J Appl Electrochem (2010) 40:1269–1279
DOI 10.1007/s10800-010-0102-1

ORIGINAL PAPER

Integrated electrokinetic-soil flushing to remove mixed organic and metal contaminants

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Received: 22 July 2009 / Accepted: 29 January 2010 / Published online: 18 February 2010
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Abstract The integrated use of hydraulic flushing and electrokinetic treatment was investigated for the remediation of silty sand contaminated by both PAHs and heavy metals. The soil was collected from a polluted former manufactured gas plant (MGP). Four bench-scale experiments were conducted to analyze the ability of the combined hydraulic flushing and the electrokinetic treatment for the simultaneous removal of PAHs and heavy metals. Sequential flushing with ethylenediaminetetraacetic acid (EDTA) or Igepal CA-720 were tested with or without the simultaneous application of a low intensity direct electric field (1 VDC cm^{-1}). The best results were obtained with 0.2 M EDTA flushing in two stages (without and with voltage gradient, 1 VDC cm^{-1}), followed by 5% Igepal flushing in two stages (without and with 1 VDC cm^{-1}). Heavy metals were removed mainly during the EDTA flushing, with removal efficiencies of about 60% for Zn, 80% for Pb, and 30% for Cu. During Igepal flushing, no heavy metals were removed, but PAHs were removed, including 40% phenanthrene, 30% pyrene, and 20% benzo[a]pyrene. Overall, this study showed that a carefully designed sequential hydraulic flushing scheme with selected chelant and surfactant is needed for the removal of both heavy metals and PAHs from MGP silty sands. Combining electrokinetics with hydraulic flushing may not necessarily improve contaminant removal from such soils.

Keywords Remediation · Pollution · Soil · Heavy metals · PAHs · Flushing · Electrokinetics

1 Introduction

In 1940 and 1950s, many manufactured gas plants (MGPs) in the United States were closed [1]. An estimate by Larsen [2] indicated that there may be more than 5,000 former MGP sites across the US that are posing significant environmental threat and require immediate remediation action. A major factor complicating the cleanup of many of these sites is the co-occurrence of organics, such as polycyclic aromatic hydrocarbons (PAHs), and heavy metals, such as lead, zinc and nickel [3–5]. Treatment processes usually employed for contaminated soils include chemical oxidation, biodegradation, thermal desorption, and incineration [6–10], but these processes do not always yield satisfactory results, especially in the case of soils with low hydraulic permeability or those soils contaminated by mixed organic–inorganic wastes. Therefore, the development of processes and technologies for the simultaneous remediation of soils contaminated by heavy metals and organics has emerged as an important area of current research in soil remediation research field.

Electrokinetic remediation has been used for the remediation of many soils contaminated with heavy metals for the last 20 years with high efficiency [11–13]. The electrokinetic treatment has been recognized as an efficient in situ process for the remediation of contaminated soils containing organic contaminants [14–17]. Recently, several attempts were carried out to test the ability of

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electrokinetics in the remediation of soils with mixed contamination [18–21]. The implementation of electrokinetic remediation involves inserting series of anode and cathode electrodes in the soil and applying an electric potential between them. The electric potential induces the mobilization and migration of contaminants towards electrode wells by two primary transport processes: *electromigration* and *electroosmosis.* Electromigration occurs in all soils, whereas electroosmosis is only significant in clay soils (low permeability soils). On the contrary, electroosmosis is not significant in sandy soils, like the one used in this study, but contaminant removal can be enhanced by water/solvent flushing.

Most of the recent studies on electrokinetic remediation have been conducted on the artificially spiked soils targeting either removal of organic species or heavy metals. It is difficult to assess the applicability of the electrokinetic method for the remediation of actual field sites based on spiked kaolinite bench scale results. Also, it is difficult to apply electrokinetic remediation to the removal of hydrophobic and strongly adsorbed contaminants from the aged soils such as those found at MGP sites. It is also well known that solubilizing agents, such as surfactants, chelants, and cyclodextrins, enhance the dissolution of a variety of hydrophobic organic chemicals as well as heavy metals in contaminated soils. Several surfactants have been examined for possible use in the electrokinetic remediation [22–24]. However, physical and chemical phenomena of using solubilizing agents in electrokinetic remediation remains complex and only few phenomenological studies are reported in literature.

Research has been on-going at the University of Illinois at Chicago (UIC) to understand the mechanism of solubilizing or extracting agents such as surfactants, chelants, and cyclodextrins to enhance the dissolution of a variety of hydrophobic organic chemicals as well as heavy metals from the contaminated soils during the application of electrokinetic remediation. Also, a major factor complicating the remediation of many MGP sites is the co-occurrence of organics and heavy metals; therefore sequential use of these extractants were examined to enhance the solubilization of these contaminants from the contaminated soils [25].

The aim of this study was to develop an effective electrokinetic remediation system for the remediation of heavy metals as well as PAHs from the MGP site soil. In particular, the efforts have been directed to determine and compare the use of electrokinetics on the sequential flushing of a chelant (EDTA) and a surfactant (Igepal CA-720) for the remediation of soil contaminated by mixed wastes. A series of laboratory experiments were conducted using an actual contaminated MGP site soil (near Chicago, IL, USA) and these test results were used to systematically evaluate the effects of flushing solution and the application of electric potential.

2 Materials and methods

2.1 Soil characterization

Contaminated soil used in this study was obtained from a highly contaminated site containing toxic metals as well as PAHs from a former MGP near Chicago (IL, USA). The soil sample was analyzed for different physical properties using the corresponding ASTM procedures (Table 1) and, heavy metal and PHA content using the USEPA SW-846 methods (Table 2). The soil was sandy material (84% sand-fraction) and has an average hydraulic conductivity of 1.6×10^{-4} cm s^{-1}. The acid buffering capacity of the soil was determined by titration with nitric acid 2 M using deionized water as control. The acid buffering capacity of the aqueous soil slurry with a solid concentration of 8.5% is found to be 3.7 eq kg^{-1} (dry soil) at the inflection point of the titration curve (pH 6.2). This indicates that the soil possesses high acid buffering capacity.

