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Electrokinetic remediation of petroleum hydrocarbon contaminated soil (I)

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ABSTRACT

The remediation of petroleum hydrocarbons (TPH) in a contaminated soil by electrokinetic (EK) treatment was studied in the laboratory. The effects of applying a constant electrical current on soil pH, moisture content, electrical conductivity (EC), temperature, and the concentrations of three fractions of TPH (C10–C16, C17–C34 and C35–C40) were investigated. The experiment was run for seven days and soil samples were collected at the end of the 7 day period for analysis of soil pH and TPH concentration. There were extreme pH conditions near the electrodes. At the end of the experiment there was around a 37% reduction of C10–C16 chain compounds compared to the initial concentration of 164 ± 18 mg/kg. The study investigated TPH remediation to a depth of 24 cm, which is significantly more than most studies of EK remediation of TPH-contaminated soils. We observed reductions in TPH concentrations even at a depth of 24 cm. The spatial distribution of reductions in TPH concentrations was also studied and it was observed that more remediation occurred near the cathodes than near the anodes. Further, the greatest reductions in TPH concentrations were recorded near the electrodes in the lowest and middle parts of the experimental set-up. The application of electrokinetics to remediate TPH-contaminated soils could be a viable option as an *in situ* remediation technology.

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1. Introduction

Total petroleum hydrocarbons (TPH) and its derivatives are persistent organic contaminants in soil that are difficult to remediate (Huang et al., 2005; Li et al., 2010). As TPH contains hazardous chemicals including benzene, toluene, ethylbenzene, xylene, naphthalene, etc, contaminated soils can be hazardous to the health of plants, animals, and humans (Liebeg and Cutright, 1999; Ting et al., 1999; Vasudevan and Rajaram, 2001). Remediating persistent organic contaminants from soils is a slow and expensive process and the high molecular weight fractions (C35–40) of TPH are extremely hard to remediate (EPA, 2000; McNicoll and Baweja, 1995). Though TPH can be biodegraded by the TPH degrading bacteria in the soils, their ability to mineralize the TPH contaminants decreases if the TPH concentration is too high in the soil (Pollard et al., 1994).

Subsurface soil contamination by TPH is difficult to remediate, due to the heterogeneity of soil properties, low TPH bioavailability, and the possibility of TPH leaching into groundwater from the contaminant plume or point. To solve the

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remediation difficulty, TPH-contaminated subsurface soils have been remediated with various conventional technologies. These include chemical, physical or biological processes (Moliterni et al., 2012). They commonly involve transporting contaminated soils to off-site treatment facilities and/or disposing of contaminated soil to landfills, or by incineration, and are generally *ex-situ*. Consequently, such *ex-situ* remediation is expensive, inefficient and unsustainable (Moliterni et al., 2012; Varjani, 2017). *In-situ* chemical oxidation is thus preferable. However, its application is limited, such as by pumping oxidant, in particular for subsurface soils with dense clay, due to the limited radius of influence of the delivery of oxidant to target contaminant areas.

Electrokinetic (EK) remediation is the application of small electrical currents between the anodes and cathodes in soil to remediate contaminants (Korolev et al., 2008; Mena Ramirez et al., 2015; Reddy and Cameselle, 2009). EK is an *in-situ* “green” technology that is economical, non-disruptive and the most viable option where all other conventional remediation technologies might have failed to clean up dense clayey vadose zone contaminated soil (Maturi and Reddy, 2006; Park et al., 2009; Reddy and Saichek, 2003; Saini et al., 2019; Schnarr et al., 1998; Wang et al., 2007).

EK acts by electrochemical transport phenomena; (i) electromigration – movement of ions in the electric field, (ii) electroosmosis – bulk movement of fluid, (iii) electrophoresis – movement of charged, dissolved or suspended particles in pore fluid, (iv) electrochemically-induced reactions within the soil, (v) redox reactions occurring on the electrode surfaces, such as electrolysis of water (Gill et al., 2014; Guo et al., 2014), as suggested below, (vi) diffusion and convection should also be taken into account. The efficiency of EK depends upon the nature of the substances present in the soil and their specific properties (Gill et al., 2014).

