



Pilot-scale electro-bioremediation of heavily PAH-contaminated soil from an abandoned coking plant site

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HIGHLIGHTS

- Electro-bioremediation was used for field-scale remediation of a coking plant site.
- The PAHs were effectively removed from the soil during electro-bioremediation.
- The total toxicity equivalent concentration of PAHs was reduced after remediation.
- Electro-bioremediation with polarity reversal maintained uniform soil properties.

ARTICLE INFO

Article history:

Received 18 July 2019

Received in revised form

15 November 2019

Accepted 24 November 2019

Available online 27 November 2019

Handling Editor: Y Liu

Keywords:

Pilot scale

Electro-bioremediation

PAHs

Abandoned sites

ABSTRACT

This study presents a systematic pilot-scale study on removal of PAHs from the abandoned site of Shenyang former Coking Plant in China (total PAH concentration of 5635.60 mg kg⁻¹ in soil). Three treatments, including the control treatment (without inoculation and electric field), bioremediation (with inoculation), and the electro-bioremediation (with inoculation and electric field), were conducted with a treatment time of 182 days to assess their PAH-removal efficiency. All the treatments were conducted from May to October under natural conditions. Results show that electro-bioremediation enhanced the removal of total PAHs, especially high-ring (>3 rings) PAHs. At 182 days, the degradation extents of total and 4–6-ring PAHs reached 69.1% and 65.9%, respectively, under electro-bioremediation (29.3% and 44.4% higher, respectively, than those under bioremediation alone). After electro-bioremediation, the total toxicity equivalent concentrations of total PAHs and 4-, 5- and 6-ring PAHs reduced 49.0%, 63.7%, 48.2% and 30.1%, respectively. These results indicate that electro-bioremediation not only effectively removed the PAHs but also reduced the health risks of soil in an abandoned coking plant site. In addition, electro-bioremediation with polarity reversal could maintain uniform soil pH, the degradation extent of PAHs and soil microorganism numbers at all sites. The environmental conditions, such as temperature and rainfall, had little influence on the process of electro-bioremediation. These findings suggest that electro-bioremediation may be applied for field-scale remediation of heavily PAH-contaminated soil in abandoned coking plant sites.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are found at high concentrations in the soils of abandoned coking plant sites (Feng et al., 2009; Zhang et al., 2011; Yin et al., 2012). Because of their toxicity, carcinogenicity and mutagenicity, remediation of soil from

these sites is a matter of great concern for many researchers and government (IARC, 1984; Leyval and Binet, 1998; Khalil et al., 2006; Balachandran et al., 2012; Wang et al., 2015). Today, there are several different technologies available for the remediation of soil contaminated with PAHs, including chemical oxidation, photo-oxidation, volatilization, desorption and microbial degradation (Liao et al., 2011; Lu and Zhu, 2012; Sun et al., 2012; Kuppusamy et al., 2017). Among these, microbial degradation is gaining wider approval as a feasible technology for remediation of PAH-contaminated soils (Khan et al., 2004; Haritash and Kaushik, 2009; Sharma et al., 2016; Redfern et al., 2019). PAHs are

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hydrophobic organic pollutants with two or more fused benzene rings. They are chronically sequestered in the soil matrix, and the more rings that a PAH has, the more easily it is sequestered (Cerniglia, 1992; Chan et al., 2006). PAHs sorbed onto or partitioned into a solid phase are not readily degraded by microorganisms, so bioremediation has limited applicability when soils are contaminated with complex mixtures of high-ring PAHs (Sun et al., 2014). The PAHs of coking plant sites have the characteristics of high concentration, complex composition and high percentage of high molecular weight polycyclic aromatic hydrocarbons (HMW-PAHs) (Ling et al., 2010; García et al., 2012). These cannot be easily degraded even after inoculation of the soil with bacteria known to be effective in decomposing PAHs (Moham and Kisa, 2006). In addition, the main challenges facing the implementation of in-situ conventional bioremediation techniques include the difficulty of effectively and precisely delivering nutrients to bacteria, low oxygen concentration in deeper soil layer, etc, particularly in soils with low hydraulic conductivity (Hassan et al., 2016). Therefore, new treatment strategies need to be developed to enhance the removal of PAHs from contaminated sites.

In recent years, electro-bioremediation (EBR) has been recognized as an efficient method of remediation for soil contaminated with hydrophobic organic compounds (Wick et al., 2007). It is based on the application of an electric potential gradient among electrodes located in a contaminated soil. The generation of an electric field in the soil makes it possible to develop various processes that, in turn, facilitate soil decontamination (Rodrigo et al., 2014; Rubén et al., 2016; Barba et al., 2017). EBR for soil contaminated with hydrophobic organic compounds can be achieved by different biological strategies such as biostimulation or bioaugmentation by enhancing the transport of bacteria or nutrients and producing the oxygen in anodes (Rabbi et al., 2000; Mena et al., 2016a; Barba et al., 2019). Suni et al. (2007) and Gill et al. (2014) reported that microbial activity was enhanced when an electric potential gradient of 0.2–2 V cm⁻¹ was used on contaminated soil. A number of successful studies on EBR for soils contaminated with organic pollutants (e.g. PAHs, petroleum, pentachlorophenol, hexachlorobenzene and perchloroethylene) have been achieved in the laboratory (Li et al., 2012; Guo et al., 2014; Mena et al., 2016b; Silvia et al., 2017; Cappello et al., 2019). Because of its high operational flexibility, EBR has gradually been applied to scale-up ex situ or in situ remediation for soil contaminated with organic pollutants. The first field application of EBR conducted in Denmark in 2012 to degrade perchloroethylene (PCE) from clay soil. The dimensions of the site investigated were 1.8 × 3 × 2.7–7.2 m in width, length and depth, respectively. However, field application are very limited because the efficiency of EBR at actual sites will be influenced by soil properties, climate and pollutant bioavailability (Gan et al., 2009; Kuppusamy et al., 2016). To our knowledge, there has been little research on EBR for actual contaminated sites, especially for the abandoned coking plant sites, which have complex contaminants and soil conditions.

In our laboratory, a 2-D electric field has been established and successfully used for the electro-bioremediation of petroleum-contaminated soils (Guo et al., 2014). In this study, pilot-scale EBR was conducted using a 2-D electric field to investigate the efficiency of EBR for contaminated soil from abandoned coking plant sites. To do this, three treatments were utilized, including the control treatment (CK) without inoculation and electric field, the bioremediation treatment (BIO) with inoculation, and the EBR treatment (EK + BIO) with inoculation and electric field. The changes of soil properties, pollutants and number of microorganisms were studied during the remediation process. Compared to previous existing works at laboratory, the application of EBR to remediate a real polluted soil in pilot scale becomes the main novelty point of this

work. These results will provide a benefit for the implementation of field-scale EBR in PAH-contaminated soils.

2. Materials and methods

2.1. Contaminated soil

In this study, to reproduce real-world conditions and increase the reliability of the results obtained, we used a natural soil from the abandoned site of Shenyang former coking plant, where coal was used as the raw material for producing coke, coke oven gas, tar, pitch, benzene and naphthalene. The soil has been continuously poisoned by coking chemicals for more than 50 years. Before remediation, 210 m³ of contaminated soil was excavated from the coking plant and cinders, stones and some of the rubbish were discarded from the contaminated soil. Contaminated soil was then air-dried and sieved through mesh 10 and soil <2 mm was homogenized using an agitator. Some soil principal properties and concentration of PAHs in the soil are summarized in Table 1 and Table 2, respectively. Heavy (four to six-ring) PAHs accounted for 85.8% of total PAHs in the soil.

