Electrochemical Stimulation of PAH Biodegradation in Sediment

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Natural attenuation of PAH in sediments is usually slow due to prevailing anaerobic conditions in sediments. Electrochemical stimulation of PAH biodegradation is proposed and demonstrated for remediation of contaminated sediment. Two graphite electrodes were placed horizontally at different depths in PAH-spiked sediments; the cathode was near the water-sediment interface and the anode was laid in the deeper sediment. An external power of 2 V was continuously applied to the electrodes to stimulate PAH biodegradation. Redox potential around the anode in powered reactors increased gradually, and was 50–150 mV higher than that in the control. pH around the anode decreased to ∼6 from an initial value of 6.4 or 6.7 in powered reactors, which reflected water electrolysis. Phenanthrene concentration at the anode decreased with time, showing a unique Z-shaped profile in the sediment in powered reactors. PAH degrading genes around the anode in powered reactor were found to increase compared to the control reactor, which provided microbial evidence of biodegradation. These findings demonstrated the capability of this novel bioelectrochemical technology for the remediation of PAH-contaminated sediment.

Keywords Sediment, PAH, bioremediation, electrochemistry

Introduction

Contaminated sediment is a longstanding problem at many sites across the United States and around the world. Contaminants detected in sediments include polychlorinated biphenyls (PCBs), heavy metals, chlorinated solvents, pesticides, polycyclic aromatic hydrocarbons (PAHs), etc. Sediments can serve as contaminant sources for transport and exposure to aquatic biota particularly with bioaccumulative contaminants. Hydrophobic organic contaminants such as PAHs typically bind strongly to organic matter in sediments and these sediment-bound pollutants serve as long-term exposure sources to aquatic ecosystems.

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PAHs may be naturally removed in sediments by microbial degradation. The ability of aerobic microorganisms to degrade PAHs is well known and has been observed in laboratory and field studies with a variety of soils and sediments for many years (Hambrick et al., 1980; Bauer and Capone, 1985; Heitkamp and Cerniglia, 1987; Boyd et al., 2005). PAH degradation in anaerobic conditions has also been reported, but the rate is much slower compared to that in aerobic conditions (Johnson and Ghosh, 1998; Rockne and Strand, 1998; Rockne et al., 2000; Chang et al., 2002; Rothermich et al., 2002). Sediments are generally anaerobic, except in the upper layer adjacent to water, ranging from millimeters to centimeters, and biodegradation of PAHs is greatly hindered by oxygen shortage in sediments. There is an urgent need to develop efficient techniques that stimulate PAH biodegradation for the management of PAH-contaminated sediment.

Recently, electrochemical remediation technologies have been shown to have great potential for contaminated soil and sediment. During electrochemical remediation, organic contaminants may be destroyed or converted by either direct or indirect processes. Numerous studies have focused on the use of direct current (DC) to oxidize or reduce organic contaminants directly (Goel et al., 2003; Alshawabkeh and Sarahney, 2005; Petersen et al., 2007). A sequential electrolytic reduction-oxidation system was developed to degrade nitrobenzene and energetic compounds (Gilbert and Sale, 2005; Sun et al., 2012). Indirect electrolysis also contributes to contaminant removal during electrochemical oxidation/reduction processes. During indirect anodic oxidation, strong oxidants such as ozone, hydrogen peroxide, and chlorine are generated at the anode instead of oxygen. The contaminant is then oxidized by these strong oxidants (Goel et al., 2003). Another widely used technique is electrokinetic remediation, which uses electric currents to extract heavy metals, certain organic compounds, or mixed contaminants from soils and slurries (Acar et al., 1995; Saichek and Reddy, 2005; Al-Hamdan and Reddy, 2008; Kim et al., 2013; Rajic et al., 2013; Ruiz et al., 2014; Zhang et al., 2014). All these approaches are based on electrochemical principles and they did not consider biodegradation potential by indigenous microbial populations in soil and sediment.

During PAH biodegradation, microorganisms require electron acceptors for the oxidation process. A novel alternative is to supply electron acceptors by direct application of electricity. Recent advances in bioelectrochemical systems (BES) show that biodegradation of aromatic hydrocarbons and chlorinated contaminants was stimulated with electrodes serving as electron acceptors and donors in a mineral medium or sediment slurry (Gregory et al., 2004; Thrash et al., 2007; Strycharz et al., 2008; Aulenta et al., 2009; Zhang et al., 2010; Chandrasekhar and Mohan, 2012; Friman et al., 2012).