Electrolysis of water occurs at the surface of electrodes (Virukyte et al., 2002):



Hydrogen (H^+) and hydroxyl (OH^-) ions are thus generated during electrolysis, and move towards electrodes of opposite charge, generating acidic and basic fronts, which might lead to heterogeneous remediation (Acar et al., 1993; Gill et al., 2014).

In principle, an applied electric field increases the contaminant bioavailability by increasing the movement of target contaminants (Guo et al., 2014). The electromigration is specifically difficult for TPH compounds since they are uncharged (Jackman et al., 2001; Wick et al., 2004). On the contrary, an electrical field applied to a soil can increase electroosmosis and electrophoresis of TPH entrenched in the subsurface (Reddy and Saichek, 2003; Schnarr et al., 1998). Moreover, EK can help in generating mass flux in regions resistant to advective transport, no matter via diffusion or convection (Jones et al., 2011). In general, EK can help remediate immobile and persistent organic contaminants in soil, including TPH (Rahner et al., 2002; Röhrs et al., 2002).

Key factors influencing EK efficiency include current density, electric field or voltage (Haidar et al., 2013; Jin and Fallgren, 2010), and other physio-chemical factors of soil, such as soil pH and moisture content (Acar et al., 1995). Another one is, when current is applied to a soil, heat is produced due to the Joule heating phenomenon. This could have an impact on the remediation efficiency as well.

The aim of this study is to investigate and validate EK remediation of TPH-contaminated subsurface soil. The study determined remediation of TPH fractions at different depth, which mimics a subsurface soil environment. Spatial contour maps were created of the TPH reduction to gain insights on the remediation mechanisms in the subsurface. The research highlights the factors governing EK remediation and suggests improvements to EK technology to increase efficiency.

2. Materials and methods

2.1. Soils

Soil was collected from a TPH-contaminated site at BHP (BHP Group Limited) in Perth, Western Australia, which consists three wastewater evaporation ponds used to store oily wastewater and runoff generated from vehicle wash-down bays, refuelling areas and mechanical workshops. Collection was carried out from one of the ponds from various depths. The soil was very wet and dense clay materials, excavated from the unsaturated subsurface zone. The soil was air-dried and then crushed, large stones or debris were removed before being passed through 2 mm sieves and stored in a cold dry place until tested. The <2 mm fraction was used for determination of the 50 μm and <2 μm fractions by the hydrometer method (Gee and Bauder, 1986). The TPH analysis of the <2 mm fraction soil was carried out by accelerated solvent extraction (see below in TPH analysis) whereas the soil physio-chemical properties were determined by standard protocols (Rayment and Lyons, 2011) and are presented in Table 1.

2.2. Apparatus and experimental method

The experimental set-up is shown in Fig. 1a. The set-up consisted of a glass chamber (50 × 50 × 50 cm) containing soil, and 10 cylindrical graphite electrodes (60 cm in length × 1 cm in diameter) distributed equally on each side. The soil was rehydrated to a moisture content of 35% by weight. Eighty-five kg of the moist soil was then placed into the glass chamber in layers, and each layer was tamped so as to minimize voids. Since the experiment was carried out to test the

Table 1

Physical and chemical properties of the soil.

Particle size	% in sample soil	pH	CEC (cmol/kg)	TC (total carbon)	TN (total nitrogen)	TS (total sulphur)
≤2 μm	17.40%	6.80 ± 0.23	1.65 ± 0.92	4.02 ± 0.34	0.03 ± 0.01	0.59 ± 0.32
2–50 μm	75.20%					
50–2000 μm	7.40%					

