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Electro-bioremediation of Contaminated Sediment by Electrode Enhanced Capping

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Abstract

In-situ capping often eliminates or slows natural degradation of hydrocarbon due to the reducing conditions in the sediments. The purpose of this research was to demonstrate a reactive capping technique, an electrode enhanced cap, to produce favorable conditions for hydrocarbon degradation and evaluate this reactive capping technique for contaminated sediment remediation. Two graphite electrodes were placed horizontally at different layers in a cap and connected to external power of 2 V. Redox potentials increased and pH decreased around the anode. Phenanthrene concentration decreased and PAH degradation genes increased in the vicinity of the anode. Phenanthrene concentrations at 0–1 cm sediment beneath the anode decreased to ~50% of initial concentration over ~70 days, while phenanthrene levels in control reactor kept unchanged. A degradation model of electrode enhanced capping was developed to simulate reaction-diffusion processes, and model results show that a reaction-dominated region was created in the vicinity of the anode. Although the degradation dominated region was thin, transport processes in a sediment cap environment are typically sufficiently slow to allow this layer to serve as a permeable reactive barrier for hydrocarbon decontamination.

Graphical Abstract

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Supporting materials

The following supporting material is available: (1) Microcosms of electrode enhanced caps; (2) Voltage and current in CtnCap1, CtnCap2 and IntmtCap reactors; (3) Vertical profiles of pH in control and powered reactors; (4) Phenanthrene porewater concentration (means and standard deviations) at different depths for CtnCap1, CtnCap2, IntmtCap and Control; (5) Sediment characteristics.

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Keywords

Sediment; PAHs; Bioremediation; Capping; Electrochemistry

1. Introduction

Contaminated sediments have become significant problems at many sediment sites both in the USA and other parts of the world. Contaminants detected in sediments include hydrophobic organics as well as metals. In situ capping is a remediation technique to contain contaminated sediments by placing a covering cap made of clean isolating materials at the water-sediment interface. Natural degradation processes for hydrophobic organics may be hindered beneath a cap due to the development of anaerobic conditions and transport processes may ultimately lead to recontamination of near surface sediments.

To encourage degradation of hydrophobic organics after conventional sand capping, it is necessary to maintain conducive conditions to contaminant degradation, e.g., nutrient-sufficient conditions, redox potentials, electron donor or acceptor levels. In organic rich sediments, often the key limitation is providing redox conditions conducive to contaminant transformation.

During recent years, electrochemical technologies have been proposed for sediment, groundwater and soil remediation. Numerous studies have demonstrated the potential effectiveness of electrokinetic remediation in the removal of soil contaminants, primarily due to direct oxidation-reduction at electrodes or induced mobility (Acar and Alshawabkeh, 1993; Franz et al., 2002; Gent et al., 2009; Kim et al., 2011; Lukman et al., 2013; Ng et al., 2014). However, for hydrophobic organic compounds (HOCs) such as polycyclic aromatic hydrocarbons (PAHs) whose mobility is not redox sensitive and with a high tendency to be adsorbed onto soil and sediment, electrokinetic remediation has limited effectiveness without the use of surfactants (Pazos et al., 2010; Hahladakis et al., 2014). Bioremediation is a reasonable alternative to treat soil and sediment polluted by PAHs but the terminal electron acceptor in sediments even a few centimeters below the sediment-water interface is typically iron (III) or sulfate, and this highly reducing conditions are not conducive to PAH degradation. Successful implementation of in-situ bioremediation sometimes requires the presence or injection of electron acceptors into the porous medium. A technology for a continuous introduction of electron acceptors and providing conditions conducive to hydrocarbon oxidation has limited bioremediation of PAH contaminated sediments. Using an electric current may be an alternative option for supplying more favorable electron

acceptors and conditions, providing a potentially viable remedial approach (Strycharz et al., 2008; Aulenta et al., 2009; Sun et al., 2010; Zhang et al., 2010; Chun et al., 2013).

