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Effect of multi-walled carbon nanotubes on phytotoxicity of sediments contaminated by phenanthrene and cadmium

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HIGHLIGHTS

- Use of MWCNTs for in situ remediation of contaminated sediments was explored.
- Phytotoxicity of contaminated sediments before and after remediation was evaluated.
- Root growth was more sensitive to the changes of pollutant concentration.
- Phytotoxicity might inaccurately indicate the changes of pollutant content.

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ABSTRACT

To implement effective control and abatement programs for contaminants accumulating in sediments, strategies are needed for evaluating the quality of amended sediments. In this study, phytotoxicity of the sediments contaminated by cadmium and phenanthrene was evaluated after in situ remediation with multi-walled carbon nanotubes (MWCNTs) as adsorbents. Adsorption experiments and measurement of aqueous concentrations of the contaminants in overlying water were used to investigate the remediation effectiveness from physical and chemical aspects. The results indicated that MWCNTs showed a much better adsorption performance towards phenanthrene and Cd(II) compared with the sediments. The in situ remediation with MWCNTs could distinctly decrease the aqueous concentrations of phenanthrene and Cd(II) released from the sediments, reducing environmental risk towards overlying water. Influences of MWCNTs dose, MWCNTs diameter, and contact time on phtotoxicity of the contaminated sediments were studied. No significant inhibition of the amended sediments on germination of the test species was observed in the experiments, while the root growth was more sensitive than biomass production to the changes of contaminant concentrations. The analysis of Pearson correlation coefficients between evaluation indicators and associated remediation parameters suggested that phytotoxicity of sediments might inaccurately indicate the changes of pollutant content, but it was significant in reflecting the ecotoxicity of sediments after remediation.

1. Introduction

In situ remediation of contaminated sediments using materials with high adsorption capacity has become a common method due to low cost, simple operation, and less impact on natural hydrological conditions (Peng et al., 2009; Gomes et al., 2013; Zhang et al., 2016). This remediation technique aims at improving the stabilization of pollutants in sediments by reducing their mobility, bioavailability, and toxicity with adsorbents. For this purpose, many nanomaterials (e.g., carbon nanotubes, nano-hydroxyapatite, nano-TiO_2, and nanoscale zero-valent iron) with stronger affinity for pollutants than traditional materials (e.g., activated carbon, biochar, and zeolite) are explored for in situ remediation of contaminated sediments (Ferguson et al., 2008; Tang et al., 2008; Feng et al., 2010; Zhang et al., 2010; Xu et al., 2012a; Tomašević et al., 2014; Zhang

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et al., 2014).

Carbon nanotubes, including single-walled carbon nanotubes and multi-walled carbon nanotubes (MWCNTs), are regarded as one of the most promising nanomaterials as adsorbents for removing pollutants (Gong et al., 2009). Recently, several studies have investigated the remediation of contaminated sediments with carbon nanotubes (Kwadijk et al., 2013; Abbasian et al., 2016; Tričković et al., 2016). The results of these studies provide evidence that carbon nanotubes can effectively decrease ecological risk of contaminated sediments. However, stabilized contaminants still remain in sediments. When the hydrological conditions change, contaminants may be released into overlying water again (Zeng et al., 2013). Therefore, it is necessary to evaluate the effectiveness of in situ remediation of contaminated sediments. Additionally, in situ remediation is a site-specific process, full-scale field applications of the remediation also calls for effective evaluation methods (Apitz et al., 2004).

Most of current evaluations focus on the total amount of contaminants. Nevertheless, it is difficult to determine the immobilized contaminants directly. Some researchers used polyethylene passive samplers (Choi et al., 2014; Pisanello et al., 2016) or Rhizon soil moisture samplers (Park et al., 2011; Sumon et al., 2012) to measure the decreased amount of contaminants in pore water. These methods are valuable for characterizing the remediation effect, but they do not illuminate the significant processes that affect the bioavailability of contaminants. Moreover, they are expensive and time-consuming. Phytotoxicity is a significant part of the ecological risk assessment of contaminants. Compared with the toxicity tests using animals, algae, and microorganisms, phytotoxicity tests during early germination have certain advantages. (1) Dry plant seeds exhibit a better applicability under harsh and rapidly changing environment. (2) Plant seeds are much cheaper and can be stored for a longer time. (3) The tests can be simple, sensitive, and fast. (4) There is no need to add plant nutrients during the tests (Wang et al., 2001; Huang et al., 2008; Kwon et al., 2016; Song et al., 2016). Thus, phytotoxicity of the sediment during early germination can be a convenient, fast, and effective way to reflect the quality of sediment.