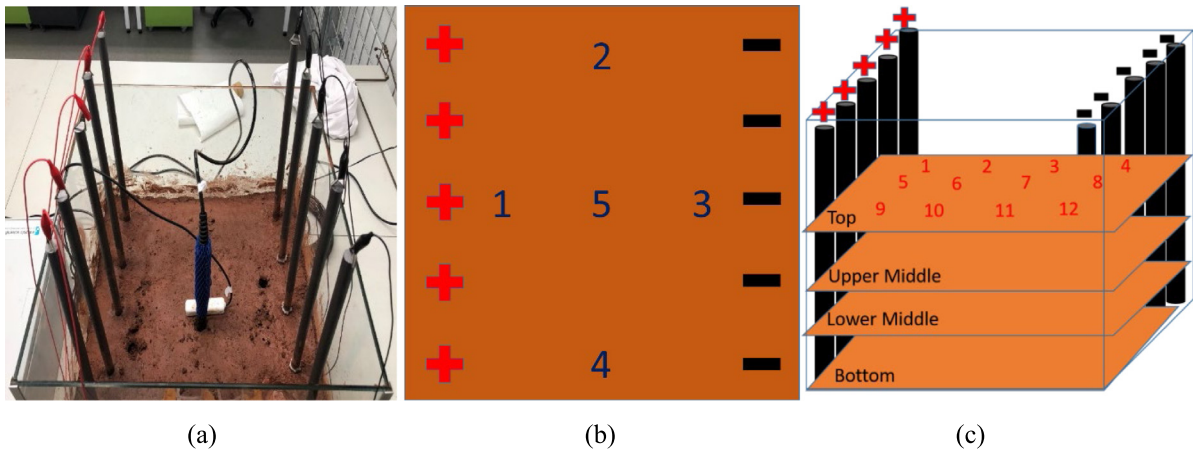


Fig. 1. Set-up for electrokinetic remediation of TPH contaminated soil – (a) Experimental set-up (b) Sensor reading points for in-situ monitoring (c) Analytical sample locations & depths at the end of the experiment.

effectiveness of EK on soil, and to make modifications for further experimentation, no control chamber was necessary. A Powertech DC regulated power supply (MP-3840, Australia) was connected to the electrodes to supply a voltage of 30 V, creating an electric field of 60 V/m for the duration of the experiment. The electric current was monitored and declined from ~1 mA at the beginning to ~0.001 mA after a week.

Soil pH was measured in-situ with an Edaphic Scientific pH-ORP sensor (France). The soil moisture content, temperature and electrical conductivity (EC) were measured in-situ using an Edaphic Scientific GS3 sensor (USA). All the sensors were calibrated according to the instruction manuals before use and placed in the soil test cell. Soil monitoring sensors were connected to a Microspider data logger system which could be connected to a laptop to read the sensor measurements.

To avoid the loss of water from the soil by Joule heating and evaporation, 2 L of deionized water was added throughout the experiment from the top soil by lightly sprinkling it on the surface on alternate days.

In-Situ readings from the soil monitoring sensors were taken from five locations (Fig. 1 b). All the readings from the sensors was taken on alternate days before the addition of water. A pH probe was used to check the pH at three locations – near the anode side (1), near the cathode side (3) and in the middle (5) (Fig. 1 b).

Since the pH probe only penetrated the upper layers of the soil in the chamber, a check of the validity of the readings in soil was made at the end of the experiment from various depths (0 cm, 8 cm, 16 cm, 24 cm, respectively, in Fig. 1c). Sampled soil was mixed with deionized water in a 1:2 ratio and shaken for 24 h to allow complete mixing. The pH of the slurry was measured using standard laboratory pH metres. The comparison was only done for the readings from the pH sensors on the last day of the experiment between the in-situ pH readings and the off-site one from the soil.

2.3. TPH analysis

After 7 days of EK, the power supply was turned off and soil was sampled from twelve locations and four depths (Fig. 1c). TPH extraction from sampled soils was performed using an accelerated solvent extraction method as described by Richter (2000). Briefly, using the accelerated solvent extraction (ASE) System (ASE350, USA) by Dionex Pvt Ltd., soil samples (0.5 g) were sandwiched between approximately 1 g of diatomaceous earth in the ASE extraction cells containing an ASE filter paper at the bottom. Acetone and dichloromethane (DCM) were used as the solvent mix (1:1 v/v) for the extraction. About 30 mL of extracts were collected per sample in 60 mL glass vials. After extraction, the samples were stored in 5°C refrigerators until further processed. All the soil samples were run in duplicates.