In this research, electrode enhanced capping is proposed and evaluated for bioremediation of sediments contaminated with PAHs (Figure 1). Two areal graphite electrodes are placed horizontally and perpendicular to contaminant transport in the cap and connected to an external power, with low current and power requirements. By water electrolysis, micromolar quantities of oxygen are produced at the anode, making the local sediment environment more oxidizing. Consequently, these redox conditions changes and produced oxygen are expected to stimulate the activity of PAH degrading microbes, and accelerate contaminant biodegradation. The objective of this study is to demonstrate the feasibility of electrode enhanced caps for remediation of PAH contaminated sediment.

2. Materials and methods

2.1 Microcosm setup and operation

Four microcosm reactors were used to investigate redox control and PAH degradation in electrode enhanced caps. The control reactor had no power applied, and the sand caps of the control was 1 mm-sieved concrete sand without any amendment (Riccelli Enterprises, Rush, NY). The external power was connected to the other three reactors through graphite electrodes in the amended sand capping layer. The composition of the amended sand caps was 80 g of siderite, 80 g of calcite, 3.6 g of NaHCO_3 and 1 L of 1 mm-sieved concrete sand. It was expected that siderite and calcite would provide long term pH buffering capacity while bicarbonate would provide short term pH buffering capacity. Studies had previously shown that an unbuffered system would exhibit pH excursions which would hinder microbial community development (Sun et al., 2010). The pH in the control cap system was stable without buffering.

The microcosms were filled with 2 mm-sieved sediment (mixture of PAH contaminated Anacostia River sediment and clean sediment, ratio 1:6). The main characteristics of the sediment including pH, redox potential, conductivity, and water content are in supporting materials. The sediment was spiked with a model PAH compound, i.e. phenanthrene, at $\sim 55 \mu\text{g/g}$ solid concentration. The phenanthrene porewater concentration (as measured by passive sampling, see below) was approximately $30 \mu\text{g/L}$. A $13\text{cm} \times 6\text{cm}$ graphite cloth (Carbon Cloth CC6 Plain, Fuel Cell Earth LLC, Wakefield, MA) was placed above the sediment layer as the anode. An amended sand layer of 3.5-cm was laid over the anode, and another graphite cloth was placed in the amended sand layer as the cathode. A 0.5 cm amended sand layer was on top of the cathode. The pictures of microcosms of electrode enhanced caps in this study are available in supporting materials. The sand layers of powered and control reactors were initially saturated with freshwater. Freshwater was made by dissolving 35 g of Instant Ocean® sea salts in 1 L of DI water and diluting by a factor of 150. A multi-channel peristaltic pump (Watson Marlow 205s, Watson-Marlow, Inc, Wilmington, MA) was used to pass the freshwater over the surface of the sand in the microcosms.

The graphite electrodes were connected to copper wires by EPO-TEK® 377H (Epoxy Technology, Billerica, MA), which is a graphite filled epoxy designed for electronic industries. The connections between the graphite cloth and copper wires were sealed with WEST SYSTEM 105 epoxy resin and 206 slow hardener (WEST SYSTEM, Bay City, MI) to prevent corrosion. Powered reactors were connected to Extech 382202 Model DC power supplies (Extech Instruments, Waltham, MA). Among the three powered reactors, two of them (CtnCap1 and CtnCap2) were operated in a continuous power mode: an external voltage of ~2 V was applied continuously except during in-situ pH and redox potential measurement; the third powered reactor (IntmtCap) was operated in an intermittent power mode: an external voltage of ~2 V was applied 16 hours continuously over a 24-hour period. The applied voltage and current for all the three reactors are available in supporting materials.

2.2 pH and ORP measurement

pH was monitored by pH microelectrode MI-405 (Microelectrodes Incorporation, Bedford, NH) and oxidation reduction potential (ORP) was quantified using platinum microelectrode. pH and ORP profiles from water-sand interface to 5.5-cm below were acquired at 0.5 cm intervals.

2.3 Phenanthrene porewater concentration measurement by PDMS-coated fiber

Porewater concentrations of phenanthrene in the sediment and sand were measured by polydimethylsiloxane (PDMS)-coated fibers (Fiberguide, Stirling, NJ), which has a 10- μ m coating on a 210- μ m core. The capability of the PDMS-coated materials to measure PAH concentrations in porewater has been demonstrated in other studies (Lu et al., 2011). The partition coefficient K_f of phenanthrene between PDMS phase (C_{fiber} , ng/L) and porewater (C_w , ng/L) was estimated to be 8910 L water/L PDMS (Lu et al., 2011).