2.2. Microorganisms

The PAH-degrading bacterial consortium used for the remediation was isolated from PAH-contaminated soil that was collected from the abandoned site of Shenyang former coking plant, China. This consortium of bacteria acclimated to PAHs degradation was enriched and maintained with an enrichment medium. The 16 S rRNA gene amplicon sequencing analysis and polymerase chain reaction-denaturing gradient electrophoresis analysis demonstrated that *Pseudomonas*, *Bacillus*, *Mycobacterium*, *Rhodococcus* and *Sphingomonas* were the main genera of consortium, and *Pseudomonas fluorescens*, *Pseudomonas aeruginosa*, *Bacillus megaterium*, *Bacillus cereus*, *Bacillus aerius*, *Bacillus licheniformis*, *Mycobacterium* sp., *Rhodococcus erythropolis*, *Sphingomonas* sp. and *Sphingopyxis terrae* were the dominate species. Among the dominate species, *Pseudomonas fluorescens*, *Bacillus cereus*, *Bacillus licheniformis*, *Mycobacterium* sp., *Rhodococcus erythropolis* and *Sphingopyxis terrae* were responsible to PAH degradation by the analysis of PAH-ring hydroxylating dioxygenase (PAH-RHD α) genes (Cébron et al., 2008). The composition of the medium per liter of deionized water was 0.20 g l⁻¹ MgSO₄, 0.02 g l⁻¹ CaCl₂, 1.00 g l⁻¹ KH₂PO₄, 1.00 g l⁻¹ (NH₄)₂ HPO₄, 0.05 g l⁻¹ FeCl₃, 1.00 g l⁻¹ KNO₃ and 500 mg l⁻¹ PAHs. The PAHs extracted from the contaminated soil as the sole carbon source. After the enrichment process, the consortium of bacteria was grown in the Bushnell–Haas Broth medium on a shaker at 25 °C and 160 rpm and collected by centrifugation at 8610 ×g when they were in the exponential growth phase. The samples were then resuspended in the mineral medium to obtain a highly concentrated bacterial suspension for the treatments.

Table 1
Principal properties of the contaminated soil sample.

Property	Value
TOC (%)	2.6 ± 0.8
Soil moisture (%)	22.45 ± 1.5
pH	6.95 ± 1.3
Conductivity (dS m ⁻¹)	0.63 ± 0.03
Total nitrogen (g kg ⁻¹)	1.56 ± 1.09
Total phosphorous (g kg ⁻¹)	3.12 ± 0.12
Cation exchange capacity (cmol kg ⁻¹)	23.5 ± 0.2
Clay (<0.002 mm) (%)	24.8 ± 1.49
Silt (0.05–0.002 mm) (%)	62.6 ± 2.39
Sand (2.00–0.05 mm) (%)	12.6 ± 0.90

Table 2
Concentration of PAHs in the contaminated soil sample.

Component	Rings	Concentration(mg kg ⁻¹)	Proportion (%)
Fluorene (Fle)	3	107.10 ± 3.45	1.90 ± 0.12
Phenanthrene (Phe)	3	525.49 ± 2.05	9.32 ± 0.07
Anthracene (Ant)	3	165.45 ± 3.21	2.94 ± 0.11
Fluoranthene (Flu)	4	1242.05 ± 4.23	22.04 ± 0.15
Pyrene (Pyr)	4	1023.52 ± 2.09	18.16 ± 0.07
Benzo(a)anthracene (BaA)	4	492.99 ± 1.45	8.75 ± 0.05
Chrysene (Chr)	4	528.70 ± 1.29	9.38 ± 0.05
Benzo[b]fluoranthene (BbF)	5	329.44 ± 0.68	5.85 ± 0.02
Benzo[k]fluoranthene (BkF)	5	193.23 ± 1.05	3.43 ± 0.04
Benzo(a)pyrene (BaP)	5	428.43 ± 0.88	7.60 ± 0.03
Dibenzo(a,h)anthracene (DahA)	5	71.11 ± 2.56	1.26 ± 0.09
Benzo(g,h,i)perylene (BghiP)	6	285.06 ± 3.44	5.06 ± 0.12
Indeno(1,2,3-cd)pyrene (IcdP)	6	243.05 ± 1.78	4.31 ± 0.06
4-6 ring PAHs	—	4837.58 ± 19.45	85.8 ± 0.68
Total PAHs	—	5635.60 ± 28.16	100.0

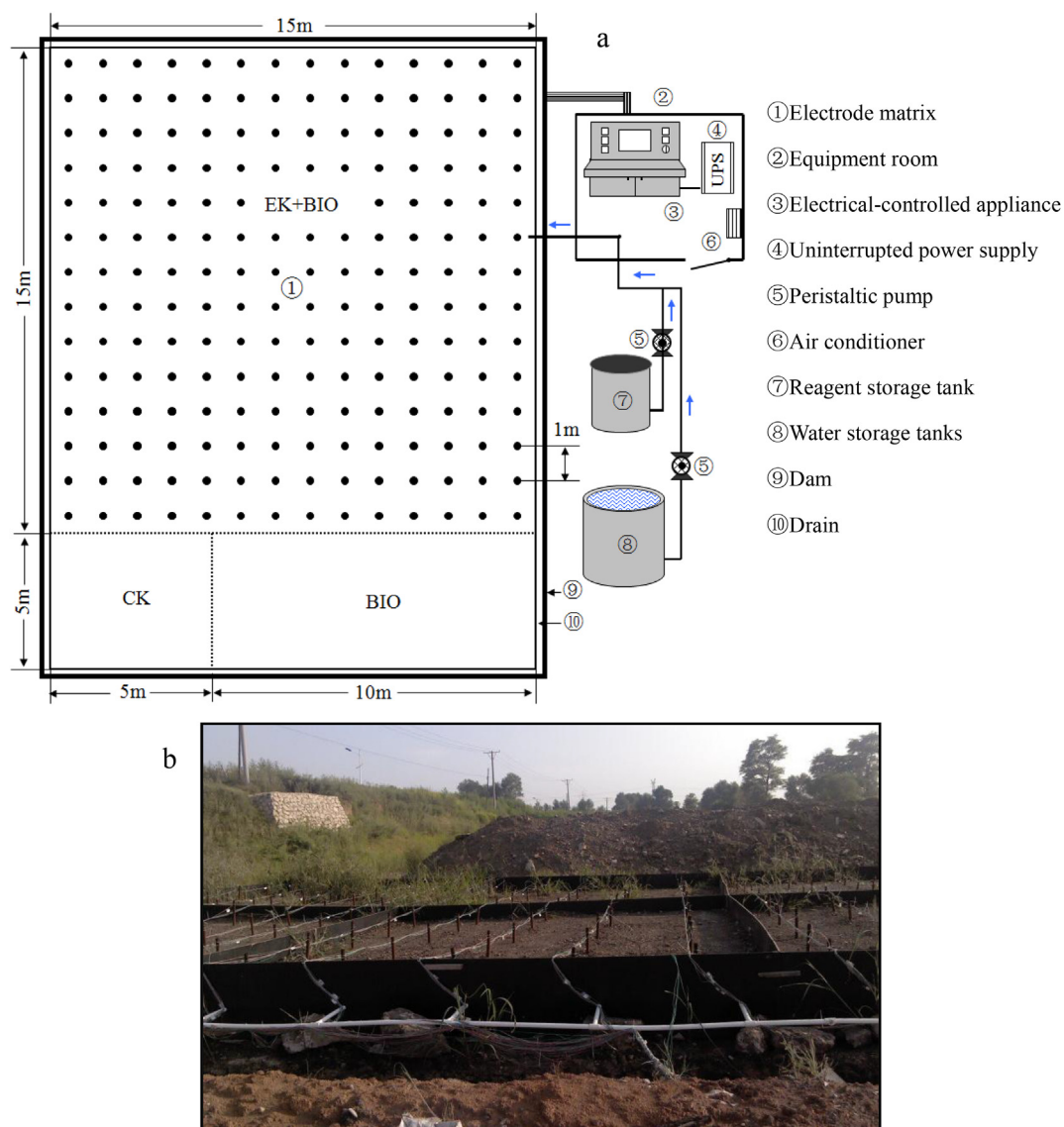


Fig. 1. Schematic diagram of pilot scale electro-bioremediation and configuration of the instrumentation.

