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Enhanced phenanthrene degradation in river sediments using a combination of biochar and nitrate

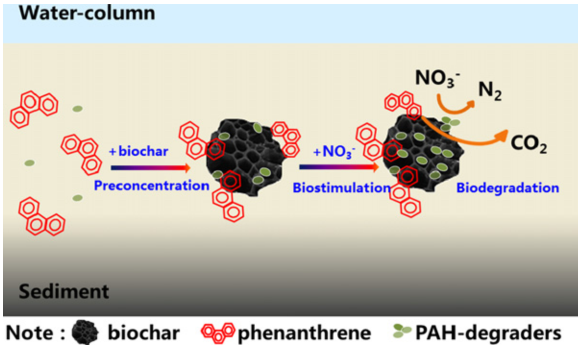
Xunan Yang [a,b,c,d,1], Zefang Chen [a,b,1], Qunhe Wu [b,*], Meiying Xu [a,c,d]

[a] *Guangdong Provincial Key Laboratory of Microbial Culture Collection and Application, Guangdong Institute of Microbiology, Guangzhou 510070, China*
[b] *School of Environmental Science and Engineering, Guangdong Provincial Key Laboratory of Environmental Pollution Control and Remediation Technology, Sun Yat-sen University, Guangzhou 510275, China*
[c] *State Key Laboratory of Applied Microbiology Southern China, Guangzhou 510070, China*
[d] *Guangdong Open Laboratory of Applied Microbiology, Guangzhou 510070, China*

HIGHLIGHTS

- PAH degradation was enhanced by biochar amendment combined with nitrate stimulation.
- Biochar enhanced the aging effects of PAHs to reduce their eco-risk in sediment.
- Biochar increased contact between phenanthrene and PAH-degraders in sediment.
- Nitrate acted as the electron acceptor to increase nitrate-reducing PAH-degraders.

GRAPHICAL ABSTRACT



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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) pollution in urban river sediments is a serious problem to ecological systems and human health. We examined novel remediation approaches, using a biochar amendment combined with bioaugmentation or/and nitrate stimulation, to degrade phenanthrene in sediment. Biochar amendment combined with nitrate stimulation enhanced phenanthrene degradation by 2.3 times that of the control and 1.9 times that of biochar alone. Nitrate stimulation altered the microbial succession and encouraged the growth of potential nitrate-reducing PAH-degraders *Thiobacillus* and *Stenotrophomonas*. Biochar was an excellent sorbent for phenanthrene and the shelter that it provided PAH-degraders increased contact between phenanthrene and PAH-degraders. Biochar also enhanced the aging effects of phenanthrene and reduced the ecological risk by 7.7% to 11%. These results suggest that biochar amendment combined with nitrate stimulation can achieve high-efficiency phenanthrene degradation in sediments.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a ubiquitous group of persistent organic pollutants in sediments. They are poorly degraded under anaerobic conditions and are threats to the health of ecosystems and humans (Dagnino et al., 2013). Therefore,

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* Corresponding author.
E-mail address: eeswqh@mail.sysu.edu.cn (Q. Wu).

[1] X. Yang and Z. Chen contributed equally to this work.

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remediation of PAHs in sediments is an important goal of urban river restoration.

In situ remediation technologies such as capping, bioaugmentation, and biostimulation are the most effective, efficient, and economical (Perelo, 2010; Megharaj et al., 2011). In situ capping is widely used and creates a barrier between the sediment and the water-column using a layer of clean material (Gidley et al., 2012). Sand has been used as capping material for delaying the breakthrough of contaminants. However, sand caps must be thick enough to block contaminant release, and thick caps could negatively impact water flow or flood capacity (Lampert et al., 2011). To minimize thickness, active materials such as activated carbon, cinder, organoclays, and zeolites, which promote contaminant sequestration and degradation, have been proposed (Viana et al., 2008; Sun et al., 2010, 2011).

Biochar has also been considered as an amendment material for in situ capping of sediment because of its capacity of organic adsorption and carbon sequestration (Rakowska et al., 2012). Biochar can adsorb organic contaminants due to its high specific surface area (Cornelissen and Gustafsson, 2005) and can reduce the toxicity of organic contaminants in sediments (Lou et al., 2011). Recently, the characteristics of biochar have been further developed. Biochar was able to increase the richness of functional soil bacteria (Wu et al., 2016) and was useful as the carrier in bacteria immobilization (Chen et al., 2012). Biochar can also capture ammonium from soils (Yang et al., 2015). These findings demonstrate that biochar can serve as a shelter for bacteria and a sorbent for nutrients. Therefore, biochar could not only be used as a clean material for organic contaminant adsorption, but also as the amending agent for the combination of bioaugmentation and biostimulation.