During the application of PDMS-coated fiber for phenanthrene porewater measurement, fibers were inserted vertically in the sediment for a period long enough to reach equilibrium (24 hours in this study). Then fibers were pulled out from the sediment, rinsed with deionized water to remove any particles, cut into 0.5 cm pieces, and placed into amber HPLC vials with HPLC-grade acetonitrile. Triplicate phenanthrene profiles were obtained during the experiment. Phenanthrene concentrations were measured by HPLC-fluorescence detector (Waters 2475). The excitation and emission wavelengths were 270 nm and 360 nm respectively. The mobile phase was composed of 15:85 water/acetonitrile (V:V) at 1.0 mL/min.

2.4 DNA extraction and qPCR analysis

At the end of the experimental study, sediment cores from each reactor were collected and dissected into 5 mm long subsamples and stored at -20 °C until further analysis. DNA from sediment samples was extracted with FastDNA™ SPIN Kit for Soil (MP Biomedicals) following manufacturer's instructions. Aromatic ring-hydroxylating-dioxygenase (RHD_a) from gram negative PAH-degrading bacteria was quantified by quantitative polymerase chain reaction (qPCR) techniques. The primer set is Forward: 5'-GAGATGCATACCACGTTGGT-3' and Reverse: 5'-

AGCTGTTGTTTCGGGAAGAYWGTGCMGTT-3' (Cébron et al., 2008). This primer set is chosen because it covers a large range of PAH degrading genes including *bphA1*, *phnAc*, *nagAc*, *nahAc*, *nahA3*, etc. Amplification reactions were carried out in 25 μ L volume containing 12.5 μ L of Power SYBR green PCR master mix (Applied Biosystems), 2.5 μ L DNA extract, 2 μ L primer at 5 μ M, 2.5 μ L of bovine serum albumin at 2 mg/mL and 5.5 μ L DI water. All qPCR samples were analyzed in triplicate in Applied Biosystems 7900HT sequence Detection System with the following temperature profiles: Step 1: 95 °C for 5 min; Step 2: forty cycles of the following procedures: (1) 95 °C for 30 s (denaturation); (2) 57 °C for 30 s (primer annealing); (3) 72 °C for 30 s (elongation); (4) 80 °C for 10 s (primer's dimer dissociation); Step 3: 72 °C for 7 min; Step 4: temperature increment from 51 °C to 95 °C (melting curve analysis).

3. Results and Discussion

3.1 Redox potential and pH change in sediment microcosms

Thermodynamically, the minimum potential for water electrolysis is 1.23 V at 25 °C and 1 atm, but actual cell voltage needed to continue the reaction is higher due to ohmic loss and overpotential. Practically water electrolyzers operate above this voltage in the range of 1.6 to 2.2 V (Abe, 2009). In this study, a potential of 2 V is applied to overcome various losses and ensure sufficient potential at the electrode for water electrolysis. A greater potential is not preferred for stimulating biodegradation since it causes a higher rate of water electrolysis, consequently resulting in severe pH changes at both anodes and cathodes. Low power was required for electrode enhanced caps in this study (current density of 22–32 mA/m² and power requirements of 45–64 mW/m²).

With the application of 2 V, electrode potentials of anode and cathode were 1.1 V and −0.7 V respectively, and ohmic loss in the system was 0.2 V. Electrode potential at the anode was large enough to produce oxygen at the anode as shown in Eq 1. pH around the anode dropped while pH near the cathode increased slightly (data is available in supporting materials), reflecting water electrolysis (Eq 1 and 2).