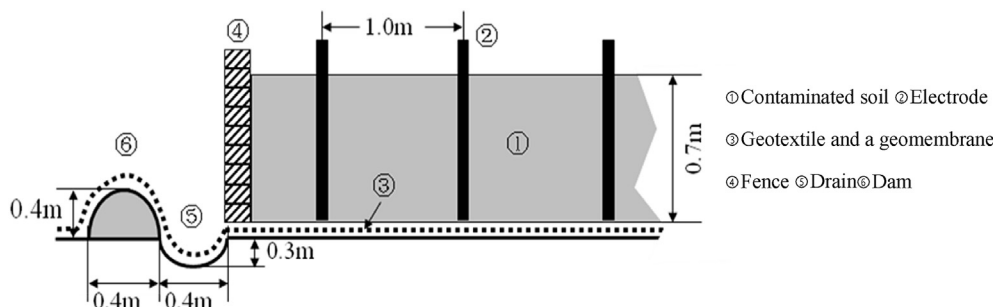


Fig. 2. Side views of the construction on site.

2.3. Experimental systems

A schematic diagram of the experimental system is shown in Fig. 1. The system consisted of three soil chambers, 225 cylindrical electrodes distributed into matrices, an equipment room, electrical-controlled appliance, uninterrupted power supply (UPS), peristaltic pump, air conditioner, nutrient storage tank and water storage tanks (Fig. 1a). The three chambers were divided by polyvinylchloride board, and all the sides and bottoms were laid with geotextile and a geomembrane (Fig. 1b).

The whole remediation area was fenced by polyvinylchloride board, and a channel and dam was set up outside the fence for avoiding contaminants leaking into surrounding areas (Fig. 2). Column-shaped stainless-steel electrodes with a length of 80 cm and a diameter of 2 cm were used to generate the electric field. The distance between two electrodes was 1 m. The electrical-controlled apparatus was capable of reversing the polarity of the electric field rotationally by each row and column in turn at an optional interval, thus generating a 2-D electric field. A UPS provided a constant direct-current electrical potential difference of 24 V for the EK-BIO treatment. During operation, peristaltic pumps were used to supplement regularly water and nutrients (N, P) to maintain soil moisture and nutrition. The electrical-controlled appliance, UPS and air conditioner were placed in the equipment room.

2.4. Experimental design

The three chambers were prepared and filled with contaminated soil (Fig. 1). They were used to conduct the three treatments (CK, BIO and EK + BIO) (Table 3). The chamber dimensions of CK, BIO and EK + BIO were 5 m (length) \times 5 m (width) \times 0.7 m (depth), 10 m (length) \times 5 m (width) \times 0.7 m (depth) and 15 m (length) \times 15 m (width) \times 0.7 m (depth), respectively. Before remediation, the soil used for BIO and EK + BIO was inoculated with the bacterial suspension at an initial inoculation in the order of 2.19×10^7 cfu (colony-forming units) g^{-1} dry soil. All contaminated soil was rehydrated to moisture content about 25% (w/w) with the mineral medium. The prepared contaminated soil was placed into the chamber in layers and each layer was tamped to minimize void space. In the EK + BIO chamber, a constant electric field gradient of 0.24 V cm^{-1} was applied. The polarity of the electric field was reversed rotationally by each row and column every 10 min. In the

CK treatment, neither an electric field nor bacterial suspension was applied.

2.5. Sample collection

In the EK + BIO treatment, sampling sites S_1 , S_2 , S_3 and S_4 were located as shown in Fig. 3a and b (near electrodes, the center of four electrodes, the middle of two electrodes, and the middle of sites S_1 and S_2). The intensity of electric field at each site is shown in Fig. 3c. In CK and BIO, the sampling sites were arranged at random. All treatments were conducted under natural conditions from May to October at State Environmental Protection Engineering Center (Shenyang) for Hazardous Waste Disposal, and daily rainfall and temperature in this region are shown in Fig. 4. Samples (20 mm diameter \times 0.7 m height) were collected once by a metal tube (20 mm inner diameter) every 14 days. For each sampling round, three samples at identical sampling sites were thoroughly mixed together to form a composite sample before analysis.

2.6. Analytical procedure

The soil pH, temperature, electric current, PAH concentration and bacterial number were analyzed during the treatments. Except for electric current, other analytical determinations were performed in triplicate, and the results were calculated as means. All data obtained in the study are presented as mean \pm standard deviation.

Soil pH was measured with a pH meter at a soil to water ratio of 1:2.5 (Lu, 2000). Soil temperature at the 30-cm depths of each sampling site was measured with a digital thermometer when sample collection. Soil electric current was monitored and recorded with an auto-controlled system every day.

The total PAHs were extracted according to the EPA Standard Method 3550C (USEPA, 1996). The concentrations of 16 PAHs (US EPA priority PAHs) were determined by high-performance liquid chromatography (HPLC; Waters Corporation, Milford Massachusetts, USA) equipped with a variable wavelength fluorescence detector (FLD, waters 2475) and a Waters PAH Column (250 mm \times 4.6 mm i. d., 5 μm particle size). Prior to injection, the extracted PAHs were filtered through a 0.22 μm Teflon filter. Aliquots of 10 μl of the sample solutions were injected into the HPLC system by an autosampler, and the column temperature was 25 $^\circ\text{C}$.

Table 3
Summary of different treatments.

Treatment	Dimensions (m)	Bacteria (cfu g^{-1} dry soil)	Electric field (V cm^{-1})	Moisture content (%)
CK	5 \times 5 \times 0.7	5.23×10^5	0	25
BIO	5 \times 5 \times 0.7	2.19×10^7	0	25
EK + BIO	15 \times 15 \times 0.7	2.19×10^7	0.24	25

