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Enhanced degradation of phenanthrene and pyrene in freshwater sediments by combined employment of sediment microbial fuel cell and amorphous ferric hydroxide

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ABSTRACT

The degradation of phenanthrene and pyrene in freshwater sediment was investigated under three kinds of treatments (addition of amorphous ferric hydroxide to sediments, employment of sediment microbial fuel cell (SMFC), and the combination of ferric addition and SMFC employment). After 240 days of experiments, it was found that the combined treatment led to the highest removal efficiencies of phenanthrene (99.47 ± 0.15%) and pyrene (94.79 ± 0.63%), while the employment of SMFC could obtain higher removal efficiencies than Fe(III) addition. The combined approach improved potentials of phenanthrene and pyrene biodegradation in sediments under anaerobic pathways except methanogenic condition, and also stimulated humification of organic matters in sediments. At the end of experiments, ratios of humic acid to fulvic acid in sedimentary organic matters reached to 2.967 ± 0.240 in the combined treatment, and were only around 1.404–1.506 in the other treatments. Thus, organic matters in sediments in the combined treatment could adsorb tightly residual PAHs with less bioavailability. Considering both enhanced biodegradation and final sequestration of PAHs in sediments, the combined application of Fe(III) addition and SMFC employment offered a new promising remediation technology for contaminated sediments.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are widespread environmental pollutants which are mainly from incomplete combustion of fossil fuels and organic compounds [1,2]. These compounds are of major public concern due to their toxicity to organisms in carcinogenic and mutagenic potential. Once in sediments, PAHs tend to adsorb on and accumulate in sediments, and undergo various degradation, transformations, and sequestration [3,4]. Biodegradation under aerobic or anaerobic condition is a major process for PAHs removal [5,6]. Nevertheless, natural attenuation cannot appreciably remove pollutants, and a lack of suitable electron acceptors is one of major factors limiting biodegradation of PAHs in sediments. Therefore, biostimulation by introducing oxygen and/or other electron acceptors could improve the native microbiological activity within sediments [7–9].

Compared with anaerobic biodegradation, aerobic degradation of PAHs would provide higher degradation rates. However, aerobic bioremediation might not be cost-effective because of the introduction of oxygen is very difficult and limited due to the low solubility and high volatility of oxygen [10]. Furthermore, aeration will cause the re-suspension of sediments and the release of excess nutrients from sediments [11]. In fact, hydrocarbon-contaminated sediments usually become anoxic with a redox gradient along water–sediment interface, and microorganisms can anaerobically degrade PAHs in polluted aquatic sediments with alternative electron acceptors, such as nitrate, sulfate, or Fe(III) oxides [10,12–14].

Nitrate or sulfate as a terminal electron acceptor in enhancing biodegradation of PAHs has been reported previously [10,12]. However, the addition of nitrate and sulfate as electron acceptors in open sedimentary environments is problematic, as these chemicals are soluble and will diffuse away from the point of application under hydrodynamic influences [10]. In comparison, the addition of insoluble Fe(III) oxides into sediments became an alternative option to stimulate degradation of PAHs [13,15]. However, the effect of Fe(III) addition on PAH degradation in sediments was sometimes vague, and it was reported that addition of amorphous ferric hydroxide did not have any significant effect on the biodegradation of PAHs in mangrove sediments [16].

Recently, it was proposed that sediment microbial fuel cell (SMFC) technology could be applied to enhance the removal of organic matter and aromatic hydrocarbons in contaminated

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sediments [8,17]. Anode in SMFC can act as a permanent, high potential electron acceptor with low-cost and continuous sink for electrons [8,18]. The microbial degradation of contaminants in sedimentary environments was not restricted by available electron acceptor after application of SMFC. Both electrodes in SMFCs and Fe(III) oxides represent insoluble and extracellular electron acceptors. However, effects of SMFC employment and Fe(III) addition on biodegradation of PAHs in freshwater sediments are unknown. In addition, it was not clear whether these two methods could be combined for sediment bioremediation.

In this study, phenanthrene and pyrene were selected as the target compounds as the two PAHs were often detected in surface sediments with high concentrations [19]. Degradation of phenanthrene and pyrene in freshwater sediments was investigated under addition of amorphous ferric hydroxide, employment of electrode in SMFC, and combined application of the two approaches as electron acceptors. Combined application of ferric oxide and SMFC was found to lead to higher removal rates of phenanthrene and pyrene in sediments compared to application of ferric addition or SMFC employment alone.

2. Materials and methods

2.1. Sediments and chemicals

Bulk samples of sediments were collected from East Taihu Lake (31°10′N, 120°24′E), a large shallow lake in China, sieved at 2 mm, and homogenized. The physical and chemical properties of the sediments were measured as follows: pH 7.8, moisture content 44.9%, total nitrogen amount 2.5030 g kg^{-1} dry sediment, and total phosphate amount 11.0827 g kg^{-1} dry sediment. Original concentrations of phenanthrene and pyrene in sediments were 0.0954 and 0.0316 mg kg^{-1} dry sediment, respectively.