The extracts were concentrated using an Xtract nitrogen evaporator in a water bath at 30°C and 151 kPa. Once concentrated, the residue in the vials was re-constituted in 2 mL of GC-MS grade hexane. These vials were then stored in 5°C refrigerators for 24 h. The vials were then vortexed to ensure all the dried concentrated residue was mixed with

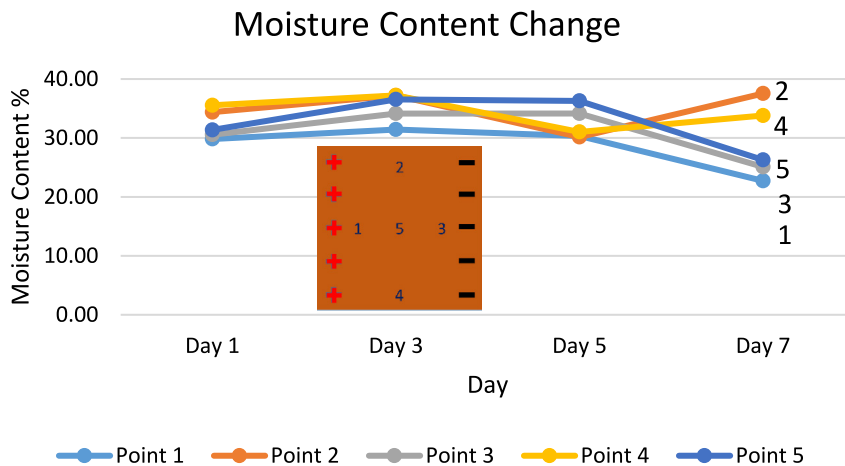


Fig. 2. Moisture change at different sensor locations during the EK treatment.

the solvent. The final solution was then filtered through 0.25 mm, 0.45 μ hydrophobic PTFE filters and transferred to 2 mL GC glass vials. These glass vials are stored in 5°C refrigerators until the GC determinations.

Analysis of TPH in extracted solution was conducted by an Agilent Technologies Gas Chromatograph fitted with a Flame Ionization Detector (GC-FID, 7890B, USA). Separation was performed on a SGE HT5 column (length – 12 m, film thickness – 0.1 μ m, maximum temperature – 380/400°C). Helium was used as the carrier gas at 2.5 mL min⁻¹, and the FID detector temperature was kept at 300°C. Splitless injection was carried out with a sample volume of 1 μ L. The oven temperature was increased from 30° to 320°C at a gradient of 10°C min⁻¹ and held at this temperature for 5 min. The total run time was 35 min with a post run time of 1 min. The hydrocarbon concentrations were quantified according to the following fractions: C10–C16, C17–C34, and C35–C40. A calibration curve ranging from 100 ppb to 50 ppm was generated using Accustandard hydrocarbon window defining standards for each of the three hydrocarbon fractions. A blank was run after every ten samples analysed. For every twenty samples a standard of 500 ppb concentration was run to check the accuracy of the GC column.

2.4. Data analysis

The GC-FID results for each sample were defined as three TPH fractions – C10–C16, C17–C34 and C35–C40. The results for each of the fractions were combined and a layered contour map was created using Golden software Grapher™. Statistical analysis was carried out to determine the significance of correlations ($p < 0.05$) between the TPH reduction in each layer (Top, UM, LM, bottom) using IBM SPSS Statistics (Version 25).

3. Results and discussion

3.1. Soil temperature, moisture content, pH, and EC

In general, the soil temperature remained stable and close to the ambient room temperature range of 22–24°C for the duration of the experiment, indicating there was little soil heating due to EK Joule heat. The minimal amounts of heating due to EK Joule heat that were measured were around the electrodes, where there was closest contact between the soil and the electrical current applied.