To date, bioelectrochemical systems for remediation have just begun to be applied to an ideal controlled environment. Most of the previous studies focused on microbial degradation by a pure or mixed culture in mineral medium, while some were extended to sediment slurry systems. These bioelectrochemical reactors are complete mixing systems with no mass transfer limitation, and redox and pH changes induced by electrochemical reactions were not addressed in these studies. Therefore, it is necessary to develop a practical bioelectrochemical technology for remediation of PAH-contaminated sediment, quantify the extent of biodegradation, and investigate redox and pH changes in stagnant sediments. In this study, a bioelectrochemical system was constructed for the bioremediation of PAH-contaminated sediment (Figure 1). Two areal graphite electrodes were laid horizontally and perpendicular to contaminant flux. A vertical layered system was designed to reduce contaminant migrating from deeper sediment, and protect both benthic and overlying water ecosystems from the impacts of sediment. A low voltage was applied to the electrodes to encourage biodegradation through the electrochemical process. Water electrolysis reaction
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Figure 1. Conceptual model for electrochemical stimulation of PAH biodegradation in sediment. Oxygen is produced at the anode to stimulate PAH biodegradation.

occurred at the electrodes and oxygen was produced at the anode. It is expected that this produced oxygen makes the local redox condition more oxidizing and stimulates biodegradation of PAH. The objective of this study is to demonstrate electrochemical stimulation of PAH biodegradation in stagnant sediments.

Materials and Methods

Microcosm Set-Up and Operation

Three 400-mL beaker reactors were constructed to study stimulation of biodegradation by electrochemical techniques in stagnant sediment. An external voltage of ~2 V was applied to two reactors (ElecR1 and ElecR2), while there was no voltage applied to the control reactor. In the control and ElecR1 reactors, 0.05 g/mL of siderite (Prince Agri Products, Inc., Quincy, IL) was mixed with sediment to provide long-term pH buffering capacity.

PAH-contaminated sediment was collected from the Anacostia River in Washington, DC, and sieved through 2 mm. A previous study showed that PAH-degrading bacteria are present in the sediment and PAH biodegradation by indigenous microbial populations could be stimulated by supplying oxygen (Yan and Reible, 2012). Clean sediment was obtained from LSU University Lake in Baton Rouge, LA, and sieved through 2 mm. Anacostia River sediment and University Lake sediment were mixed at a volume ratio of 1:5.6 prior to spiking with PAH. The sediment was spiked with phenanthrene and naphthalene at a level of ~20 μg/g concentration for both compounds. The reactors were filled with PAH-spiked sediment to a depth of about 7 cm.

A 5 cm × 5 cm woven graphite felt (Graphite felt, Wale Apparatus Co, Hellertown, PA) was placed at 3 cm below the sediment water interface as the anode, and a second, identical graphite felt was placed at 0.5 cm below the sediment-water interface as the cathode. The control reactor had graphite felts but no power connection. Deionized water was applied on top of the sediment as overlying water, and periodically refilled to compensate for evaporation and other water losses.

The graphite electrodes were connected to copper wires by a graphite-filled epoxy: EPO-TEK® 377H (Epoxy Technology, Billerica, MA). The graphite power component in the epoxy ensured its electrical conductivity. The connections between the graphite felt and
copper wires were sealed with Gardner Bender LTW-400 liquid electrical tape (Gardner Bender, Milwaukee, WI).

An external power of 2 V was supplied to powered reactors by Extech 382202 DC power supply (Extech Instruments Corp., Waltham, MA) for 12 weeks, except during microelectrode measurement.

**pH and Redox Potential \((E_H)\) Measurement**

Vertical profiles of pH in sediment at different times were measured by a MI-405 standard pH microelectrode (Microelectrodes Inc, Bedford, NH). The pH microelectrode was calibrated with pH 4, pH 7, and pH 10 standard buffer solution (Fisher Scientific, Fair Lawn, NJ) before and after each measurement. The vertical profile was from the water-sediment interface to a depth of 45 mm with 5-mm intervals.

