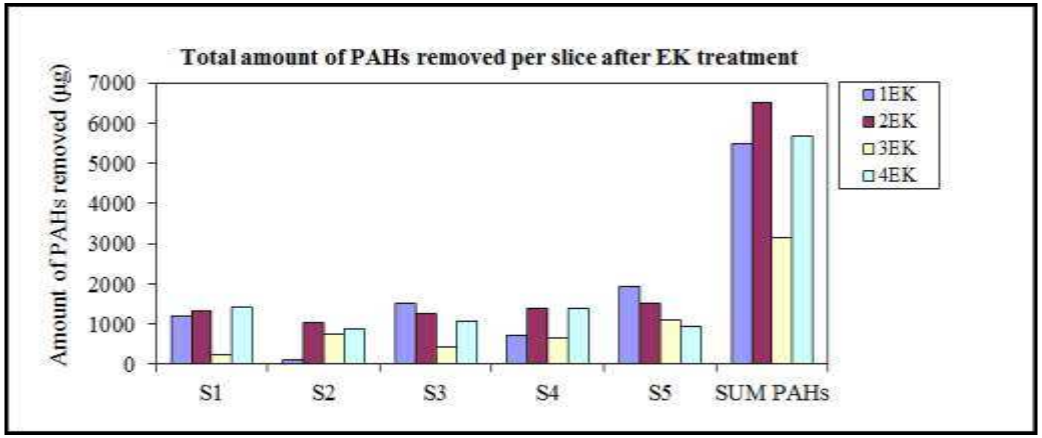
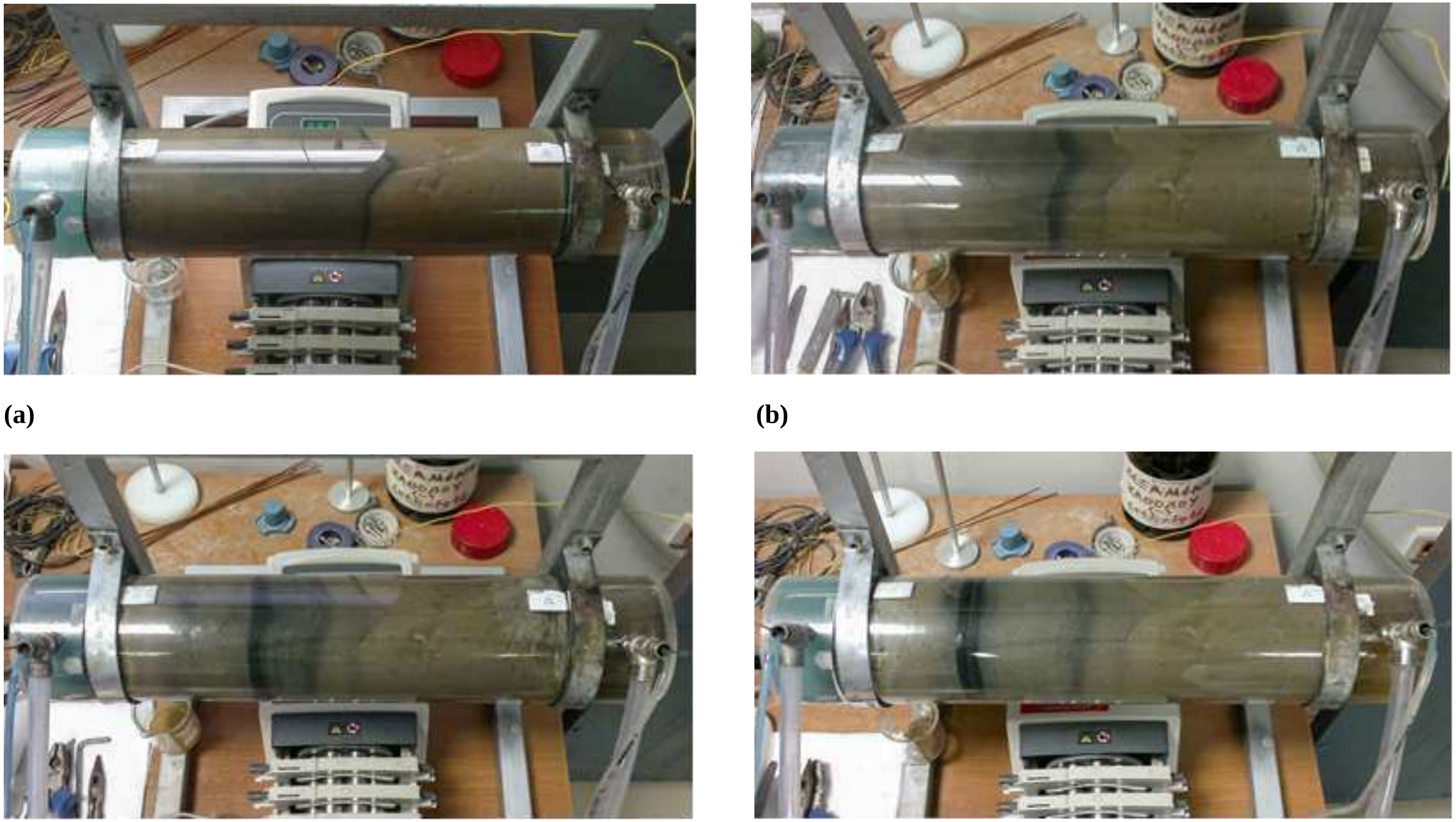