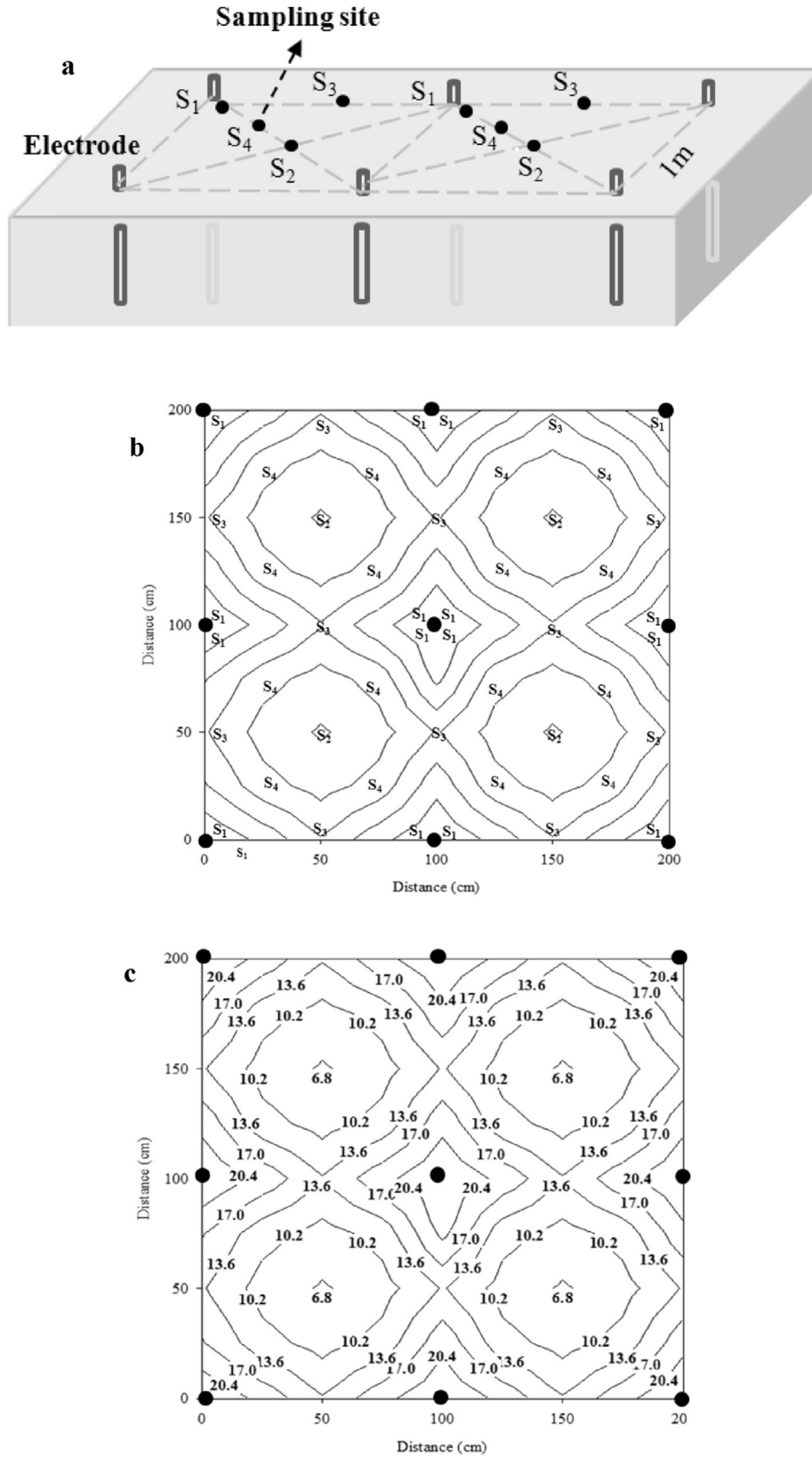


Fig. 3. Distribution of sampling sites (a, b) and intensity of electric field (c) in the EK-BIO treatment.

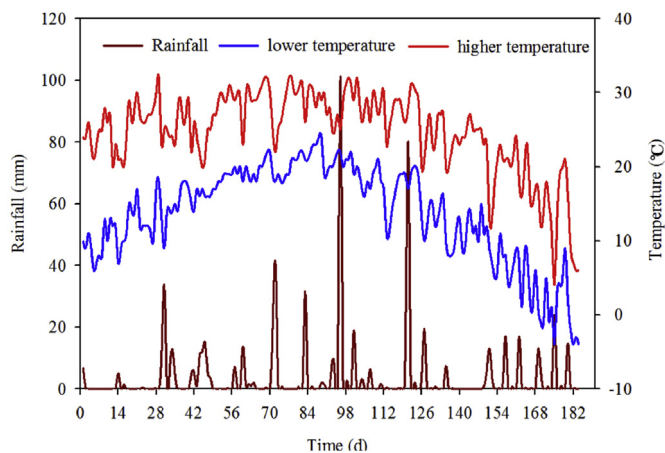


Fig. 4. Daily rainfall and temperature during the treatment process (Data from Shenyang Meteorological Service).

The HPLC running protocol was as follows: the gradient elution program used consisted of 60% water and 40% acetonitrile for 2 min, then programmed to 100% acetonitrile in 12 min at a flow rate of 1.0 ml min^{-1} .

Genomic DNA was extracted from freeze-dried soil (0.5 g) using Fast DNA® spin kit for soils (MP Biomedicals) following manufacturer instructions. Total bacteria numbers were measured by real-time PCR of 16SrRNA genes. Real-time PCR was performed in a 25 μl volume using the SYBR® Premix Ex Taq™ II kit with SYBR green I (Takara, Japan) on an ABI 7000 real-time PCR detection system (Applied Biosystems, Foster City, CA, USA). The bacteria number was estimated by using the primers 8 F (5'-GAGAGTTT-GATCCTGGCTCAG-3') and 518 R (5'-ATTACCGCGGCTGCTGG-3') and the amplification procedure was 95 °C for 15 s, 55 °C for 30 s, then 40 cycles at 95 °C for 15 s, 55 °C for 30 s, and 72 °C for 45 s, with a final extension at 72 °C for 5 min.

2.7. Toxicity equivalent concentrations of soil PAHs

The toxicity equivalency factors (TEFs) have been developed for assessing the toxicity equivalent concentrations (TEQ_{BaP}) of soil PAHs (Nisbet and LaGoy, 1992; USEPA, 1993). The factor for each of the PAHs expressed its toxicity relative to benzo[a]pyrene, which has a TEF of unity (Table 4). The concentration of the individual PAHs is multiplied by its TEF, and these values are summed to yield total toxicity equivalent concentrations (TEQ_{BaP}). By this means, the concentrations of a suite of PAHs can be represented by a single concentration, which reflects the overall toxicity of the PAHs within the sample for which TEFs have been assigned. The equation is as follows:

Table 4
Toxicity equivalence factors (TEFs) of 16 PAHs

Component	TEFs	Component	TEFs
Naphthalene(Nap)	0.001	Benzo(a)anthracene (BaA)	0.1
Acenaphthylene(Any)	0.001	Chrysene (Chr)	0.01
Acenaphthene(Ane)	0.001	Benzo[b]fluoranthene (BbF)	0.1
Fluorene (Fle)	0.001	Benzo[k]fluoranthene (BkF)	0.1
Phenanthrene (Phe)	0.001	Benzo(a)pyrene (BaP)	1
Anthracene (Ant)	0.01	Dibenzo(a,h)anthracene (DahA)	1
Fluoranthene (Flu)	0.001	Benzo(g,h,i)perylene (BghiP)	0.01
Pyrene (Pyr)	0.001	Indeno(1,2,3-cd)pyrene (IcdP)	0.1

$$\text{TEQ}_{\text{BaP}} = \sum_{i=1}^n C_i \times \text{TEF}_i \quad (1)$$

where i is the individual PAH, TEQ_{BaP} is total toxicity equivalent concentrations (mg kg^{-1}), C_i is the measured concentration of individual PAH (i) (mg kg^{-1}), and TEF_i is the toxicity equivalency factors of individual PAHs (i).

2.8. Energy consumption and cost

The additional costs (compared to conventional bioremediation) mainly include cost of electrode materials and energy consumption. The energy consumption (kWh/m^3) is calculated using Equation (2).

$$\text{Energy consumption} = \int \frac{IE}{V_{\text{soil}}} dt \quad (2)$$

where I is the electric current (mA), E is the applied electric potential (V), V_{soil} is the volume of the treated soil (m^3) and t is the time of treatment (d).

2.9. Statistical analysis

Statistical analysis was performed with SPSS for Windows Ver. 11.5 (SPSS Inc, Chicago, IL, USA). The graphs were plotted with Sigma Plot 10.0 (Systat Software Inc., USA). Bacterial number was calculated per gram of freeze-dried soil and log-transformed (\log_{10}^x) to improve the homogeneity of the variance of the data.

3. Results and discussion

3.1. Soil pH and temperature

Lear et al. (2007) reported that changes in microbial community and activity were mainly caused by the changes of soil pH under the constant electric field. Therefore, the pH control was the most critical parameter for survival of microorganisms during the EBR process (Yeung and Gu, 2011; Gill et al., 2014). The temporal and spatial changes of soil pH in the three treatments are shown in Fig. 5. The results indicate that soil pH decreased slightly as treatment time increased in EK + BIO; it reduced 0.33 after 182 days compared with the initial value of 6.95 (Fig. 5a). In contrast, soil pH remained constant in CK and BIO. Fig. 5b also shows that soil pH at each site in EK + BIO was slightly reduced. Although the soil pH reduced the most at site S_1 , it decreased only 0.41 after 182 days (Fig. 5b). It is well known that pH changes are caused by the transport of protons and hydroxyl ions generated by water electrolysis on the electrode surfaces. To maintain a suitable pH in the soil during EBR processes, periodic polarity reversal has been used in some different treatments such as electro-remediation of soils with emerging contaminants (Yang et al., 2016) and EBR of petroleum and diesel-polluted soils (Guo et al., 2014; Mena et al., 2016a, 2016b). In these studies, successful results were obtained, and pH was controlled by automatically neutralizing protons and hydroxyl ions. In the present study, the duration of electric field rotational reversal for each row and column was 10 min, which was beneficial for maintaining a constant pH.