As the chamber was not covered at the top, loss of moisture can be attributed to evaporation and Joule heating to some extent. At the start of the experiment, the soil moisture ranged between 30%–35% w/w. With the progress of the experiment, this value reduced, by the end of the 7 days, to a range of 22%–37% w/w (Fig. 2). The mean moisture content calculated from the data sampling points decreased from 32.3% w/w to 29.1% w/w, which is not significant. That is because water was sprinkled on the soil during the experiment, the loss of water was very minor.

While the overall change in moisture content was minor, there were significant changes around the electrodes and the centre. The moisture content (Points 1, 3, 5) there was lower than at the beginning of the experiment, whereas on the edges of the chamber (Points 2 and 4) there was higher moisture content than day 1. This could be attributed to electroosmosis. As mentioned earlier, electrolysis of water occurs at the electrodes during EK (Eqs. (1) and (2)), generating H⁺ and OH⁻ ions. These ions under the applied electric field move towards their reciprocal electrodes to meet somewhere in the middle to cause a pH jump (Saini et al., 2019), which will be studied below.

During the experiment the soil pH started to deviate from the initial value of 6.8 after 3 days, and finally to pH 14 (Point 3) and pH 2 (Points 1, 5) after 7 days, suggesting the reaction of Eq. (1) happened around the anode to decrease

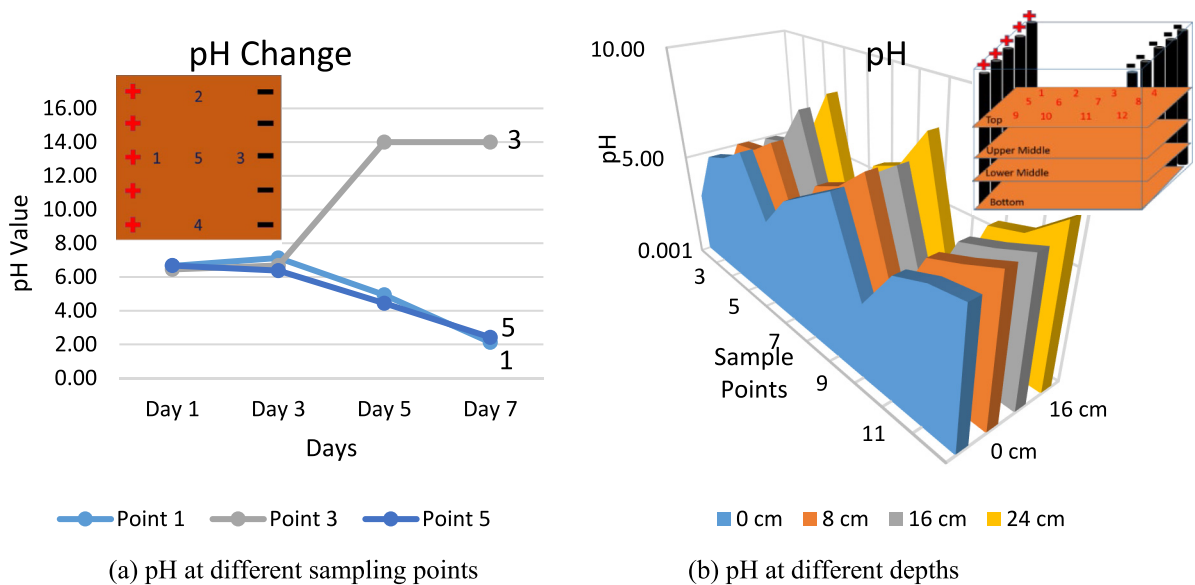


Fig. 3. Measure of pH variation during the EK treatment.

the pH value, while Eq. (2) happened around the cathode to increase the pH value. The electroosmosis from anode to cathode transport H^+ from Point 1 to Point 5, thus lead the pH value decrease there as well.