Vertical profiles of reduction potential \((E_H)\) in sediment were measured by a platinum (Pt) microelectrode against a saturated Ag/AgCl reference electrode. The Pt microelectrode for \(E_H\) measurement was calibrated in a pH-buffered, saturated quinhydrone solution before and after each measurement (Sparks, 1996). The vertical profile of redox potential was also from the water-sediment interface to a depth of 45 mm with 5-mm intervals.

**Voltammetric Determination of Redox-Sensitive Species**

Redox-sensitive species \((O_2, Fe^{2+}, Mn^{2+}, \text{and } S^{2-})\) were analyzed electrochemically at discrete depths within the sediment by inserting voltammetric microelectrodes into the sediment porewater. All voltammetric measurements were performed using an Au/Hg solid-state microelectrode, a platinum counter electrode, and an Ag/AgCl reference electrode. The Au/Hg microelectrodes consisted of a 100-μm-diameter gold wire housed in glass tubing filled with nonconductive epoxy and connected via copper wire. They were fabricated according to methods developed by Brendel and Luther (1995) and Luther et al. (1999).

The gold surface was first polished with diamond pastes of 15, 6, 1, and 0.25 μm (Buehler, Lake Bluff, IL), then plated with mercury at \(-0.1\) V (vs Ag/AgCl reference electrode) in acidic Hg(NO₃)₂ solution for 120 s. The gold amalgam was stabilized by polarizing the microelectrodes at \(-9\) V for 120 s.

Each Au/Hg microelectrode was calibrated for dissolved oxygen by linear sweep voltammetry, and then for manganese, ferrous iron, and sulfide by square wave voltammetry (SWV) in 2 mM acetate or HEPES buffers.

Voltammetric analyses for redox-sensitive species were performed by a DLK-100A potentiostat and a micromanipulator capable of vertical movements at the sub-millimeter scale (Analytical Instrument Systems, Inc, Flemington, NJ). The small size of the working microelectrode, and the precise control of vertical movement, allowed repeated vertical profiling with high spatial resolution while minimizing bulk sediment disturbance. Scan parameters and detection limits were the same as those reported in Brendel and Luther (1995). Triplicate electrodes were used for the measurement and vertical profiles from the sediment-water interface to a depth of 45 mm with 5-mm intervals were obtained (the same depth as pH and redox potential profiles).

**Phenanthrene Porewater Concentration Measurement by PDMS-Coated Fiber**

Vertical profiles of phenanthrene porewater concentration were obtained by polydimethylsiloxane (PDMS)-coated fibers (Fiberguide Industries, Stirling, NJ). An attempt was made
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to measure naphthalene porewater concentration by PDMS fibers, but it was not successfully performed because naphthalene is not strongly adsorbed to PDMS and is very volatile. The diameter of PDMS-coated fiber is 230 μm, and the thickness of PDMS coating is 10 μm. The PDMS fibers have been tested in the laboratory to verify their ability to quantify PAH porewater concentrations as described by Lu et al. (2011). The partitioning of phenanthrene between the PDMS and the pore water was found to be linear and characterized by a partition coefficient $K_f$ of 8910 (Lu et al., 2011).

Phenanthrene was separated by high-performance liquid chromatography (HPLC) with a 250 × 4.6 mm column (Phenomenex Luna 5u C18(2) 100A). An isocratic flow of 1.0 mL/min with mobile phase acetonitrile:water 15:85 (V:V) was used for separation. All analyses were performed in accordance with EPA method 8310. Detection was achieved using a Waters 2475 multiwavelength fluorescence detector. The excitation and emission wavelengths for phenanthrene are 270 nm and 360 nm, respectively.

DNA Extraction and qPCR Analysis

At the end of the experiment, sediment cores were collected and dissected into 0.5-cm-long subsamples and stored at −20°C until further analysis.