Temperature is also a very important parameter affecting the microbial activity during the process of EBR. The increase in temperature occurs due to the water electrolysis reaction (exothermic reaction) occurring in the electrode and ohmic resistance by soil that acts as electrical resistance (Barba et al., 2017; Ramadan et al., 2018). For EK-BIO treatments it is an additional mechanism to

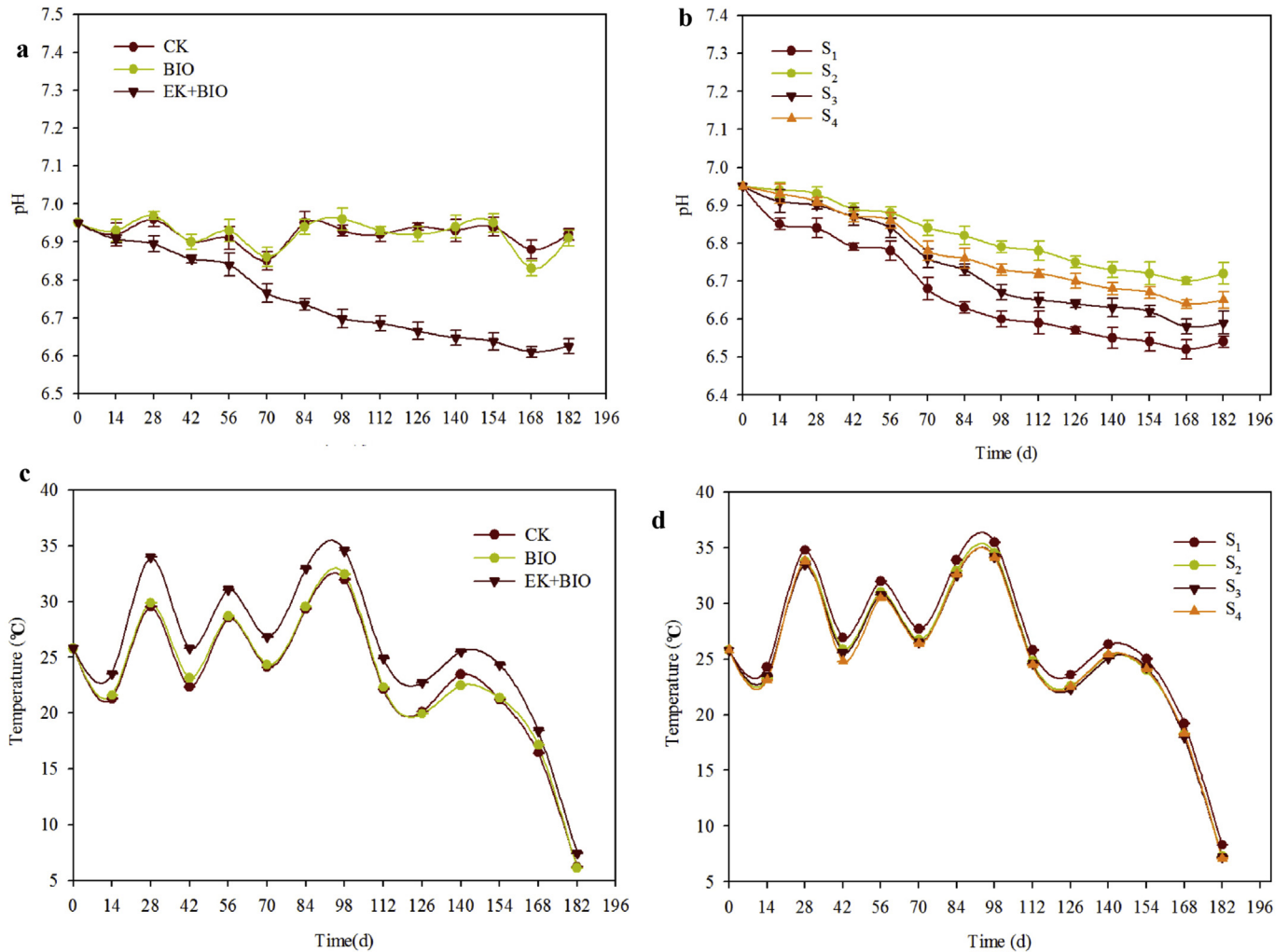


Fig. 5. Changes of soil pH and temperature at different times and sites (a: pH changes in three treatments; b: pH changes in EK + BIO treatment; c: temperature changes in three treatments; d: temperature changes in EK + BIO treatment).

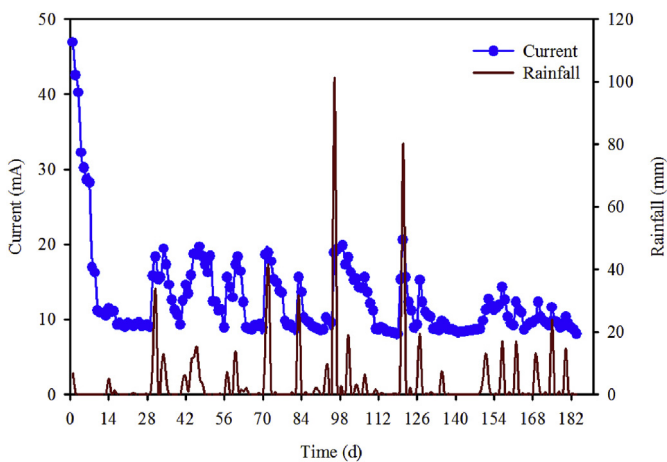


Fig. 6. Variations of soil current during the EK + BIO treatment.

enhance bioremediation, and Suni et al. (2007) observed temperature increase from ambient 6 °C to 16–50 °C when electric current was 1–1.5 A in a field trial. Fig. 5c shows the temporal changes of soil temperature in the three treatments. The results indicate that

soil temperature in EK-BIO was higher 1.2–4.4 °C than that in CK and BIO. Temperature rises occurring on the pilot-scale EBR is not high enough when compared with laboratory-scale studies where the temperature can rise from 7.6 °C to maximum of 12.1 °C in 1 V cm⁻¹ of electric field (Li et al., 2016). This may be related to the processes such as losses of heat to environment and the evaporative cooling. In general, the largest temperature rise in the reactor is located in the area around anode (Ramadan et al., 2018). However, in this study the temperature values were nearly identical at each site in EK-BIO (Fig. 5d). Barba et al. (2017) reported that polarity reversal was an efficient option for pH, moisture and temperature control. In the present study, the results showed that the operation mode of electric field could also control the constant temperature at all sites during field-scale remediation.

3.2. Soil electric current

The electric current was monitored on-line throughout the EBR, as shown in Fig. 6. The electric current is inversely proportional to soil resistance, which is determined by the conductive ion content, soil moisture content and temperature (Chen et al., 2017). Under the electric field, soil ions migrate to the vicinity of the cathode and anode, causing the soil resistance to change substantially (Jin, 2013). The electric current declined from 46.9 to 16.2 mA in the

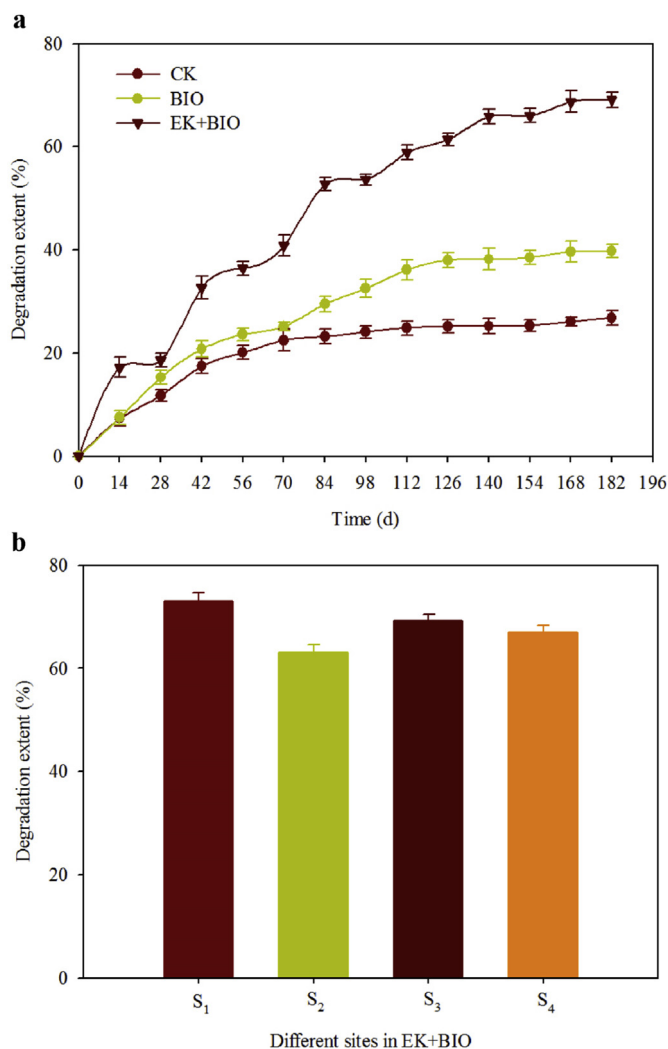


Fig. 7. Changes of PAH degradation extent at different times and sites (a: in three treatments; b: in EK + BIO).