2.2 Test set-up

Figure 1 shows the schematic of the test setup [26] used for this study to perform hydraulic flushing or combined hydraulic flushing-electrokinetic experiments. The test setup consisted of an electrokinetic cell, two electrode compartments, two electrode reservoirs, a power source, and a multimeter. The electrokinetic cell was made of Plexiglas® with 6.2 cm inside diameter and 19.1 cm length. Each electrode compartment consists of a valve to control the flow into the cell, filter paper, a porous stone, and a perforated graphite electrode. The filter paper was placed between the soil and the porous stone and both were

Table 1 Characterization of the contaminated soil from the MGP site

Property	Test method	Value
Water content	ASTM D 2216	14.0%
Specific gravity	ASTM D 854-92	2.63
Grain size distribution	ASTM D 422-63	Gravel: 0%
		Sand: 84%
		Fines: 16%
Atterberg limits	ASTM D 4318	Non-plastic
pH	ASTM D 2974	7.05
Redox potential	ASTM D 2974	185.3 mV
Electrical conductivity	ASTM D 2974	3.08 mS cm^{-1}
Organic content	ASTM D 2974	11.10%
USCS classification	ASTM D 2488	Organic silty sand, SM

Table 2 Contaminant concentrations in the soil from the MGP site

Total metal content[a]		Polynuclear aromatic hydrocarbons[b]	
Chemical	Concentration (mg kg^{-1})	Chemical	Concentration (mg kg^{-1})
Aluminum	1640	2-Methylnaphthalene	2.93
Arsenic	3.81	Acenaphthene	37.7–44.8
Barium	197	Acenaphthylene	0.72–2.63
Beryllium	0.3	Anthracene	22.6–32.8
Cadmium	8.39	Benz(a)anthracene	8.65–11.8
Calcium	47000	Benzo(a)pyrene	0.419–1.45
Chromium	19.5	Benzo(b)fluoranthene	1.71
Cobalt	4.33	Benzo(g,h,i)perylene	0.286–0.729
Copper	263	Benzo(k)fluoranthene	1.86–2.28
Iron	25000	*Bis*(2-ethylhexyl)phthalate	5.34
Lead	1160	Chrysene	4.81–11.2
Magnesium	19800	Dibenz(a,h)anthracene	0.124–0.367
Manganese	294	Dibenzofuran	26.8
Mercury	9.31	Fluoranthene	56.8–58
Nickel	18.6	Fluorene	39–46.5
Potassium	201	Indeno(1,2,3-cd)pyrene	0.345–0.825
Silver	1.48	Naphthalene	6.03–8.35
Sodium	226	Phenanthrene	110–128
Vanadium	3.53	Pyrene	35.1–40.2
Zinc	1100		

[a] Determined with the USEPA Method SW6020A and SW7471B

[b] Determined with the USEPA Method SW8270D

placed in front of the electrode. Plexiglas® reservoirs were connected to the electrode compartments using Tygon® tubing. Gas vent ports were provided in the electrode compartments to allow gases resulting from the electrolysis reactions to escape. Tubing was attached to gas vent ports to collect any liquid that was removed along with the gases. A power source was used to apply a constant voltage to the electrodes.

2.3 Experiment design and testing procedure

Table 3 shows the details of the four experiments conducted in this study. Deionized water, 0.2 M EDTA, or 5% Igepal CA-720 were used as flushing solutions using a constant hydraulic gradient of 0.2 or 1.2. A constant voltage gradient of 1.0 VDC cm^{-1} was used as it is shown in Table 3.

Approximately 1200 g of wet soil (moisture content: 30% in wet basis) was used for each test. The soil was placed in the electrokinetic cell in layers and compacted uniformly using a hand compactor. The exact weight of soil used in the cell was determined for each experiment in order to assure the accuracy in the contaminant removal results and mass balance. Anode and cathode reservoirs were filled with the selected flushing solutions for each experiment (Table 3). The liquid level in both reservoirs was maintained constant throughout the testing to assure a constant hydraulic gradient across the soil specimen. Each test was run to collect predetermined number of pore volumes of hydraulic or combined hydraulic and electroosmotic flow. At the completion of each test, aqueous solutions from the reservoirs and the electrode compartments were collected and analyzed. The soil specimen was weighed and divided in sections and analyzed for metal and PAH content.

2.4 Chemical analyses

Representative samples of reservoir solutions, soil sections, and the initial soil for each test were analyzed for total metals and the PAHs using the following USEPA Methods: method 6020A (Inductively Coupled Plasma-Mass Spectrometry), method 7471B (Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique), and method 8270D (Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)). The chemical analysis was conducted with stringent quality control by the STAT Analysis, Inc. (Chicago, IL, USA), a USEPA certified laboratory. To ensure accuracy of the test results, new tubing were used for each experiment, and the electrokinetic cell