ORP in the sediment around the anode increased with the application of electrode enhanced caps (Figure 2). ORP in CtnCap1 reactor was over 50 mV higher than that in control, and the increase of redox potential in the other two powered reactors (CtnCap2 and IntmtCap) was about 10–40 mV compared to control. Although an increased redox potential was observed near the anode, ORP near the surface at the cathode did not decrease notably and redox potentials around the cathode were still above 300 mV. The cathode was placed near sand-water interface and redox condition near this interface was generally controlled by diffused oxygen from the atmosphere. It suggests that the oxidized condition at the surface of the cap was not altered by the electrodes, but the redox condition at the deeper sediment became more oxidized in favor of PAH degradation.

The pH changes induced by water electrolysis were minimized by the amendment of sodium bicarbonate in the sand cap. pH around the anode was buffered above 6 in all the three powered reactors. Compared with control reactor, only a small drop of pH from 6.4 to 6 was observed in the powered reactors. With pH maintained at near neutral pH, PAH biodegradation rates were expected to be accelerated by the oxygen produced at the anode with less influence of pH shift.

3.2 Phenanthrene concentrations and PAH degrading genes

Phenanthrene porewater concentrations were measured with a vertical resolution of 0.5 cm during a period of 70 days. Phenanthrene porewater concentration remained fairly constant at approximately 30 µg/L in the deeper sediments (1–3 cm below the anode) in all the powered reactors and control (data is available in supporting materials). However, phenanthrene concentration in the 1 cm vicinity of the anode displays different trends over time between powered reactors and control (Figure 3). In the powered reactors, the phenanthrene porewater concentrations at 0.5–1 cm sand above the anode remained very low (<1 µg/L); the concentrations at 0–0.5 cm sand above the anode were initially ~ 2 µg/L and decreased to less than 0.2 µg/L at the end. On the contrary, in the control reactor phenanthrene porewater concentrations increased over time in the sand up to as much as ~15 µg/L above the anode (at both 0–0.5 cm and 0.5–1 cm) due to the diffusion of phenanthrene from the underlying sediment. The electrode enhanced capping effectively reduced phenanthrene porewater concentrations from 15 µg/L (control) to 0.2 µg/L (powered reactors) at 0–0.5 cm above anode. In the sediments immediately beneath the anode, phenanthrene porewater concentrations decreased over time in powered reactors to less than 5 µg/L, while they remained approximately constant in the control reactors. The average porewater concentrations of phenanthrene in the 1 cm vicinity of sediment (at the end of the experiment) were 49%, 56% and 53% of initial concentrations for CtnCap1, CtnCap2, and IntmtCap, respectively.

The amount of PAH degrading genes was quantified by qPCR for sediment at 0–0.5 cm below the anode (Figure 4). All PAH degrading genes were reported as an increase from the level of genes in the control. The normalized copy numbers increased by almost one order of magnitude in powered reactors compared to those in control, indicating that electrode enhanced capping stimulated microbial PAH biodegradation.

The IntmtCap reactor was running in an intermittent mode: two third of the time with power and one third of the time with no power, to provide a preliminary evaluation of this mode of operation. The results of phenanthrene concentration show that the biodegradation rates of IntmtCap were almost the same as those of continuous reactors. In addition, IntmtCap even shows a slightly higher level of PAH degrading genes. The intermittent operation might reduce pH excursions under some conditions and should require less power input.

In a preliminary sediment slurry test, electrochemical degradation of phenanthrene was not observed under 3.5 V in a completely mixed reactor (data not shown). In the simulated cap 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. So the

chance of electrochemical degradation of phenanthrene to occur in the present study was very slim if not impossible.

Three mechanisms for stimulation of PAH biodegradation were proposed in electrode enhanced caps: 1) Oxygen produced by electrolysis of water can provide electron acceptors for organisms oxidizing PAHs. Aerobic bacterial degradation of PAHs is known to occur at a much faster rate than anaerobic degradation (Cerniglia, 1992). Previous study suggested that even at very low oxygen concentration, biodegradation of organic contaminant is significantly accelerated (Gossett, 2010). 2) Direct electron transfer from anodes to stimulate microbial degradation of PAHs. The possibility of accelerating anaerobic oxidation of organic contaminants in this manner has been demonstrated for aromatic hydrocarbons (Zhang et al., 2010; Friman et al., 2012). 3) Electron shuttling can stimulate microbial degradation. Electron shuttles are chemical compounds that stimulate biodegradation of contaminants by facilitating electron transfer to and from bacteria. In this way, electrons are “shuttled” between bacteria and electrodes. Common chemicals in sediment such as humic substances and iron are able to serve as electron shuttles to encourage biodegradation (Lovley et al., 1996; Ohmura et al., 2002). Among these three mechanisms, the first mechanism is most likely to be dominant in this study, because the qPCR assay mainly targets PAH degrading genes involved in the first mechanism and qPCR results revealed an increase of genes. The evidence of the other two mechanisms remains unknown but all the three mechanisms could coexist in sediments, and were not necessarily mutually exclusive.