first 9 days, then maintained at around 10 ± 1 mA from 10 to 29 days. The phenomenon was also reported by Kim et al. (2009) and Cheng et al. (2017). The investigation of Cheng et al. (2017) showed that electromigration which contributed to the ionic transportation dominated in the first 10 days, and the current decreases rapidly with the attenuation of electromigration. However, the attenuation of electromigration is related to the reduction of conductive ions. After 9 days, the decrease of conductive ions in the soil matrix led to the increase of actual soil resistance. Over 30–182 days, the electric current fluctuated according to the rainfall. Seasonal variations will cause changes of soil resistance. Rainfall and temperature are the most obvious factors affecting soil resistance; the soil resistance decreases or increases because of the infiltration of rainfall or the freezing effect of soil (Baraud et al., 1999; Li, 2013). In this study, the treatment process was conducted under natural conditions, thus the change of electric current was not only affected by the change of soil ions, but also by rainfall and temperature. Fig. 6 shows that the temperature had no influence on the change of current. Thus, it can be concluded that the changes of soil current in the EK + BIO treatment were influenced mainly by soil ions and the rainfall.

3.3. Degradation extents of total PAHs

Fig. 7a shows the cumulative degradation extents of PAHs during the treatment period. The results demonstrate that the degradation extents of PAHs were higher in EK + BIO than those in BIO and CK at 182 days. The degradation extent of PAHs in EK + BIO reached 69.1%, representing an enhancement of 29.3% and 42.2% compared with those in BIO and CK, respectively. The approximate results were observed by Guo et al. (2014) that EBR significantly enhanced the removal of total petroleum hydrocarbons (TPH). Compared with CK, the increase of the PAH degradation extent in EK + BIO was more than twice as that in BIO. This indicates that the utilization of an electric field could improve the degradation efficiency of PAH-degrading microorganisms despite the low degradation efficiency of biological remediation alone in situ field-scale remediation. This is because electrokinetics can deliver nutrients to the bacteria in the soil and increase mixing between bacteria and contaminants (Elektorowicz and Boeva, 1996; Schmidt et al., 2007). However, the efficiency of EK + BIO in pilot scale in this study is lower than that at laboratory reported by Li et al., (2012) and Martínez-Prado et al., 2014. This may be related to the complex environment of sites and low pollutant bioavailability.

Some studies have indicated a positive relationship between the degradation extents of pollutant and electric intensity (Niqui-Arroyo et al., 2006; Fan et al., 2014). The degradation extents of PAHs at different sites in EK + BIO in the current study are shown in Fig. 7b. At 182 days, the maximum degradation extent of PAHs (73.0%) was achieved near the electrode (site S₁), with the strongest intensity of electric field. The minimum degradation extent of PAHs (63.1%) was observed at the center of the four electrodes (site S₂) with the weakest electric intensity. Although the degradation extent of PAHs at site S₃ was higher than that at site S₄, there was little difference between them. On the whole, the electric field with alternating polarity in EK-BIO kept the degradation extent of PAHs relatively uniform during the process of remediation at the field site. The result is consistent with the research by Guo et al. at laboratory (2014).

3.4. Degradation extents of different-ring PAHs

It is well known that microbial degradation can effectively remove low-ring (2–3-rings) PAHs, but the degradation of high-ring (>3 rings) PAHs is difficult because their strong stability, low aqueous solubility and high sorption to soil particles (Kanaly and Harayama, 2010; Mohan and Kisa, 2006). The degradation extents of individual extracted PAHs were analyzed at 182 days, as shown in Fig. 8a. The degradation extents of 13 PAHs gradually decreased with the increase of ring number, and considerable difference existed in degradation extents of different-rings PAHs in the three treatments. In general, the degradation extents of different-ring PAHs in EK + BIO were higher than those in BIO and CK. The total degradation extents of 3-, 4-, 5- and 6-ring PAHs in EK + BIO were 88.4%, 76.2%, 48.2% and 35.5%, respectively. The total degradation extents of 4–6-ring PAHs in EK + BIO (65.9%) enhanced by 65.3% and 44.4% compared with those in CK and BIO, respectively. In contrast, there was little difference in 3-ring PAH degradation extent in all treatments. Li et al. (2012) demonstrated in the laboratory that the application of an electric field is conducive to 4–6-ring PAH degradation. Shi et al. (2008) reported electroosmotic flow could enhance desorption of contaminants by creating flow within the double layer (Shi et al., 2008). In the present study, the increase of 4–6-ring PAH degradation extent in EK + BIO may be related to the role of electroosmotic flow in stimulating desorption of high-ring PAHs. The above analysis suggests that EBR could be a potentially useful approach for the treatment of sites contaminated