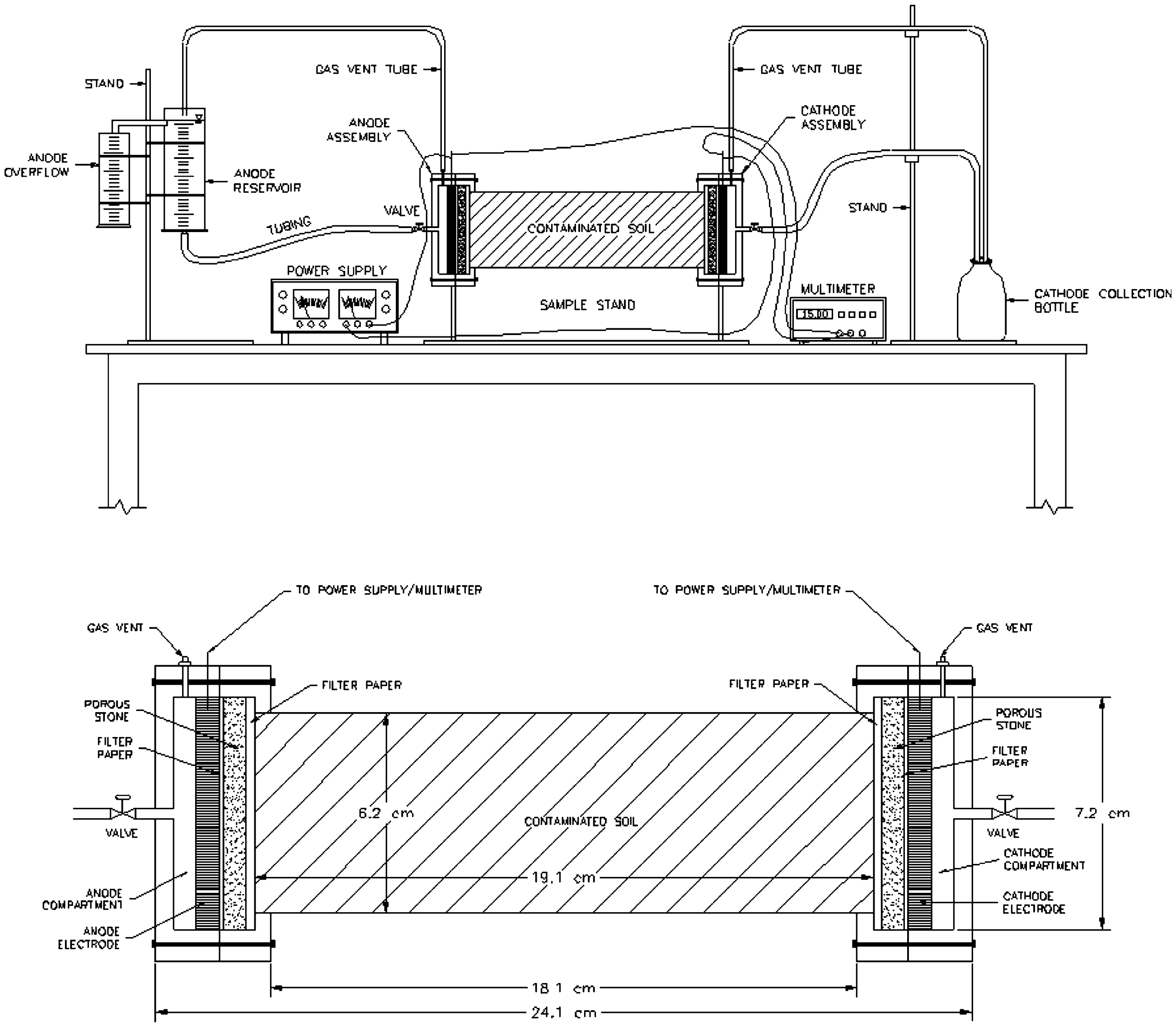

Fig. 1 Schematic of the electrokinetic test setup and cell details

and compartments were washed thoroughly to avoid cross contamination between the experiments.

3 Results and discussion

This study presents the treatment of a heavy metal and PAH contaminated soil from a former MGP site. The soil was treated with a hydraulic flushing combined with electrokinetics in an attempt to evaluate the couple technology for the remediation of contaminated soils with mixed contamination (organic and inorganic). Due to the different chemical nature of the contaminants, a complexing agent, EDTA, and a surfactant, Igepal CA-720, were used as sequential flushing solutions in order to enhance the extractability and solubility of the contaminants. A constant voltage gradient (1 VDC cm^{-1}) was applied with the objective of increasing the extraction of the contaminants and their transport out of the soil. Table 3 shows the operating conditions of the experiments.

3.1 Cumulative flow

Figure 2 shows the cumulative flow results for all the tests reported in this study. Exp. 1 shows steady increase of the cumulative flow, due to the constant hydraulic gradient used. No influence of the voltage gradient was found in Exp. 1. The cumulative flow in Exp. 2 largely differs from the results of Exp. 1 mainly due to the low hydraulic gradient used (i.e., 0.2) and only marginal effect of the chemical nature of flushing solutions (EDTA and Igepal) can be attributed to the decrease in the flow.

Table 3 Integrated electrokinetic flushing testing program using the soil from the MGP site

Test designation	Voltage gradient (VDC cm^{-1})	Hydraulic gradient	Flushing solution	Pore volumes	Treatment time (h)
Exp. 1	0.0	1.2	Deionized water	11.2	28.7
	1.0	1.2	Deionized water	10.0	31.2
Exp. 2	0.0	0.2	5% Igepal CA-720	6.6	258.1
	0.0	0.2	0.2 M EDTA	5.8	247.5
Exp. 3	1.0	0.2	5% Igepal CA-720[a]	5.6	270.9
	1.0	0.2	0.2 M EDTA[b]	6.5	87.9
Exp. 4	0.0	1.2	0.2 M EDTA	6.0	33.9
	1.0	1.2	0.2 M EDTA[b]	5.5	27.4
	0.0	1.2	5% Igepal CA-720	5.6	24.1
	1.0	1.2	5% Igepal CA-720[a]	5.8	24.8