Previous studies on bioelectrochemical systems (BES) has focused on microbial degradation by a pure or mixed culture in mineral medium (Gregory et al., 2004; Thrash et al., 2007; Strycharz et al., 2008; Aulenta et al., 2009; Friman et al., 2012) or contaminant degradation in bulk sediment (Zhang et al., 2010; Chandrasekhar and Mohan, 2012; Chun et al., 2013). To our knowledge, the present study is the only one that incorporated bioelectrochemical systems with an engineering application, e.g. sediment capping, and monitored high resolution contaminant profiles. This promising result demonstrated the effectiveness of the electrode enhanced capping as a biobarrier for remediation of contaminated sediment, at least under the negligible upwelling flow condition tested in these experiments. By placing the anode at the sand-sediment interface, migration of phenanthrene from the underlying sediment was prevented or inhibited considerably. While contaminant may breakthrough conventional sand capping over time, electrode enhanced capping could overcome this limitation by creating a biobarrier at the cap-sediment interface.

3.3 Degradation model of electrode enhanced capping

The experimental conditions were limited to diffusion migration of contaminants only. A first-order degradation rate model is widely used for PAH degradation and it offers a realistic prediction of phenanthrene concentration reduction. Degradation of phenanthrene in an electrode enhanced cap with diffusion only was modeled by a one-dimensional reaction-diffusion equation as follows:

$$\frac{\partial c}{\partial t} = \frac{D_{ef}}{R} * \frac{\partial^2 c}{\partial x^2} - \frac{k}{R} * c \quad (3)$$

Where R is the retardation factor of phenanthrene in sediment and sand, D_{ef} is the effective diffusion coefficient of phenanthrene in porous media, k is the first order reaction constant, and c is phenanthrene porewater concentration.

Electroosmosis in a pore occurs due to the drag interaction between the bulk of the liquid in the pore and a thin layer of charged fluid next to the pore wall, so liquid moves under the action of the electric field in a direction parallel to it. The thin layer of charged fluid, or electric double layer, has a typical thickness between 1 and 10 nm (Probstein and Hicks, 1993). In the application of electrode enhanced capping, sand is used as the capping material. Coarse sand is a very porous soil type and lacks capillary capacity (Sun and Romantschuk, 2004). Furthermore, it has a very low surface charge and zeta potential, which makes electroosmosis negligible in the sand (Haran et al., 1997; Li et al., 1997). Electroosmotic flow was not taken into consideration in the degradation model.

It is assumed that the sediment and sand in an electrode enhanced cap are divided into four different zones (from the top to the bottom): 1) non-reactive sand in the upper layer (0.5–4 cm above the anode); 2) reactive sand in the vicinity of the anode (0–0.5 cm above the anode); 3) reactive sediment in the vicinity of the anode (0–0.5 cm below the anode); 4) non-reactive sediment in the deeper layer (0.5–3 cm below the anode). Phenanthrene was not detected in the sand layer at 1 cm or more above the anode (initial no phenanthrene), and its concentrations at 1 cm or more below the anode remained constant with time. So it is assumed that diffusive flux is zero at both upper and lower boundaries. Initial conditions were specified according to experimental results. The coupled reaction and transport processes in reactive sediment and sand were characterized by a dimensionless number, Damkohler number (Da), which is defined as follows:

$$Da = \frac{\text{Reaction rate}}{\text{Diffusion mass transport rate}} = \frac{kL^2}{D_{ef}} \quad (4)$$

Where L is the thickness of reactive sediment or sand, i.e. 0.5 cm in this study.