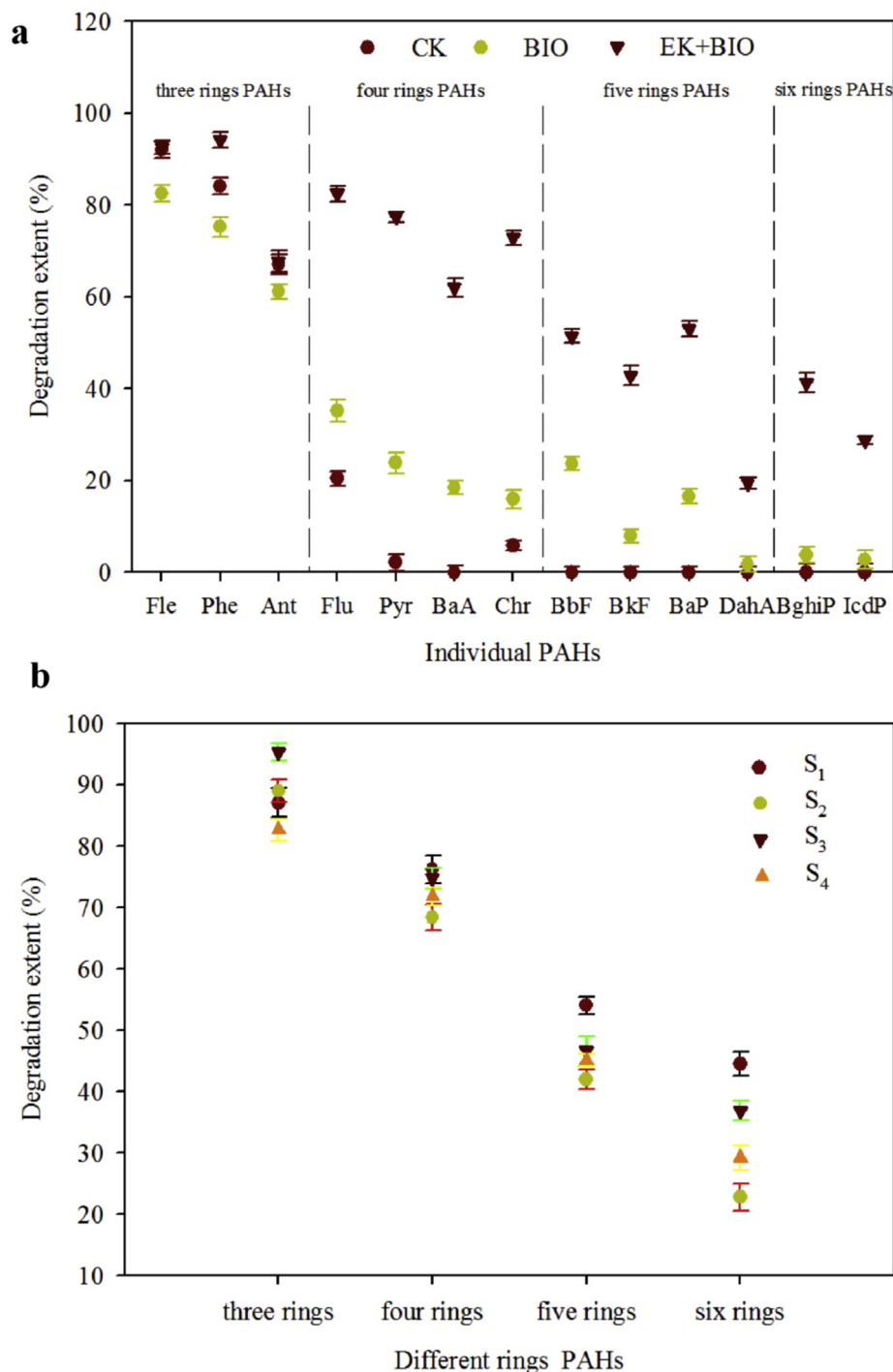


Fig. 8. Degradation extents of individual PAH in all treatments (a) and degradation extents of different-ring PAHs at different sites in EK + BIO treatment (b).

with high-ring PAHs.

The difference of total degradation extents of 3-, 4-, 5- and 6-ring PAHs at different sites in EK + BIO were analyzed (Fig. 8b). Except for 3-ring PAHs, the degradation trend of 4-, 5- and 6-ring PAHs in different sites, the degradation trend of total PAHs. The degradation extents of 4-, 5- and 6-ring PAHs at the different sites decreased in the order $S_1 > S_3 > S_4 > S_2$. There were no significant differences among the degradation extents of 4- and 5-ring PAHs at all sites. However, for 6-ring PAHs, the differences in degradation

extent were significant ($P < 0.05$) at all sites. The results indicate that the electric field intensity had a strong influence on the degradation of 6-ring PAHs. The stronger the electric field intensity, the higher the degradation extents of 6-ring PAHs. It may be due to synergistic effect of electric field and degradation microorganisms, and that further research into these particular effects is required. It is important to note that, to our knowledge, there are few publications available about the relationship between electric field and the degradation of high-ring PAHs.

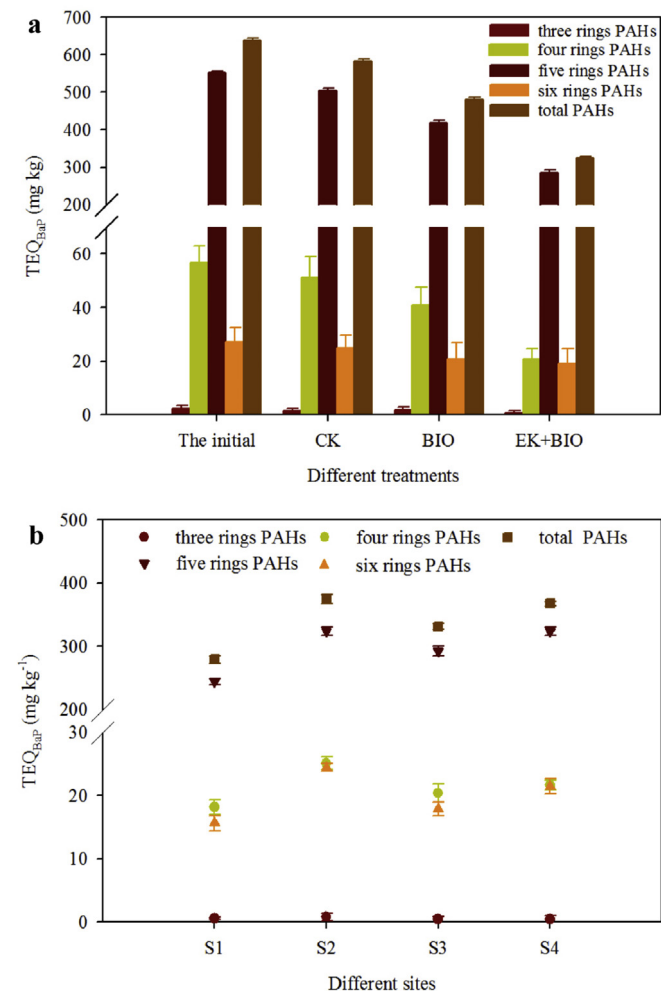


Fig. 9. Changes of toxicity equivalence concentration of PAHs (a: in different treatments; b: at different sites in EK + BIO).

3.5. Toxicity equivalent concentrations of soil PAHs

The toxicity of contaminated soils was often assessed by analyzing the TEQ_{BaP} of PAHs. Fig. 9a shows the TEQ_{BaP} of total and different-ring PAHs in the three treatments before and after remediation. The TEQ_{BaP} of total PAHs in the initial soil was $638.10 \text{ mg kg}^{-1}$, the contribution of 3-, 4-, 5- and 6-ring PAHs accounted for 0.36%, 8.91%, 86.47% and 4.26%, respectively. This indicates that there was a large potential health risk associated with the soil of the abandoned coking plant site, and the risk was almost entirely caused by 5-ring PAHs. At 182 days, the TEQ_{BaP} of total and different-ring PAHs was lowest in EK + BIO. The TEQ_{BaP} of total PAHs reduced $312.07 \text{ mg kg}^{-1}$ and the TEQ_{BaP} of 4-, 5- and 6-ring PAHs reduced by 63.7%, 48.2% and 30.1%, respectively. The TEQ_{BaP} of total and different-ring PAHs at different sites in EK + BIO is shown in Fig. 9b. The TEQ_{BaP} of PAHs was lowest at site S₁ (near the electrodes), and highest at site S₂ (the farthest from the electrodes). These findings indicate that EBR can effectively reduce the risks of soil at abandoned coking plant sites and the intensity of the electric field affects the TEQ_{BaP} of soil PAHs. Istrate et al. (2018) evaluated the remediation effect with regard to the electrochemical technique used for soil decontamination using the incremental lifetime cancer risk (ILCR), the results indicated that the health risks from hydrocarbon contaminated soils was reduced by using electric field-based treatment. TEQ and ILCR are all the means

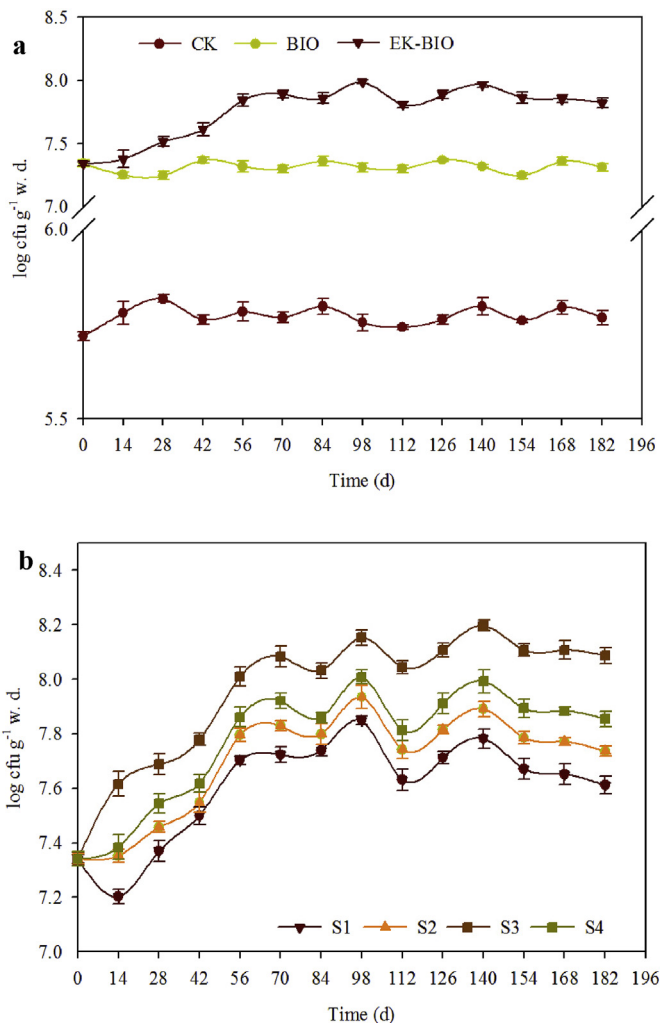


Fig. 10. Changes of bacterial numbers as treatment time increased (a: in three treatments; b: at different sites in the EK + BIO treatment).

of assessing and managing potential risk to human and ecosystem health. To our knowledge, there has been little research on the changes of TEQ of PAHs under electric field.