[a] In flow location used as anode and outflow location as cathode

[b] Inflow location used as cathode and outflow location used as anode. Electromigration from cathode to anode, electroosmosis from anode to cathode, electroosmosis effects are considered insignificant

In Exp. 3, the same flushing solutions with the same hydraulic gradient as in Exp. 2 were used; with the only difference that 1 VDC cm^{-1} voltage gradient was superimposed to the hydraulic gradient. During the Igepal flushing, the combined hydraulic and electroosmotic flow was slightly higher in the beginning of the experiment (up to 100 h of treatment, Fig. 2) and then it reduced marginally. Comparing the results for the Igepal flushing in Exp. 2 and 3, it can be concluded that the electroosmotic flow towards cathode was not significant in this soil, and the hydraulic gradient is the only cause for the cumulative flow collected. Igepal is not expected to favor the variables that affects the electroosmotic flow (i.e., zeta potential, dielectric constant of the fluid, viscosity,…), nor to dissolve salts that may increase the ionic strength of the interstitial fluid. Moreover, it is widely recognized that the electroosmotic flow is not very important in sandy soils. However, in the second stage of Exp. 3 nearly 6.5 pore volumes were collected in just 88 h treatment time (Table 3). This is a noticeable increment compared to Exp. 2-stage 2. This can be explained by the increase in the ionic strength in the pore fluid due to the dissolution of salts, which increases the hydraulic conductivity of the soil that governs the overall enhanced flow behavior of the studied system. Furthermore, it was reported by several authors that the presence in the soil of organic compounds such as EDTA or citric acid can modify the superficial soil particle charge, and therefore the zeta-potential, resulting in a rapid increase of the electroosmotic flow during the electrokinetic treatment. This phenomenon was reported especially for citric acid and EDTA [27, 28]. Thus, it can be concluded that the cumulative flow collected in the second stage of the Exp. 3 was the combination of the hydraulic and the electroosmotic flow.

The cumulative flow of Exp. 4 is similar to that of control experiment since both experiments used the same

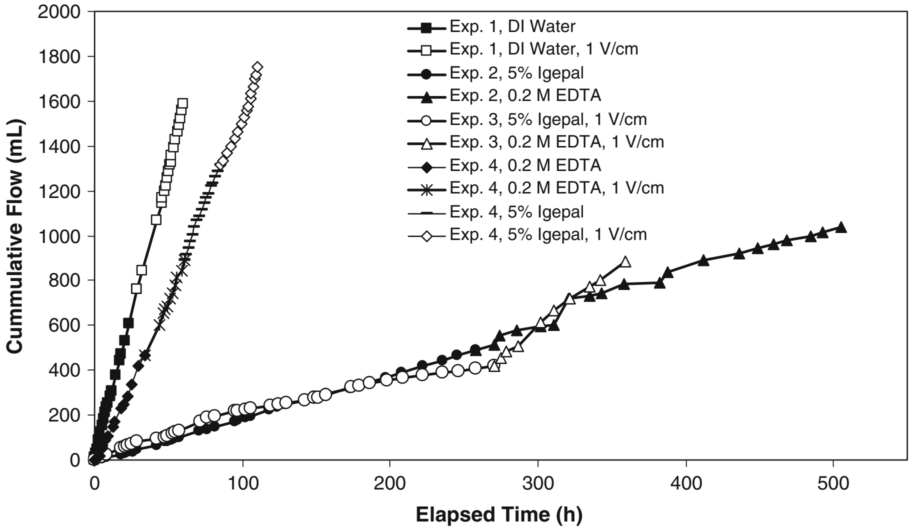

Fig. 2 Hydraulic and electroosmotic cumulative flow

hydraulic gradient. During the EDTA flushing, the electroosmotic flow suffers a slight increase due to the application of voltage gradient (stage 2). However, in stages 3 and 4 with Igepal flushing, no change in the electroosmotic flow was observed. These findings further suggest that the application of voltage gradient induces the surface charge of the soil and enhances the solubilization of salts during EDTA flushing ensuring the increased electromigration of the ions present in pore fluid that enhances electroosmotic flow. On the other hand, the solubilization and mobilization of PAHs by Igepal is governed by the hydraulic conductivity of the soil and it is independent to charge density of surface soil particles. It is pertinent to mention here that the hydraulic permeability of the soil remained constant and did not change due to the application of DC current or change in purging solution. Thus, it can be concluded that the cumulative flow in the stages 1, 3, and 4 was due to the hydraulic gradient alone, while in stage 2, electroosmotic flow affected the flow behavior.

3.2 Contaminant removal

The soil sampled at the MGP site was contaminated with metals and PAHs. Figure 3a–c shows the mass of total metals, total toxic metals, and total PAHs removed in all the experiments reported in this study. The initial total metal and PAH concentrations in the soil are listed in Table 2. In Fig. 3b, toxic metals correspond with all the analyzed metals from Table 2 except: Al, Ca, Fe, Mg, K, and Na.

3.2.1 Metal removal

As seen from Fig. 3a and b, deionized water flushing at neutral pH (Exp. 1) did not contribute for the removal of metals with or without the application of voltage gradient. This indicates that metals are in the form of precipitates or they are strongly sorbed to the soil matrix, which corresponds with an aged contamination accumulated in the soil for a long period of time. Probably, the exchangeable fraction of the contaminants was already removed in the site by natural process such as rain or groundwater washing of the soil matrix.

Figure 3a and b reveals that Igepal did not affect/enhance desorption of metals from the soil. The flat concentration profiles in Igepal flushing stages in Exp. 2 and 3 demonstrate that this surfactant does not provide the adequate chemical environment for the solubilization of metals, especially when Igepal was used before EDTA. However, a significant removal of metals was detected in Exp. 4 when Igepal was used after EDTA flushing.