DNA was extracted from three replicate samples of each sediment using FastDNA SPIN Kit for Soil (MP Biomedicals) following the manufacturer’s instructions. The primer set used in the quantitative polymerase chain reaction (qPCR) targets aromatic ring-hydroxylating-dioxygenase (RHD$_{α}$) for gram-negative PAH-degrading bacteria, which covers a large range of functional genes, including $bphA_1$, $phnAc$, $nagAc$, $nahAc$, $nahA_3$, etc. (Cebron et al., 2008). The sequence of the forward primer is 5′-GAG ATG CAT ACC ACG TKG GTT GGA-3′, and the reverse primer is 5′- AGC TGT TGT TCG GGA AGA YWG TGC MGT T-3′. All qPCR was performed in a total volume of 25 μL using the Applied Biosystems 7900HT Sequence Detection System. The composition of amplification is 12.5 μL of the Power SYBR green PCR master mix (Applied Biosystems), 2 μL of mixed forward and reverse primer (5 μM), 2.5 μL DNA extract (2.5 μL water for negative control), 2.5 μL of bovine serum albumin (2 mg/mL), and 5.5 μL water. All DNA samples were analyzed in triplicate. qPCR thermal cycling includes the following steps: Step (1) initial dissociation: 95°C for 5 min; Step (2) 40 cycles of the following four steps: (1) Denaturation: 95°C for 30 s; (2) Primer annealing: 57°C for 30 s; (3) Elongation: 72°C for 30 s; (4) Dissociation of the primer’s dimers: 80°C for 10 s; Step (3) 72°C for 7 min; Step (4) Melting curve analysis: 0.5°C temperature increment every 10 s from 51°C to 95°C.

Results and Discussion

Redox Control, pH Changes, and Redox-Sensitive Species

When an external power of 2 V is applied to the electrodes in the sediment for ElecR1 and ElecR2, water electrolysis reaction occurs as shown in Eq. (1) and Eq. (2). An external power voltage of 2 V was selected to ensure water electrolysis at the electrodes. Obviously, a larger voltage increases reaction rate of water electrolysis and generates more oxygen per time, but also produces more H$^+$ at the anode and more OH$^-$ at the cathode. Under a large voltage, severe pH changes may be introduced by water electrolysis if there is not enough buffer in the sediment (Sun et al., 2010). A large voltage is not preferred for stimulating
Figure 2. Vertical profiles of redox potential ($E_H$) in (a) ElecR1, (b) ElecR2, and (c) control reactors. $E_H$ values were versus standard hydrogen electrode (SHE). Depth zero was the water-sediment interface. Cathode was at $d = 0.5 \text{ cm}$ and anode was at $d = 3 \text{ cm}$.

An increment of redox potential was observed in two powered reactors compared to the control (Figure 2). The redox potential around the anode ($d = 3 \text{ cm}$) increased gradually from an initial value of $\sim 100 \text{ mV}$, and finally reached $\sim 200 \text{ mV}$ after about one month of operation for both powered reactors. The redox potential at the same depth in the control reactor was about 80–160 mV during the course of the experiment. The changes in redox conditions were not limited to the vicinity of the anode, but also took place in the sediment below the anode. As shown in Figure 2, the redox potential below the anode ($d = 3–4.5 \text{ cm}$) was about 50–150 mV higher in powered reactors than that in the control. To determine the statistical significance of $E_H$ below the anode between the powered reactor and control, a two-sample t-test was conducted using MATLAB. This test was performed on $E_H$ data.

Biodegradation due the detrimental effect of extreme pH on microbes.

Anode: \[ 2\text{H}_2\text{O} = \text{O}_2 + 4\text{H}^+ + 4e^- \quad E^0 = 1.229\text{V} \quad (1) \]

Cathode: \[ 2\text{H}_2\text{O} + 2e^- = \text{H}_2 + 2\text{OH}^- \quad E^0 = -0.827\text{V} \quad (2) \]
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at \( d = 3–4.5 \) cm at day 13, 21, 40, 68, and 76, and test results revealed that there were statistically significant differences between ElecR1 and control (\( p < 0.001 \)), and between ElecR2 and control (\( p < 0.001 \)). Although redox potential increased in the vicinity of the anode, the redox potential at the cathode did not decrease notably. Redox potential around the cathode was maintained above 300 mv for all three reactors, though redox potential in the control was slightly higher than that in the powered reactors. Oxidizing conditions at the sediment-water interface were due to the diffusion of oxygen from the atmosphere, and these were not altered by the upper cathode. Redox condition at the deeper sediment became more oxidized in favor of PAH degradation.