Total amount of PAHs removed per slice after EK treatment
Amount of PAHs removed (µg)
7000
6000
5000
4000
3000
2000
1000
0
S1
S2
S3
S4
S5
SUM PAHs
1EK
2EK
3EK
4EK

Fig. 6c



(a) (b)

(c) (d)

Fig. 7

List of Tables

Table 1

Physicochemical properties of the sediment

“<” below detection limit

* Measurements below detection limit were taken as half the limit

Table 2

Detailed parameters of the EK experiments

[a] Initial voltage: 20 V (0.7 V cm^{-1}), reduced to 15 V (0.5 V cm^{-1}) mainly due to foaming phenomena and/or electric current peak.

Table 1

Physical Properties	**Value**
Moisture (%)	24.5
pH	8.05
Redox (mV)	85
Electrical conductivity (mS cm^{-1})	13.88
Organic matter (%)	5.86
Specific gravity	2.01
Cation exchange capacity (meq 100gr^{-1})	1.76
Main minerals	**Percentages (%)**
Quartz	30
Calcite	48
Dolomite	6
Mica	5
Chlorite	4
Feldspars	4
Hematite	2
Kaolinite	1
Particle size distribution	**Percentages (%)**
Sand	81
Silt	9
Clay	0
USCS classification	Sand (S)
Initial toxic metal content	**Concentration (mg kg^{-1} dw, average of three replicates)**
Cr	31.79
Ni	18.17
Cu	59.11
Zn	218.27
As	4.29
Pb	80.42
Initial PAH content	**Concentration (ng g^{-1} dw, average of three replicates)**
Naphthalene	70
Acenaphthylene	<50*
Acenaphthene	<50*
Fluorene	80
Phenanthrene	660
Anthracene	<50*
Fluoranthene	1100
Pyrene	1150
Benzo(a)anthracene	790
Chrysene	540
Benzo(b)fluoranthene	770
Benzo(k)fluoranthene	240
Benzo(a)pyrene	460
Dibenzo(a,h)anthracene	90
Benzo(ghi)perylene	330
Indeno(1,2,3-cd)pyrene	360
Sum PAHs	6700

Table 2

Test code name	Anodic solution	Cathodic solution	pH control	Voltage gradient [a] (V cm^{-1})	Voltage (V)	Duration (d)
1EK	DI water	Acetic acid 0.1M	No	0.7-0.5	20-15	20
2EK	5% wt. Nonidet P40	Acetic acid 0.1M	No	0.7-0.5	20-15	20
3EK	0.1M EDTA in 1M NaOH	Acetic acid 0.1M	No	0.7-0.5	20-15	21
4EK	3% wt. Poloxamer 407	Acetic acid 0.1M	No	0.7-0.5	20-15	18

Highlights

Article title: Performance of electroremediation in real contaminated sediments using a big cell, periodic voltage and innovative surfactants.

- Innovative surfactants, periodic voltage and a big electrokinetic (EK) cell were used.
- The EK efficiency in removing PAHs and toxic metals from sediments was assessed.
- Maximum PAHs removal efficacy was obtained by the use of Nonidet P40.
- Arsenic, nickel and chromium obtained the highest removal percentages.
- Periodic application of voltage favoured the efficiency of the overall EK process.