The Damkohler number describes the effect of reaction (k) relative to that of diffusion (D_{ef}/L^2). At high Damkohler numbers ($Da \gg 1$), reaction times are much faster than transport times for a given length scale.

The degradation model was implemented using Earth Science Module of COMSOL MULTIPHYSICS 3.5a. The parameters D_{ef}/R and k/R were calibrated by fitting the model to experimental measurements, and Da was calculated based on calibration results (Table 1). Figure 5 shows the comparison of experimental and model results in control and powered reactors. A reasonable agreement between experimental and model results is observed for both control and powered reactors. The model predicted the increase of phenanthrene concentration in the sand layer in control reactor, implying an accurate description of diffusion only process. For reaction-diffusion processes, the model predicted the low level of phenanthrene concentration in sand layer and the decrease of concentration in sediment layer in powered reactors, demonstrating its ability to model the biobarrier in an electrode enhanced cap. High values of Da in reactive sediment ($Da = 21.4$) and sand ($Da = 8.6$) show

that an electrode enhanced cap could create a reaction-dominated region in the vicinity of the anode.

With groundwater upwelling, the electrode system, as operated, may not provide sufficient residence time for degradation of phenanthrene. The effect of flow conditions on phenanthrene degradation and transport was investigated by a one-dimensional advection-reaction-diffusion model:

$$\frac{\partial c}{\partial t} = \frac{D_{ef}}{R} * \frac{\partial^2 c}{\partial x^2} - \frac{v}{R} * \frac{\partial c}{\partial x} - \frac{k}{R} * c \quad (5)$$

Where v is interstitial velocity.

The dimensionless Peclet number (Pe) can be calculated from the upwelling interstitial velocity v :

$$Pe = \frac{\text{Advection rate}}{\text{Diffusion rate}} = \frac{vL}{D_{ef}} \quad (6)$$

Figure 6 illustrates the phenanthrene flux into non-reactive sand layer for a range of Peclet numbers with or without the biobarrier created by electrode enhanced caps. It is assumed that the Damkohler numbers remained unchanged (as calibrated in Table 1) in the biobarrier cases and $Da = 0$ without the biobarrier. Electrode enhanced caps could significantly reduce contaminant flux when Pe is small ($Pe < 1$), and the contaminant removal efficiency decreases when Pe number increases. For advection-dominant transport ($Pe = 10$), the electrode enhanced cap reduces the contaminant flux by about 15% due to insufficient residence time for degradation.

3.4 Cost analysis

It is too early to develop verifiable cost scenarios for electrode enhanced capping at this initial stage in the development of the technology. However, certain preliminary estimates have been attempted to assess the potential cost-effectiveness of this technology. The additional costs (compared to conventional capping) mainly include cost of electrode materials and energy cost. There are numerous graphite suppliers worldwide and the cost of graphite cloth can be as low as \$1–\$6/m² (Changzhou Airan Materials Co., Ltd, China). In this study, the energy costs for three powered reactors ranged from 0.35 to 0.5 mW. Considering an electrode area of ~78 cm², the energy cost per unit area was only 45–64 mW/m², i.e. 0.39–0.56 kWh/(yr*m²). The average retail price of electricity to ultimate customers of US in 2013 was 10.08 cents per kWh (U.S. Energy Information Administration, 2014). So the additional cost for energy of electrode enhanced capping is about 3.9–5.6 c/(yr*m²), i.e. \$158–\$227 per acre per year. Considering typical costs of field scale cap applications are between \$17/m² and \$21/m² plus the cost of materials (Reible, 2004), the energy cost is still only a very insignificant portion of the total cost of in-situ capping. In total, the placement cost of an electrode enhanced cap is about \$20–\$30/m². Another type of reactive capping, coke-filled reactive core mat, has an overall placement

cost of \$29–\$33/m² (McDonough et al., 2007). The cost of the electrode enhanced capping technique is comparable to reactive core mat, making it a cost-effective method for remediation of contaminated sediment.