Noticeable metal removal was observed in EDTA flushing in Exp. 2 and 3. Better results were obtained in Exp. 2 with no voltage gradient. It can be explained by considering flushing of Igepal in first stage may have lowered the capillary forces [29, 30] within the pores due to the formation of micelles. Thus, the EDTA flushing in stage 2 of Exp. 2 requires 247 h to flush 5.8 pore volumes, a comparatively longer time than in Exp. 3. The longer flushing time permits a longer interaction of the EDTA with the solid surface releasing, dissolving and complexing the contaminant metals that are flushed out of the soil. Unlike, in Exp. 3 upon the application of the voltage gradient, micelle stability diminishes soon, favoring the electroosmotic flow, which resulted in a comparatively high flow through the soil that flushed 6.5 pore volumes in 88 h. The EDTA flushing in such a short time do not result effective enough for the movilization and complexation of contaminant metals strongly sorbed to the soil matrix.

Exp. 4 was conducted in four distinct stages. In stage 1 with EDTA, total metal or toxic metals are not mobilized in early stages of flushing confirming that the metals are strongly sorbed to the soil matrix. But shortly, the removal of metals increases in stage 1 and continued to increase on the further application of voltage gradient at stage 2. Noticeable concentrations of metals and toxic metals were measured in stage 3, when Igepal was used as flushing solution. This indicates that organically bound metals were released by the introduction of Igepal. No further increase in the removal of metals and toxic metals was detected in the fourth stage. These results show that maximum removal of metals can be achieved with the selection of the adequate flushing sequence, in this case employing EDTA before Igepal.

The coupled electrokinetic-hydraulic flushing technology was evaluated following the removal of three selected heavy metals: copper, lead, and zinc. These metals are strongly absorbed to the soil matrix at the MPG site, so the DI water flushing (Exp. 1) was not effective in their removal. However, in Exp. 2, the hydraulic flushing removed nearly 64% of lead, 43% of zinc, and 8% of copper from the soil. The simultaneous application of a voltage gradient (Exp. 3) resulted in lower removal for lead and copper but a similar value for zinc (removal in Exp. 3: 46% of lead, 40% of zinc, and 4% of copper). These findings reflect that the stability of the lead and copper–EDTA complexes decreased with the application of voltage gradient in comparison of Zn–EDTA complexes [31].

In Exp. 4, slow removal of copper, lead, and zinc was observed in the initial phase of stage 1 when EDTA was flushed in. Further, application of voltage gradient in stage 2 increased the metal removal. Small but noticeable removal of metals was observed in stage 3 when the Igepal was flushed in the absence of any voltage gradient and became constant in stage 4 of the operation when the voltage gradient was applied. These results confirm that