At the end of the experiment, the anode end and the middle of the chamber had very acidic pH, whereas the cathode had a highly basic pH. The pH results for the soils from different depths after the end of the experiment, measured using the pH metre off-site, were in agreement with the pH readings obtained by the soil pH sensor (Fig. 3b). Even though the pH sensor probe only penetrated the top layer, the readings received from it estimate the pH in deeper layers as well. This enhances the soil pH measurement process as we do not need to excavate the set-up to get the readings. Even after taking multiple readings at the sensor reading locations, the sensors gave values with a standard deviation of only ± 0.1 of the figure; hence all the graphs presented are without error bars.

The EC at the beginning of the experiment was within the range of 1400–1600 $\mu S/cm$. As also shown by the pH readings, deviation in the EC readings from the original values appeared from day 3 onwards (Fig. 4). On day 5 the EC values were still within a small well-defined range (1000–1800 $\mu S/cm$). However, on the final day of the experiment, the EC values showed significant ranges (300–2800 $\mu S/cm$), with lower values in the middle/near the cathode, and higher values near the anode. As we can see from the pH results, the soil near the anode had very acidic pH values as H^+ ions were generated by Eq. (1), which increased EC values near the anode (Fig. 4). The main contributors to EC were H^+ and OH^- (with molar conductivity of 0.35 S L $mol^{-1}cm^{-1}$ and 0.20 S L $mol^{-1}cm^{-1}$, respectively, much higher than Na^+ of 0.05 S L $mol^{-1}cm^{-1}$ or Cl^- 0.08 S L $mol^{-1}cm^{-1}$, for example) and this is the reason why significant EC increase at Point 1. In the meantime, a contribution from the movement of other ions present in the soil cannot be ignored (Mena Ramirez et al., 2015).

3.2. Effects of EK on TPH remediation

3.2.1. C10–C16 remediation

The initial concentrations for C10–16 compounds in the repacked contaminated soil were 164 ± 18 mg/kg. After 7 days of EK, there was an overall reduction of 37% in the concentration of C10–C16 chain compounds in soil. To see if there was any linear relationship between the TPH reduction at a particular sampling point in all the different layers, we correlated the mean of the TPH reduction at a particular sampling point to the mean of the TPH reduction of the sampling point in each of the layers. For the C10–C16 fraction there was statistically significant correlation in all the four layers (Table 2), particularly when considering the short-term remediation of 7 days.

Most of the reduction in TPH concentrations occurred in the soil surrounding the electrodes (Fig. 5a). Reductions of TPH concentrations in soil around the anodes were greater than near the cathodes. Looking at the different layers, the two bottom layers had higher reduction than the two top layers. The possible reason is the higher moisture content in the bottom, which can aid in electroosmosis. Since the experimental chamber was not covered, some of the reduction of moisture content in the top layer would be caused by evaporation. The median remediation of each fraction of TPH at different depths is presented in Table 3.

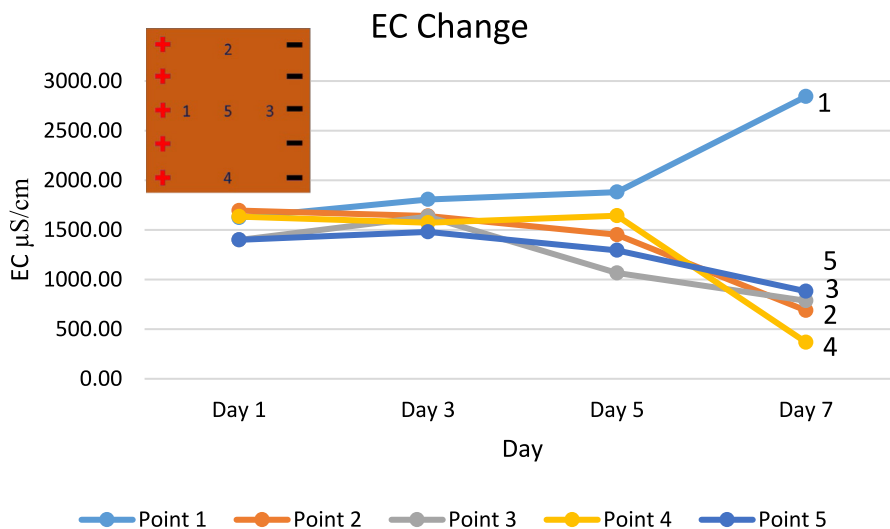


Fig. 4. Measured soil EC variability.