To spike PAHs into sediments, the solutions of PAH mixture, containing phenanthrene and pyrene (98% purify, Alfa Acsar Co., UK), was firstly prepared in methanol, and then added drop-wise to wet sediments followed by mixing mechanically at low speed for 2 h [20,21]. The amounts of phenanthrene and pyrene to sediment were 10 and 5 mg kg^{-1} dry sediment, respectively. Prior to experiments, the spiked sediment samples were stored in the dark for 12 days for partial aging.

2.2. Setup of sediment column bioreactors

Five plexiglass columns with approximately 4-L volume (12 cm × 35 cm, diameter × height) were used as sediment column bioreactors (SCBs) to perform the biodegradation experiment in a dark environment at 25 °C. Each bioreactor contained 1600 g wet sediment and 1 L overlying water. The compositions of the mineral salts medium in the overlying water was (g L^{-1}): $K_2HPO_4{\cdot}3H_2O$, 0.0001; KH_2PO_4, 0.0002; NH_4Cl, 0.0115; $MgCl_2{\cdot}6H_2O$, 0.1; $CaCl_2{\cdot}2H_2O$, 0.1; and $FeCl_2{\cdot}4H_2O$, 0.02. SCB0 served as sterile control in which sediments were autoclaved twice at 121 °C for 30 min. SCB1 was applied to mimic the natural attenuation without addition of electron acceptor. In SCB2, amorphous ferric hydroxide with a 16 g of wet weight, prepared according to the method described elsewhere [22], was mixed and homogenized with sediments to test effect of iron amendment. SCB3 and SCB4 were operated with an electrode serving as the electron acceptor through deployment of SMFCs as described below. In addition, amorphous ferric hydroxide with the same amount as that amended to sediments in SCB2 was added to sediments in SCB4.

Two set of SMFCs were installed in SCB4 and SCB5 according to detailed description in previous study [23]. The anode, composed of two stainless steel cylinders (80 mesh, 1 mm thickness) was buried 2 cm below the sediment surface. The space between external stainless steel cylinder (9.6 cm × 10 cm, diameter × height) and internal cylinder (4.8 cm × 10 cm, diameter × height) was about 2.4 cm. The cathode, composed of a stainless steel cylinder (9.6 cm × 4 cm, diameter × height), was placed 6 cm above the sediment. The voltage signal between the anode and cathode across an external load of 100 Ω was measured using a multimeter (model 2700, Keithley Instruments, Cleveland, OH, USA).

2.3. Measurement of PAH degradation potential in sediments under various anaerobic redox conditions

At the end of experiments, sediment samples with a 0.5 g wet weight were transferred from the SCBs into 100 mL serum bottles in an anaerobic chamber filled with ultra-high purity nitrogen in order to measure PAH degradation potential of sediments under various anaerobic redox conditions. Test bottles were then filled with 50 mL medium with a compositions consisting of (g L^{-1}): K_2HPO_4, 0.27; KH_2PO_4, 0.35; NH_4Cl, 2.7; $MgCl_2{\cdot}6H_2O$, 0.1; $CaCl_2{\cdot}2H_2O$, 0.1; and $FeCl_2{\cdot}4H_2O$, 0.02.

The concentrated phenanthrene and pyrene solution, which were prepared through firstly dissolved in methanol and then mixed with deionized water, was added to test bottles with initial phenanthrene and pyrene concentrations in serum bottles of 0.5 mg L^{-1}, respectively. Four different anaerobic redox conditions (nitrate-reducing, iron-reducing, sulfate-reducing, and methanogenic) were maintained through adding four different electron acceptors (20 mM sodium nitrate, 50 mM ferric citrate, 20 mM sodium sulfate, and 20 mM sodium hydrogen carbonate) to serum bottles, respectively. The pH of liquid medium in bottles was adjusted to 7.0. After capped with butyl rubber stoppers, serum bottles were incubated at 25 °C in the dark without shaking for anaerobic treatments. Sterile controls were autoclaved twice at 121 °C for 30 min. Those test bottles were sampled daily with a syringe for determination of residual PAHs concentrations. All above operations were carried out under anaerobic chamber, and experiments were performed in duplicate.

2.4. The potential Fe(III)-reducing microbial activity in sediments

At the end of experiments, sediment samples (2 g) taken from each SCB were added to 100 mL serum bottles, followed by supplement of 60 mL of freshwater medium containing 12 mM glucose and 4 mM ferric citrate as electron donor and acceptor, respectively. Serum bottles were sealed with butyl rubber stopper and incubated at 25 °C in the dark. Sampling was done using syringes and needles. All manipulations of culture samples were carried out under strictly anoxic conditions. The reduction of Fe(III) was measured as the production of Fe(II) in HCl extracts using the colorimetric reagent ferrozine under strictly anoxic conditions [24]. Reduction rates were determined by the linear least square regression of the Fe(II) concentration versus time.

2.5. Fractionation and characterization of sediment organic matter

At the end of experiments, sediments from SCBs were sampled. Fulvic acid (FA), humic acid (HA) and biopolymer (BP) were isolated from sediment organic matter (SOM) samples using NaOH and HCl extraction procedure [25]. Organic carbon contents in three SOM fractions were quantified as total organic carbon (TOC) concentrations, which were measured using a Fisons CHN analyzer (Model EA1108, UK). The molecular structures and functional groups of FA and HA from SOM were further analyzed by Fourier transform infrared (FTIR) spectroscopy (Model NEXUS870, USA).