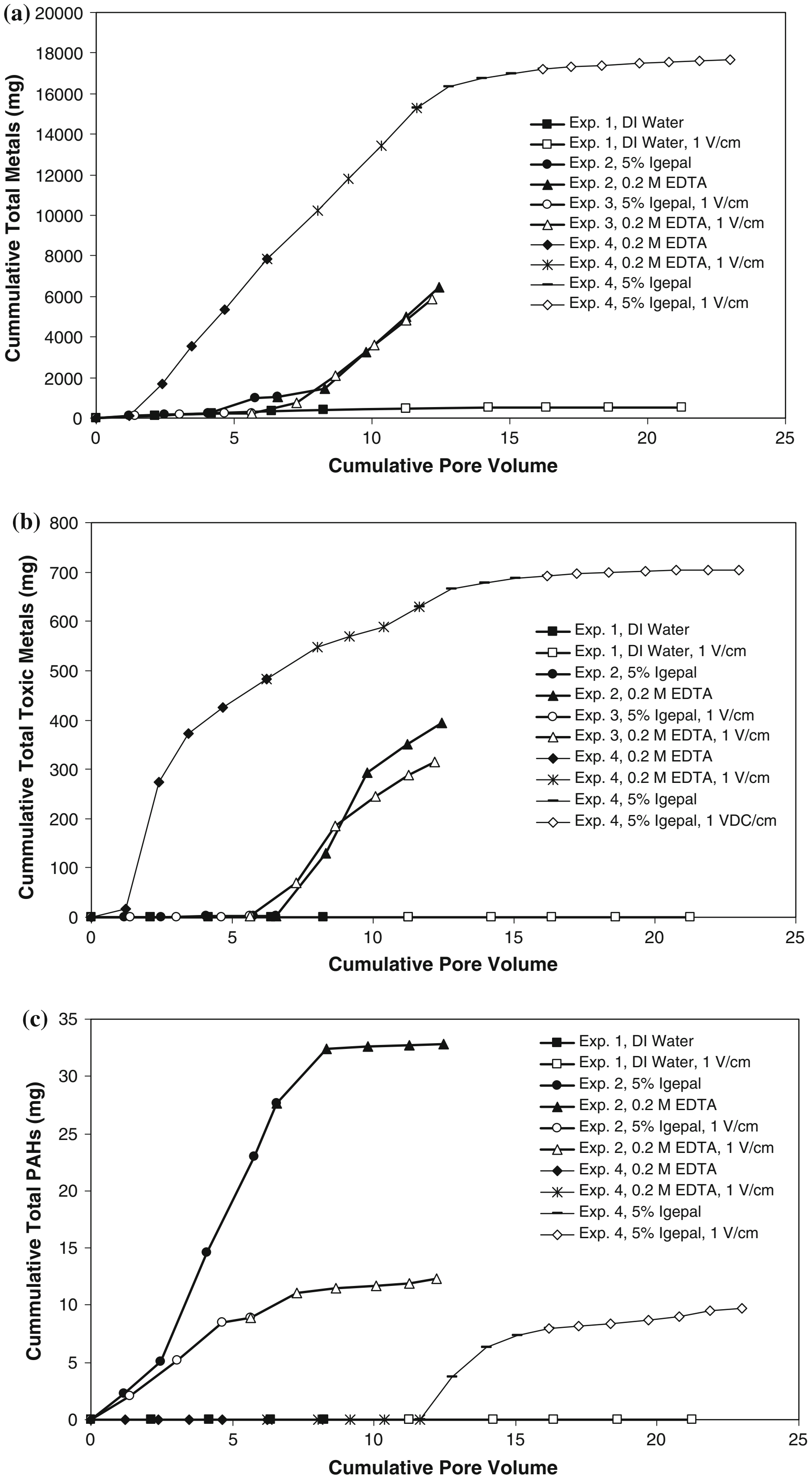

Fig. 3 Effect of hydraulic and voltage gradients with alternating flushing solutions on removal of (**a**) total metals, (**b**) toxic metals and, (**c**) PAHs

periodic application of voltage gradient favors the remediation of copper, lead, and zinc from the soil in sequentially enhanced systems [21, 32]. Slight removal of metals in the third stage upon the application of Igepal indicates the desorption of organically bounded metals from the soil; this may be due to the action of Igepal and also due to the change in the charge of the solid particles induced by the application of voltage gradient in the second stage. Overall, in Exp. 4, nearly 80% of lead, 60% of zinc, and 32% of copper were removed from soil in less than 120 h. These results showed the efficacy of the tested system in comparison of the other tests conducted where lower removal was achieved in longer treatment time.

3.2.2 PAH removal

Figure 3c shows that Exp. 1 did not show any noticeable removal of PAHs from the soil due to the hydrophobic nature of the PAHs that prevents them to be mobilized by DI water flushing. However, it is observed in Exp. 2 that PAHs removal occurred by Igepal flushing. In Exp. 3, the the application of voltage gradient decreases the removal of PAHs from the soil as the flow was decreased, as it is shown in Table 3 and Fig. 2. No apparent solubilization of PAHs takes place when EDTA is flushed through the soil in both Exp. 2 and 3. Overall, these results revealed that the solubilization of the contaminants depends upon the type of the flushing agent and the permeability governs the mobilization of the contaminant. Application of voltage gradient for the enhancement of electrokinetic process was not found to be effective due to low electroosmotic flow. Similarly, in Exp. 4 no removal of PAHs was observed in stages 1 and 2 with EDTA flushing. The removal of PAHs occurs with Igepal flushing at stage 3 and was increased upon the periodic application of voltage gradient in stage 4.

The removal of three selected PAHs, namely phenantherene, pyrene, and benzo[a]pyrene, was followed to assess the capability of the coupled electrokinetic-hydraulic flushing technology for their removal. Only important removal of PAHs was found during the Igepal flushing. Thus, Exp. 2 showed that nearly 60% of phenantherene, 55% of pyrene, and 17% of benzo[a]pyrene can be remediated from the soil. However, the simultaneous application of the voltage gradient (Exp. 3) decreases the affinity of the flushing solution and only 42% of phenantherene, 30% of pyrene, and 12 of benzo[a]pyrene were removed.

A slight but noticeable removal of PAHs was registered when EDTA is sequentially flushed in, mainly due to the dissolution of soil minerals by EDTA and also due to change in charge of solid particles that releases the additional PAH content. It is observed that in Exp. 3 nearly 30% of the phenantherene, 19% of pyrene, and 8% of benzo[a]pyrene is removed in the Igepal flushing stage, while 12% of phenantherene, 11% of pyrene, and 4% of benzo[a]pyrene is removed in the sequentially EDTA enhanced remediation.

In Exp. 4, no PAH removal was observed during the EDTA flushing, but in the third and fourth stages with Igepal maximum remediation of phenantherene, pyrene, and benzo[a]pyrene from the soil was achieved that increases upon the application of voltage gradient at stage 4, except of benzo[a]pyrene that remains constant (no increase in the removal was observed). Nearly 40% of phenantherene, 30% of pyrene, and 19% of benzo[a]pyrene were released from the soil. Theses results are slightly lower that those obtained for Exp. 2. Thus, a close examination of these results confirms that the removal efficiency of PAHs depends upon the sequence of purging solutions and applied hydraulic gradient as well as voltage gradient.

3.2.3 Effect of flushing solution and electric field on contaminant removal

Figure 4a and b was plotted to compare the removal efficiency of Exp. 1, 2, and 3 for all the metals and PAHs present in soil. It can be seen in Fig. 4a that all the metals are effectively removed under hydraulic gradient governed system (Exp. 2) and their removal considerably decreased with the application of voltage gradient (Exp. 3). This clearly indicates that more stable metal–chelate complexes are formed in Exp. 2 due to the long residence time of EDTA in the pores comparatively to the less flushing time that have been employed in Exp. 3 to collect approximately same pore volumes (Table 3). On the other hand, Fig. 4b shows up to 60% removal of PAHs from the soil in Exp. 2, which decreased to 35% in Exp. 3 when the voltage gradient was applied. No removal was observed in the DI water flushed systems.