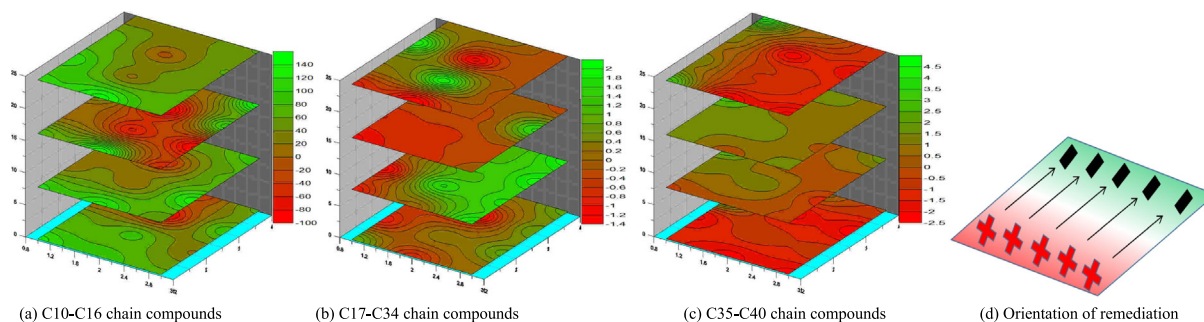


Fig. 5. Spatial display of remaining TPH concentrations after EK-remediation at different depths.

Table 2
Statistical correlation of reduction in TPH concentrations with depth.

		Top			Upper middle			Lower middle			Bottom		
		C10-16	C17-34	C35-40	C10-16	C17-34	C35-40	C10-16	C17-34	C35-40	C10-16	C17-34	C35-40
Overall	r	.839**	.439	.925**	.799**	.558	.771**	.794**	.836**	.808**	.741**	.525	.310
	p	.001	.154	.000	.002	.059	.003	.002	.001	.001	.006	.080	.326

*Correlation is significant at the 0.05 level (2-tailed), ** Correlation is significant at the 0.01 level (2-tailed).

3.2.2. C17-C34 remediation

The initial concentration for the C17-C34 compounds was 7.10 ± 1.03 mg/kg. Overall there was no significant change in the concentrations mainly due to short duration of 7 days. Again statistically there was no significant correlation, as listed in Table 2. When we look into the minor variations that occurred in the concentrations, there was more reduction in concentrations around the electrodes than in the middle, which is assumed to have occurred due to electroosmosis (Fig. 5b).

3.2.3. C35-C40 remediation

The initial concentrations for C35-C40 TPH fraction compounds was 7.13 ± 0.84 mg/kg. After 7 days, there was only a minor reduction by 1.26% from the initial concentrations. Even though the reduction was only minor, it was statistically significant in all the layers except the bottom layer (Table 2). Most of this reduction occurred in the lower middle layer (Table 3). Just like the other two fractions, C35-C40 chain compounds were remediated more around the electrodes than in the middle of the chamber (Fig. 5c). Given that the duration of EK was very short, the minor reduction of these long chain compounds reinforces the efficacy of EK for *in-situ* TPH remediation.

In summary, the maximum decreases in TPH concentrations were observed near the electrodes, and the minimum was found near the middle of the chamber. Beyond the electroosmosis, another possible reason could be attributed to

Table 3
TPH concentrations before and after EK remediation.