The use of solar panels (photovoltaic modules) as a power supply for chemical/electrochemical systems and remote sensors has previously been reported (Hart and Martinez, 2006). Solar panels as a power supply have almost zero pollution, low maintenance cost and a long life, and can be used as a power source for electrode enhanced capping either directly in an intermittent (daylight) mode or with a storage battery in continuous mode. The output of a single solar panel (size: 1000–5000 cm²) with 40 solar cells ranges from 10 to 300 watts. Because of its low power requirement, a single solar panel can power a large area of electrode enhanced capping. If the power requirement is 45–64 mW/m² as previously discussed, a solar panel with a capacity of 100 W can power an area of 1560–2229 m². So a one-acre area needs only 2–3 solar panels of 100 W for the application of electrode enhanced capping.

These analyses show that electrode enhanced capping can be a cost-effective and sustainable remediation technology for the management of contaminated sediment. Of course, to successfully apply an electrode enhanced cap at a specific sediment site, site hydraulics and geochemical parameters, contaminant levels, etc. need to be determined in feasibility study. It is also necessary to optimize operating parameters before scaling up the system from bench scale to field scale.

4. Conclusions

A novel electrode enhanced capping was proposed and demonstrated for bioremediation of PAH contaminated sediment. Two graphite cloth electrodes were placed horizontally within a thin sand layer and an external voltage of 2V was applied. pH dropped and ORP increased near the anode reflecting water electrolysis. Phenanthrene concentration decreased and PAH degrading genes increased around the anode. A degradation model shows that a reaction-dominated region was created in the vicinity of the anode. With low costs of energy and materials, electrode enhanced capping can be a cost-effective and sustainable remediation technology for the management of contaminated sediment.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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- Electrode enhanced capping is developed for remediation of PAH contaminated sediment.
- ORP increases and pH drops around the anode reflecting water electrolysis.
- Phenanthrene concentration decreases slowly with time in the vicinity of the anode.
- The increase of PAH degrading genes provides microbial evidence.
- A reaction-dominated region is created in the vicinity of the anode.

Figure 1. Conceptual model for an electrode enhanced cap for remediation of PAH contaminated sediment. PAH biodegradation is stimulated by the oxygen produced at the anode.

Figure 2.

Vertical profiles of ORP at (a) Day 20, (b) Day 28, (c) Day 42 and (d) Day 56. ORP values were versus standard hydrogen electrode (SHE). Depth zero was the water-sand interface. Cathode was at $d = 0.5$ cm and anode was at $d = 4$ cm.

Figure 3.

Phenanthrene porewater concentration at (a) 0.5–1 cm above the anode, (b) 0–0.5 cm above the anode, (c) 0–0.5 cm below the anode and (d) 0.5–1 cm below the anode. The results are the means of triplicate samples, and error bars are not shown for simplicity.

Figure 4.

PAH degrading gene abundance by qPCR quantification at the depth of 0–0.5 cm below the anode in CtnCap1, CtnCap2, IntmtCap and control reactors. The PAH-RHD α GN gene levels were normalized by the weight of dry sediment. All the values were reported as an increase from control reactor. The results are the means of triplicate, and error bars represent standard deviation.

Figure 5.

Experimental and model results of normalized phenanthrene porewater concentration in control and powered reactor: (a) 0.5–1 cm above the anode, (b) 0–0.5 cm above the anode, (c) 0–0.5 cm below the anode and (d) 0.5–1 cm below the anode. Phenanthrene concentration was normalized by the average concentration in the deeper sediment. The experimental results are the means of triplicate samples, and error bars represent standard deviation.

Figure 6. Phenanthrene flux into non-reactive sand under different flow conditions (Peclet Number, Pe) with or without the biobarrier (electrode enhanced caps).

Table 1Parameters D_{ef}/R and k/R at different zones in an electrode enhanced cap

	D_{ef}/R (cm ² /day)	k/R (1/day)	Da
Non-reactive sand	8.46×10^{-3}	0	0
Reactive sand	8.46×10^{-3}	2.90×10^{-1}	8.57
Reactive sediment	8.64×10^{-5}	7.38×10^{-3}	21.4
Non-reactive sediment	8.64×10^{-5}	0	0