The difference in contaminant removal in Exp. 2 and 3 can be explained on the basis of the fact that surfactant enhanced solubilization relies on micellar-enhanced contaminant solubility in the pore fluid. The ability of surfactant to mobilize and remove contaminants will depend upon the number and stability of micelles formed. The results from Exp. 2 and 3 indicate that in Igepal enhanced system, more micelles are formed at hydraulic gradient condition resulting in the efficient PAHs removal. When the voltage gradient is applied (Exp. 3) the surfactant is capable of producing other structured phases [33]. Some of these phases are undesirable for subsurface remediation (e.g., liquid crystals, gels, colloids, etc.) which are not useful for PAH remediation, explaining the limited results obtained. In the second stage of Exp. 3, the application of voltage gradient and EDTA flushing is apparently effective in the mobilization of these PAHs phases to a certain

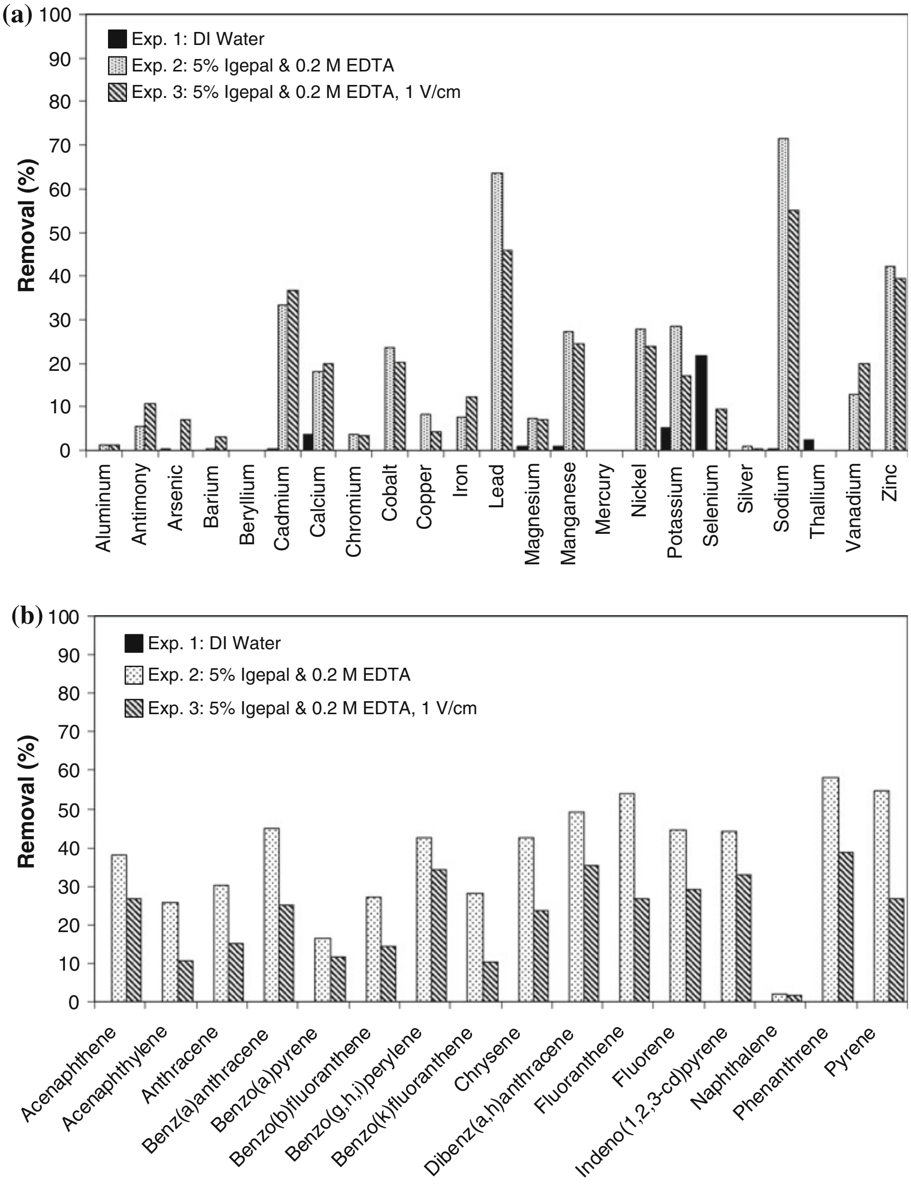

Fig. 4 Effect of flushing solution and electric field on (**a**) metal removal, (**b**) PAH removal

extent, while the EDTA flushing alone (second stage of Exp. 2) was ineffective for PAH removal.

Polyaminocarboxylate chelates such as EDTA form soluble complexes with free metal ions in the soil pore solution. In addition, they dissociate exchangeable cations attached to mineral surfaces and also dissolve soil minerals. Thus, the EDTA enhanced system relies on the interaction of the EDTA ions with the soil matrix and the stability of the EDTA–metal complexes. Thus, at low hydraulic gradient, the high removal of metals indicates that EDTA–metal complexes attain maximum stability at low hydraulic gradient condition. It can be concluded that dissolution of mineral surface may be highest at low hydraulic gradient that results into the physical perturbation of the soil resulting in the mobilization of PAHs. Further, the decrease in the removal behavior upon the application of voltage gradient can be explained on the following basis. It is seen that the flow is found to be increased in the EDTA flushed system upon the application of voltage gradient and also the effluent is collected at anode end in the EDTA flushed system, indicating permanent negative charge of soil particles and the EO flow is due to the electromigration of ions. This may further induce following interaction of metal–EDTA complexes and soil surface: (1) Negatively charged metal complex and EDTA could be specifically adsorbed on the soil surface, thereby increasing the negative charge of the surface, and (2) EDTA is able to mask all multivalent cations present in the pore fluid as a result of formation of double layer at the soil surface. This may decreases the stability of the toxic-metals complexes. For this reason, the removal of lead and copper was found to be decreased on the application of voltage gradient.