Bioaugmentation is used to introduce appropriate species for degradation of specific contaminants (Hu et al., 2016). Biochar inoculated with bacteria can effectively improve the removal of PAHs in soil (Chen et al., 2012). However, the efficiency of this strategy may be limited in sediment remediation. Generally, there are abundant electron acceptors such as Fe(III) and oxygen in the unsaturated soils. But polluted sediments are always anaerobic and lack electron acceptors which limit the biodegradation of organic contaminants (Eriksson et al., 2006). Biostimulation is used to encourage the indigenous microbial population by injecting essential electron acceptors or donors which maximize the catabolic ability of existing microbes to remove contaminants. Nitrate is an ideal electron acceptor, which could be used by a variety of PAH-degraders. Yang et al. (2013) demonstrated that sediment bacteria could metabolize pyrene as the sole carbon source in nitrate-reducing conditions. Xu et al. (2015) found that the metabolism of PAH-degrader could be encouraged when nitrate was added to sediments.

We studied biochar addition in combination with bioaugmentation and/or biostimulation to enhance phenanthrene (a representative PAH) degradation in sediment. We hypothesized that phenanthrene would first be concentrated on the biochar surface. Then the potential bacterial PAH-degraders settling in the biochar pores would expediently use phenanthrene as the carbon source. Addition of nitrate may also be captured by biochar and serve as an electron acceptor to stimulate phenanthrene degradation. Our goals were to (1) study the feasibility of using biochar amendment combined with bioaugmentation and/or biostimulation in sediments; (2) explore the effects and roles of biochar on phenanthrene removal in sediment by observing bulk and mild-extracted phenanthrene; and (3) correlate the results of combined remediation with microbial community succession.

2. Materials and methods

2.1. Sediment collection and pre-treatment

Surface sediment (0–5 cm) samples were collected with a grab from the Pearl River at a site (Zhongda Wharf, Guangzhou, China) with reported high PAHs levels (Yang et al., 2016). The wet samples were sieved through the 0.2-mm sieve and mixed into river water to form a slurry (v/v = 1:1). Under stirring, three aliquots of phenanthrene (Sigma-Aldrich, Shanghai, China) in an acetone solution were spiked into the slurry every 5 min, followed by continual stirring for 15 min. The spiked sediments were stored in continuous darkness for 120-day aging. Sediments were re-homogenized prior to being used in degradation experiments.

2.2. Biochar preparation and characterization

Biochars were pyrolyzed granules (φ = 0.5–1.0 mm) sieved from crushed macadamia nut shells. The pyrolysis process was conducted under nitrogen in a tubal furnace with the pyrolysis temperature that ramped at 10 °C min^{-1} from 250 to 500 °C, then maintained at 500 °C for 1 h. Weights of the granules before and after pyrolysis were used to calculate the production rates of the biochar (32.6%). The carbon (77.5%) and hydrogen (3.69%) content were analyzed with an elemental analyzer (Vario EL cube, Elementar, Germany).

2.3. Inoculum enrichment and immobilization

Enrichment of the phenanthrene degraders was inoculated with the sediments. The enrichment was conducted as Yang et al. (2013) described. Briefly, the enrichment was conducted in an anaerobic mineral

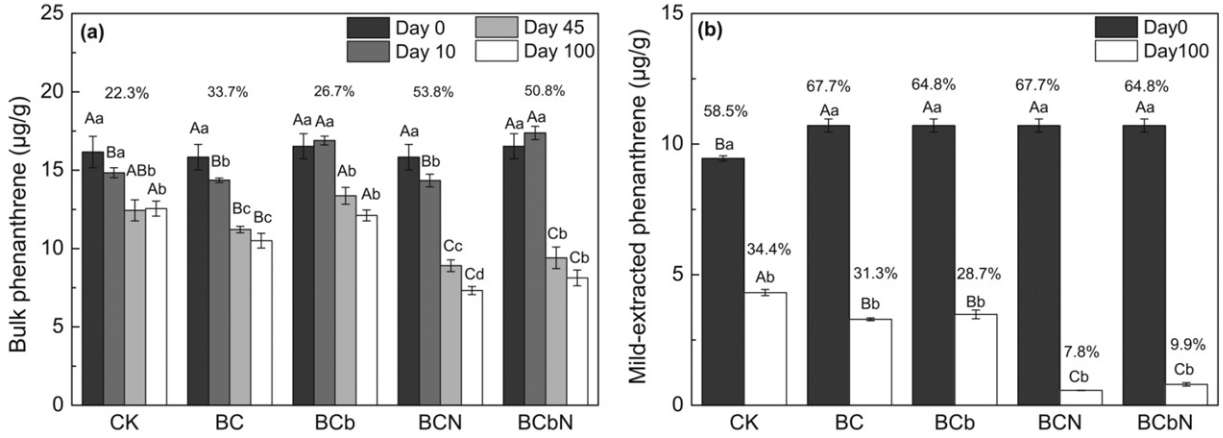

Fig. 1. Concentrations of (a) bulk and (b) mild-extracted phenanthrene during the incubation period. Significant difference level (α = 0.05) is indicated by using capitals for different treatments and lowercases for different sample times in one treatment. The percentages in (a) were represented the 100 d removal ratios and in (b) were the ratios of the mild-extracted fraction to bulk phenanthrene.