Polycyclic aromatic hydrocarbons (PAHs) and heavy metals (HMs) are two widespread pollutants in sediment. Their fates are of great environmental concern due to their toxic, mutagenic, and carcinogenic properties (Hong et al., 2016; Sá et al., 2016; White et al., 2016). In this study, cadmium and phenanthrene are selected as model compounds of HMs and PAHs. The objectives of the study were (1) to carry out in situ remediation of sediments contaminated by phenanthrene and cadmium with MWCNTs, and (2) to assess phytotoxicity of the contaminated sediments with and without addition of MWCNTs by selected plants with short germination period as bio-indicators.

2. Materials and methods

2.1. Chemicals, carbon nanotubes and sediments

Phenanthrene ($C_{14}H_{10}$, purity > 97%) was purchased from Xiya Chemical Industry Co., Ltd., Shandong, China. Cadmium chloride ($CdCl_2 \cdot 2.5H_2O$, analytical grade) was obtained from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. Three MWCNTs (purity > 95%) with different outer diameter (10–20 nm, 30–50 nm, >50 nm) were used in this study. They were purchased from Chengdu Organic Chemistry Co., Chinese Academy of Sciences, Chengdu, China.

Surface sediment samples (0–15 cm) were collected from the Xiangjiang River in Changsha, Hunan Province, China. All sediment samples were air-dried at room temperature and crushed in a porcelain mortar. Then the samples were sieved over a 2 mm mesh sieve and homogenized prior to use. Sediment properties including pH, cation exchange capacity, organic carbon content, zeta potential, electrical conductivity, and texture were measured according to previously reported methods (Bouyoucos, 1928; Gillman and Sumpter, 1986; Yeomans and Bremner, 1988; Su et al., 2016).

2.2. Adsorption experiments

Adsorption of the two contaminants on sediments and MWCNTs was conducted in 50 mL glass bottles with Teflon-lined screw-cap. For the adsorption of phenanthrene, 2 g L^{-1} sediments or 0.1 g L^{-1} MWCNTs were mixed with phenanthrene solutions of various concentrations (0.1–4 mg L^{-1}) on a shaker for 48 h at 180 rpm, 25 ± 1 °C. After equilibrium, the suspension was centrifuged and the phenanthrene concentration in supernatant was determined by high performance liquid chromatography (HPLC, Agilent 1100, USA). Initial phenanthrene solutions of various concentrations were prepared by diluting concentrated phenanthrene stock solutions using methanol as solvents. The final concentration of methanol in the aqueous solution was kept below 0.1% (v/v) to minimize the cosolvent effect (Nkedi-Kizza et al., 1985; Chen et al., 2007). For the adsorption of Cd(II), the experiments were carried out by mixing 0.5 g L^{-1} sediments or 0.5 g L^{-1} MWCNTs with Cd(II) solutions of varying initial concentrations (2–20 mg L^{-1}) on a shaker for 12 h at 180 rpm, 25 ± 1 °C. After equilibrium, the supernatants were taken out and filtered through filter membranes with 0.45 μm pore size. The Cd(II) concentration in the filtrate was measured by an atomic absorption spectrometer (AAS, Agilent 3510, USA).

2.3. Sediment-spiking procedures

Quantitative phenanthrane or cadmium chloride was spiked into the sediments to reach desired concentrations according to previously reported methods with appropriate modifications (Brinch et al., 2002; Simpson et al., 2004; Jiang et al., 2015). For thorough mixing of phenanthrane and sediments, penanthrane was dissolved in dichloromethane and then added to 25% of the total weight of dry sediments, followed by stirring every 15 min to evaporate the solvent completely. Subsequently, the treated sediments were mixed with the rest 75% of sediments. After manual homogenisation, the moisture content of spiked-sediment was adjusted by adding 50% (v/w) ultrapure water. Following that, the blending container was sealed and stored in darkness to avoid evaporation and photolysis of phenanthrene. The Cd(II) was artificially added into sediments by adding contamination solutions using deoxygenated water as homogenising solvent. Spiked sediments were homogenized using a glass stirring rod. After that, the mixture was deoxygenated by bubbling with nitrogen for 2 h to minimize oxidation reactions that cause the pH value to decrease (Simpson et al., 2004). The spiked sediments were shaked periodically and aged for 6 weeks to achieve equilibrium of diffusion processes within the sediments (Oliver, 1987). Samples were taken out to determine final concentrations of Cd(II) and phenanthrene in the sediment after spiking procedure. According to the consequences of measurement, sediments with actual concentration of 1.42 mg Cd(II) or 2.56 mg phenanthrene per gram of dry weight sediment were used for the following experiments.

2.4. Amendment of contaminated sediments

To determine the effect of MWCNTs dose on remediation effectiveness of the contaminated sediments, MWCNTs were mixed with the sediments at the dose of 0.5%, 1.0%, or 1.5% (w/w). In the