3.2.4 *Effect of flushing solutions and periodic electric field*

Figure 5a and b shows the removal efficiency of each stage flushing conducted in Exp. 4 for all the metals and PAHs present in soil. It can be seen in Fig. 5a that metals were predominantly removed in stage 1 and stage 2 corresponding with EDTA flushing. However, a slight but noticeable removal of some metals was observed in stage 3 and 4 (Igepal flushing). Overall 80–30% of toxic metals (lead, zinc, and copper) were removed in Exp. 4. In contrast, the removal of PAHs from the soil is solely happened in stage 3 and 4 when the Igepal was introduced in the system, as shown in Fig. 5b. Nearly 48–25% of the PAHs were removed from the soil in Exp. 4. The results show that maximum removal of PAHs was achieved in stage 3.

The contaminant removal in Exp. 4 can be explained on the basis of the fact that EDTA mobilizes and complexes contaminated metals as it is flushed through the soil (sage 1). The metal removal continues in stage 2 (EDTA flushing with 1 DCV cm^{-1} voltage gradient) due to the formation of negatively charged complexes migrating towards the anode under the effect of the electric field. The minor metal removal observed in stages 3 and 4 (Igepal flushing) reflects desorption/mobilization of organically bounded metals from the soil due to the physical perturbation of surfactant.

On the other hand, surfactant enhanced solubilization of PAHs relies on the formation of micelles and their

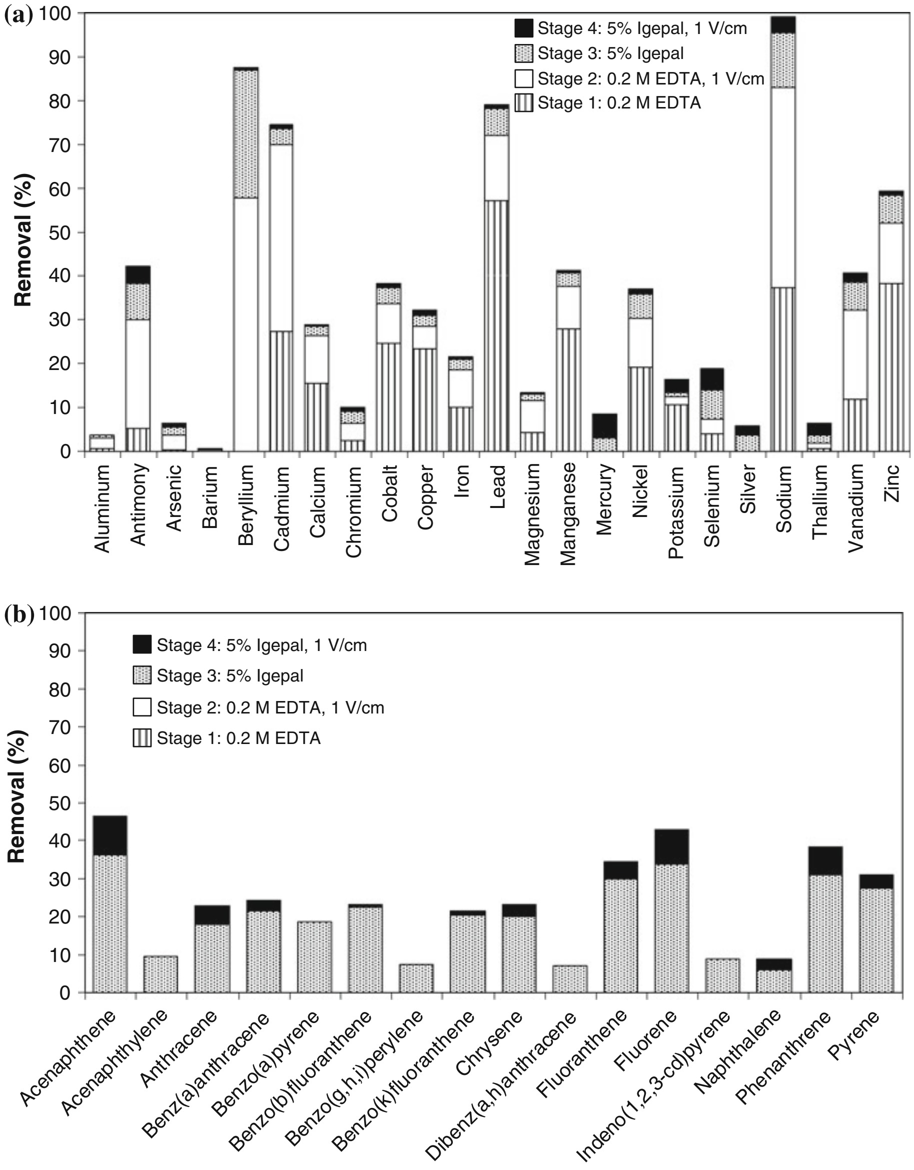

Fig. 5 Effect of flushing solutions and periodic electric field application on (**a**) metal removal, (**b**) PAH removal, for Exp. 4

interaction with the solid surface, where the contaminants are sorbed. When the voltage gradient is applied, the surfactant is capable of producing other structured phases that limit the number and stability if the micelles, and therefore the PAH removal efficiency.

4 Conclusions

The removal of PAH and metal contaminants from a former MGP polluted soil is influenced by the type of flushing solution and application of voltage gradient. Igepal surfactant is shown to remove PAHs, while EDTA chelant is shown to remove heavy metals from the soil. Sequential application of surfactant and chelant removed both PAHs and heavy metals present in the soil and the efficacy of the process depends on the order of flushing. Application of voltage gradient is found to retard the removal of PAHs and enhance the removal of metals from the soil. The experiments conducted only for a short duration in this study but the removal results reveal a good removal of both types of contaminants. Longer duration tests may be required to establish this as a potent technology for the remediation of soil contaminated by mixed wastes. Soil composition can have a profound effect on the contaminant removal; therefore, site-specific soil investigations must be conducted to develop sequential process that will be effective to remove mixed contaminants from the soil.

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