Hydrocarbon fraction	Soil layer	Initial concentration	Concentration after 7 days of EK
C10–C16	Top	164 ± 18 mg/kg	109 ± 54 mg/kg
	Upper middle		129 ± 80 mg/kg
	Lower middle		94 ± 58 mg/kg
	Bottom		97 ± 68 mg/kg
C17–C34	Top	7.10 ± 1.03 mg/kg	6.96 ± 0.61 mg/kg
	Upper middle		7.55 ± 0.61 mg/kg
	Lower middle		7.46 ± 1.27 mg/kg
	Bottom		6.82 ± 0.98 mg/kg
C35–C40	Top	7.13 ± 0.84 mg/kg	8.35 ± 2.28 mg/kg
	Upper middle		7.25 ± 1.39 mg/kg
	Lower middle		6.56 ± 0.98 mg/kg
	Bottom		6.83 ± 1.29 mg/kg

the location of the application of the electrical field (Fig. 5d). Guo et al. (2014) found that soil around their electrodes had a high field intensity, leading to more pH and EC changes and greater reductions in TPH concentrations. The pH and EC variations in our experiment were more prominent near the electrodes, signifying that the soil near the electrodes had more contact, leading to more electrochemically-induced reactions, than the soil further away.

A comparison of the pH of the soils at the two locations near the electrodes showed highly acidic pH values near the anodes and a highly basic pH values near the cathodes. The difference in pH of soil at the anode and cathode might be favourable for electrokinetically induced reactions for the different TPH fractions. In addition, oxidizing and reducing zones that might have been created due to the electrolysis of water around the electrodes are favourable for bioremediation and this may have activated indigenous bacteria in the contaminated soil decompose TPHs (Kim et al., 2010; Lohner et al., 2011), which deserves further research.

4. Conclusions

The results show that there was a 37% reduction in the concentration of C10–C16 chain compounds within a 7-day EK remediation period which was statistically significant in all the layers. The reductions in the TPH concentrations at three depths up to 24 cm, show that EK can be effective even at deeper layers of soil. There was little heat generated during EK and the temperature of the soil remained around the room temperature with only minor fluctuations around the electrodes. At the end of the 7-day period there were extreme pH conditions at the electrodes. Several researchers have carried out different techniques to overcome this like addition of pH neutralizing solutions (Gonzini et al., 2010; Kim and Lee, 1999), switching polarities (Huang et al., 2013; Li et al., 2015), approaching anode/cathode (Zhang et al., 2014; Zhou et al., 2014), similarly we shall research the best option to avoid the extreme pH conditions.

The greatest reductions in TPH concentrations were attained around the electrodes, and the least was found in the middle of the chamber, which indicates the positive effects of electric intensity on remediation efficiency. The C10–C16 fractions were remediated more at the anodes than the cathodes, under very acidic conditions at the end of the experiment. The C17–C34 and C35–C40 fractions were remediated more at the cathodes than the anodes which had highly basic pH conditions at the end of the experiment. The shorter carbon chain compounds were remediated more at acidic pH values, whereas the longer carbon chain compounds were remediated more under basic pH conditions. Around anode there are redox reactions occurring which help in the degradation of TPH, whereas around the cathode oxidation reactions occur which are not that helpful for the degradation, hence more reductions in the TPH concentrations was observed around the anodes. The results are consistent with those of Guo et al. (2014) who showed that electrical intensity is the driving force for mass transfer and ultimately leads to more extensive electrochemical reactions in the soil, hence more reduction in the TPH concentration.

A stronger electric field intensity also leads to more chances for interactions between the contaminants and bacteria in the soil. Even though we did not consider the microbial community of the soil, the indigenous bacteria could have been activated to consume TPH fractions, which would have helped in reducing the TPH concentrations in the soil.

Although there was not much reduction in the concentrations of the longer carbon chain compounds fractions (C17–C40), the 37% reduction in the shorter carbon chain compounds (C10–C16) is a very promising result. The experiment was run for a period of 7 days and if extended there could have been reduction of longer carbon chain compounds. With further experimentation and research, the technology could be considered as an effective *in situ* remediation technology and trialled for field remediation of TPH.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Anish Saini, Dawit Nega Bekele, Sreenivasulu Chadalavada, Cheng Fang, Ravi Naidu

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