With the application of potential, pH in the sediment for powered reactors changed with time. As shown in Figure 3, pH around the cathode (\( d = 0.5 \) cm) increased with time and reached the highest value after about 40 days. The peak pH of ElecR1 and ElecR2 was 9.7 and 8.9, respectively. pH around the cathode dropped to about 7.5 and stayed at this level until the end of the experiment. pH around the anode decreased to \(~6\) from an initial value of 6.4 or 6.7 for powered reactors, and pH in this acidic zone remained relatively steady with time. Compared to the pH changes induced by electrodes in powered reactors, pH in the control reactor remained relatively steady with time and depth.

The profiles of redox-sensitive species were measured at day 79 when steady state was achieved (Figure 4). Oxygen concentrations at the sediment water interface for powered

![Figure 3. Vertical profiles of pH in (a) ElecR1, (b) ElecR2, and (c) control reactors. Depth zero was the water-sediment interface. Cathode was at \( d = 0.5 \) cm and anode was at \( d = 3 \) cm.](image)
and control reactors were 53–80% of saturation level and reached less than 5% immediately at the depth of 1 cm. There was no observable difference between the powered reactors and control in oxygen level in the superficial sediments. Dissolved oxygen penetration depth in sediments was controlled by aerobic heterotrophic activity, reoxidation of reduced compounds produced by anaerobic mineralization, and transport by diffusion, advection, and bioturbation (Burdige, 2007). Beneath the oxic layer, concentrations of Mn$^{2+}$ increased steadily with depth, while modest concentrations of Fe$^{2+}$ concentrations were observed from $d = 2$ cm. The levels of ferrous iron in the deeper sediment in both powered reactors were considerably higher than that in the control. The increased level of ferrous iron in powered reactors resulted from the metal released in the acidic conditions as follows:

$$\text{Fe(OH)}_3(s) + 3\text{H}^+ + e = \text{Fe}^{2+} + 3\text{H}_2\text{O}$$ (3)

Because of the prevalence of ferrous iron and the absence of sulfide in the sediment, it was determined that the predominant terminal electron accepting process (TEAP) was ferric iron reduction for all of the powered reactors and control. Freshwater sediment
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(i.e., Anacostia River sediment and University Lake sediment) was used in this study. In freshwater sediment with low sulfate concentration, sulfate reduction is generally low and limited by the availability of electron donors (i.e., sulfate), resulting in the absence of sulfide in the sediment porewater (Holmer and Storkholm, 2001). Although an increase of redox potential was observed in all of the powered reactors, the predominant TEAP in the sediments did not change with embedded electrodes.

Voltammetric techniques are able to detect dissolved oxygen with a detection limit of 5–25 μM (Brendel and Luther, 1995). However, in this study, the voltammetric techniques failed to detect any dissolved oxygen around the anode, though oxygen was produced at the anode by water electrolysis reaction. Due to the high sediment oxygen demand, only a very thin layer of sediment around the anode had detectable levels of oxygen. The thickness of this thin layer with oxygen present remained unknown in this study, but it should be in the order of millimeters or less. It is very possible that the microelectrodes did not reach the sediment with detectable levels of oxygen. These practical or operational limitations of the instruments made it very difficult for in-situ monitoring of oxygen concentration.

Phenanthrene Concentrations and PAH-Degrading Genes

A study of the uptake kinetics of phenanthrene by fiber revealed that the concentration of phenanthrene in the PDMS coating reached equilibrium in about 10 hours (data available in the Supplemental Information). In this study, 24 hours of equilibration time were used during each measurement.

Porewater concentrations of phenanthrene were determined at different depths every two weeks during the experiment (Figure 5). In the superficial sediments (d = 0 and 1 cm), phenanthrene concentration decreased with time in both powered and control reactors due to biodegradation in the oxic environment and volatilization loss. The phenanthrene levels in powered reactors were consistently higher than those in the control in the superficial sediments because of the difference in initial conditions. Some operational inconsistency during the set-up of the experiment might cause the difference in initial conditions.

In the control reactor, phenanthrene concentration in the anode zone (d = 3 cm) did not change notably, whereas phenanthrene concentration decreased over time around the anode in both ElecR1 and ElecR2 (Figure 5). The phenanthrene concentrations were 60% and 71% of their initial concentrations at the end of the experiment for ElecR1 and ElecR2, respectively, but phenanthrene concentration still remained at 90% of initial concentration for the control.