3.6. Bacterial numbers

Fig. 10 shows the changes in bacterial numbers during the treatment process. The results of real-time PCR show that the total bacterial numbers expressed by 16 S rRNA gene copy numbers fluctuated by the same order of magnitude (10^7) both in EK + BIO and BIO (Fig. 8a). The bacterial numbers in BIO decreased slightly compared with the initial amount (0 days), which may be related to the environmental impact or indigenous bacteria (Blasco et al., 1997). In contrast, in EK-BIO, the bacterial numbers clearly increased and were approximately 1–5 times those in BIO during the whole process. Xu et al. (2010) reported that the exchange polarity technique resulted in an even distribution of nutrients and electrokinetics was successful in delivering nutrients to the bacteria in the soil compared with one-direction electric fields.

The bacterial numbers all increased, except those at site S₁, decreased during the first 14 days in EK-BIO (Fig. 10b). The bacterial numbers were not significantly different ($P > 0.05$) among sites S₁, S₂, S₃ and S₄. Zhao et al. (2009) reported that the fluctuation of soil pH near the electrode can be effectively reduced if the electrode

Table 5Pearson correlation analysis among degradation extent, TEQ_{BaP} and Bacterial numbers at different sites in EK + BIO.

Sites	Variable	Degradation extent (%)	TEQ _{BaP} (mg kg ⁻¹)	Bacterial number (log cfu g ⁻¹ w.d)
S ₁	Degradation extent (%)	1	-0.975 ^b	-0.711
	TEQ _{BaP} (mg kg ⁻¹)	-0.975 ^b	1	0.760
	Bacterial number(log cfu g ⁻¹ w.d)	-0.711	0.760	1
S ₂	Degradation extent (%)	1	-0.957 ^a	0.863 ^b
	TEQ _{BaP} (mg kg ⁻¹)	-0.957 ^a	1	-0.910 ^a
	Bacterial number(log cfu g ⁻¹ w.d)	0.863 ^b	-0.910 ^a	1
S ₃	Degradation extent (%)	1	-0.985 ^b	0.858 ^a
	TEQ _{BaP} (mg kg ⁻¹)	-0.985 ^b	1	-0.829 ^a
	Bacterial number(log cfu g ⁻¹ w.d)	0.858 ^a	-0.829 ^a	1
S ₄	Degradation extent (%)	1	-0.929 ^a	0.842 ^a
	TEQ _{BaP} (mg kg ⁻¹)	-0.929 ^a	1	-0.823 ^a
	Bacterial number(log cfu g ⁻¹ w.d)	0.842 ^a	-0.823 ^a	1

^a Correlation is significant at the 0.05 level (2-tailed).^b Correlation is significant at the 0.01 level (2-tailed).

switching period is less than 10 min, thus eliminating the effect of pH caused by electrode reaction on the number of microorganisms. In this study, the application of periodic polarity reversal was favorable to keep soil properties and microorganisms uniform. In addition, a recent study explored the possibility of providing oxygen (electron acceptor) to polluted soils by electrokinetics for aerobic bioremediation treatments of the soils, which is required for aerobic microbial growth (Ramirez et al., 2014).

3.7. Relationships of degradation extent, TEQ_{BaP} and bacterial number at different sites in EK + BIO

The present study has shown that the changes of degradation extents of total PAHs (Fig. 7b), TEQ_{BaP} of total PAHs (Fig. 9b) and bacterial numbers (Fig. 10b) at different sites in EK + BIO. In order to further study their relationships, Pearson correlation analysis among degradation extent of total PAHs, TEQ_{BaP} of total PAHs and bacterial numbers was performed, as shown in Table 5. The results show that degradation extent and TEQ_{BaP} have significant negative correlation at all sites, reaching -0.975, -0.957, -0.985 and -0.929 respectively ($p < 0.05$). However, there were differences in correlations between degradation extent and bacterial number at all sites. Except for the negative correlation between degradation extent and bacterial number at site S₁, there was a significant positive correlation between degradation extent and bacterial number at other sites (Site S₂, S₃ and S₄) ($p < 0.05$). Luo et al. (2004) and Zeyoudi et al. (2015) reported that electrochemical reaction in the vicinity of the electrodes inevitably produces a negative effect on soil microorganism. In this study, electrochemical reaction at site S₁ (near the electrodes) which generated a variety of chemical oxidants or causes the changes of soil conditions, thus affecting the soil bacterial number and activity, which in turn influenced the degradation extent of PAHs. Nevertheless, there was little difference in degradation extent at all sites (Fig. 7b), which illustrated that the degradation of PAHs at site S₁ not only depended on biodegradation but also electrochemical reactions. In addition, it could be concluded that the removal of PAHs mainly depends on the microbial degradation according to the positive correlation between degradation extent and bacterial number at other sites (Site S₂, S₃ and S₄). The results are consistent with the researches by Guo et al. (2014) and Li et al. (2016).

3.8. Cost analysis

The costs of energy consumption and electrodes were calculated at the end of 182-day remediation period. According to Equation (2), the energy consumption was estimated as 8.52 kWh/m³ of

contaminated soil. Also, the price of electrical energy was 0.14 dollars per kWh (China). So, the cost of energy consumption was 1.19 dollars/m³ in this study. The price of each stainless-steel electrode was 5.69 dollars, which were provided by the manufacturer (Shenyang Shangpin Stainless Steel Co., Ltd, China). Thus, the cost of electrode was 8.13 dollars for per m³ contaminated soil. These findings have important economic implications, particularly in consideration of the fact that the energy cost was only a very insignificant portion of the total cost of electro-bioremediation. In view of the removal efficiencies of PAHs, power consumption and cost of electrode materials, the EBR approach can be a cost-effective and feasible alternative for the treatment of soil from abandoned coking plant sites.

4. Conclusion

The findings of this study suggest that EBR may be used to repair the soil from abandoned coking plant sites. Under natural conditions, the degradation extents of total PAHs and high-ring (>3 rings) PAHs were apparently enhanced under EBR compared with bioremediation alone. There was little difference in the degradation extents of PAHs at all sites in the electric field, which indicates that the electric field with alternating polarity was favorable to maintain uniform degradation of PAHs. In addition, the TEQ_{BaP} of PAHs was reduced after the application of electric field. With low costs of energy and materials, EBR can be a cost-effective approach for remediation of the heavily PAH-contaminated soil in abandoned coking plant sites.

Author contribution statement

Fengmei Li: carried out experiments, analyzed samples, wrote the manuscript. Shuhai Guo: designed experiments, revised the manuscript. Bo Wu: carried out experiments, analyzed data. Sa Wang: carried out experiments, analyzed samples.

Declaration of competing interest

No conflict of interest declared.

Acknowledgements

This research was supported by the National Natural Science Foundation of China (21677150 and 21507144). We thank anonymous reviewers for their constructive comments that helped improve this manuscript.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2019.125467>.

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