As shown in Figure 5, phenanthrene concentration at the anode (d = 3 cm) decreased with time, whereas phenanthrene concentration at 1 cm above the anode (d = 2 cm) remained almost unaffected throughout the study period in the powered reactors. As a result, phenanthrene concentrations at the anode (d = 3 cm) were lower than those at 1 cm above the anode (d = 2 cm) after several weeks, showing a unique Z-shaped profile in the sediment (Figure 6). This phenomenon was not observed in the control reactor. The phenanthrene profile in the control reactor displayed a down-gradient from the deeper sediment toward the sediment water interface. The decrease of phenanthrene at the anode and the unique Z-shaped profiles provided evidence that the anode placed in the sediment could effectively decrease phenanthrene porewater concentration around the anode in the sediment.

PAH-degrading genes were quantified by qPCR for sediment at a depth of 0–0.5 cm above the anode and 0–0.5 cm below the anode for ElecR1 and control (sediment sample in ElecR2 was contaminated after collection and not analyzed). To compare biodegradation
activity between different sediment samples, it is only necessary to determine the relative abundance of PAH-degrading genes across the samples. Thus, quantification of the absolute number of gene copies was not attempted and the copy number relative to each other was quantified. An arbitrary number of $1 \times 10^8$ was assigned to the control reactor to facilitate the comparisons. Figure 7 shows that two sediment samples in the control (above and below the anode) had about the same numbers of gene copies. However, the gene copy number in the sediment above the anode in ElecR1 was 2.3 times higher than the control, and that below the anode in ElecR1 was 1.5 times higher than the control. The increase of PAH-degrading genes near the anode in ElecR1 provided microbial evidence of PAH biodegradation, indicating that microbial biodegradation played an important role in PAH decontamination. In a preliminary sediment slurry test, electrochemical degradation of phenanthrene was not observed under 3.5 V in a completely mixed reactor (Yan and Reible, 2012). In the stagnant sediment experiment, as in the present study, the applied voltage was only 2 V and mass transfer limitations in sediments also reduced the possibility of electrochemical reactions. The chance of electrochemical degradation of phenanthrene to occur in the present study was very slim, if not impossible. In this novel bioelectrochemical system, electrochemical reduction is not the major mechanism to remove contaminants, but

Figure 5. Phenanthrene porewater concentration at different depths for (a) ElecR1, (b) ElecR2, and (c) control. The results are the means of duplicate samples, and error bars represent standard deviations.
Figure 6. Vertical profiles of phenanthrene porewater concentration in (a) ElecR1, (b) ElecR2, and (c) control reactors. Depth zero was the water-sediment interface. Cathode was at $d = 0.5$ cm and anode was at $d = 3$ cm. The results are the means of duplicate samples, and error bars are not shown for simplicity.

Figure 7. PAH-degrading gene abundance by qPCR quantification at the depth of 0–0.5 cm above and below the anode in the ElecR1 and control reactors. The PAH-RHD$_\alpha$ gram-negative gene levels were normalized by the weight of dry sediment. The results are the means of triplicate, and error bars represent standard deviation.
it provides an effective means to generate oxygen and stimulate biodegradation of PAH by indigenous microorganisms.

Conclusions

An electrochemical technique was proposed and developed to stimulate PAH biodegradation in sediments. Two graphite electrodes were placed horizontally in the sediment and an external voltage of 2 V was applied to produce conditions more favorable for PAH degradation at the anode. Reduction potential increased and pH dropped around the anode, reflecting water electrolysis. Phenanthrene concentration at the anode decreased with time in the powered reactor and was about 60–70% of initial concentrations. Due to the decontamination of phenanthrene at the anode, a unique Z-shaped profile was developed in the sediment in the powered reactor. qPCR results showed an increase of PAH-degrading genes around the anode in the powered reactor compared to the control, which is an indicator of microbial PAH degradation. This electrochemical technique requires low energy input and could be a cost-effective remediation method for remediation of contaminated sediment.

Supplemental Information

The following supporting information is available: (1) microcosms of bioelectrochemical system for stimulation of PAH biodegradation in sediment; (2) concentration of redox-sensitive species in ElecR1, ElecR2, and Control reactors; (3) uptake kinetics of fiber for phenanthrene.

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