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Restoration of manufactured gas plant site soil through combined ultrasound-assisted soil washing and bioaugmentation

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HIGHLIGHTS

- EDDS + MCD could efficiently remove PAHs/heavy metals simultaneously.
- Inoculation enhanced enzyme activity and PAH removal.
- Ultrasonication promoted pollutants desorption.
- Biodegradation activity was inhibited by the presence of toxic metals.

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ABSTRACT

An effective ex situ soil remediation technology was developed in this study to remove polycyclic aromatic hydrocarbons (PAHs) and heavy metals in a mixed contaminated site. Ultrasonication (20 kHz, 45 min) combined with methyl-β-cyclodextrin (75 g/L) and S,S-ethylenediaminedisuccinic acid (25 g/L) were efficient in extracting mixed pollutants from the soil. After two successive washing cycles, the removal efficiency of PAHs and heavy metals were approximately 84.5% and 81.3%, respectively. The high removal of metals remarkably reduced soil microtoxicity and thus activated biodegradation activity towards PAHs. Inoculation of PAHs-degrading bacterial strains with nutrients addition further removed 86.8% of residual PAHs in 16 weeks. These results were indicated by the significant increase in the number of PAH degraders and soil enzyme activity. After treatment, the residual levels of individual PAHs and heavy metals could meet Chinese soil quality standard for residential use. The proposed combined cleanup strategy proved to be effective and environmentally friendly for remediation of mixed-contaminated site.

1. Introduction

Manufactured gas plant (MGP) sites are known for significant release of polycyclic aromatic hydrocarbons (PAHs) into the surrounding soil. It is urgently desirable to remediate such contamination due to the hazardous nature of PAH compounds and the urge for urbanization.

One of the general common solution for remediation of MGP sites is to excavate the contaminated soil and bury it in landfill sites. However, the offsite burial is not an appropriate option because it merely shifts the pollution elsewhere and has proved to be expensive due to the recent increment in the landfill levy (EPA Victoria, 2009).

Due to their relatively low costs and environmental friendship relative to physical and chemical processes, bioremediation approaches have been extensively studied and applied for restoration of PAHs-contaminated soils (Haritash and Kaushik, 2009). However, it is often difficult to reach remediation endpoints and to meet regulatory soil quality criteria through bioremediation alone, due to strong sorption and sequestration of PAHs to soil organic matter (SOM) (Reichenberg et al., 2010). Moreover, a fact often overlooked is that PAHs often co-exist with heavy metals (such as As, Cr, Cu, Pb, Ni, Zn, etc) in MGP sites due to similar pollution sources (Thavamani et al., 2011). Biodegradation of PAHs in MGP sites could be inhibited by the presence of high levels of toxic metals (Thavamani et al., 2011). These situations present a complex and challenging problem for remediating MGP sites, since the chemical

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processes and remediation technologies are different for toxic metals and PAHs (Sandrin and Maier, 2003).

One of the commonly employed and efficient techniques for soil remediation is soil washing using chemical agents. Recently, some studies have been performed on remediation of soil co-contamination with hydrophobic organic contaminants (HOCs) and toxic metals. For example, saponin showed higher capability than Triton X100 and citric acid did on desorbing phenanthrene and Cd from artificial soil (Song et al., 2008). Glycine-β-cyclodextrin prepared by Wang et al. (2010) could remarkably increase phenanthrene solubility and efficiently complex with Pb in artificial soil. Sun et al. (2013) used methyl-β-cyclodextrin solution to enhance extraction of PAHs and metals from a coking plant soil. Nevertheless, the removal efficacy of HOCs and heavy metals in the case of coexistence is limited for a washing agent alone, because these two types of pollutants have different natures and partitioning mechanisms in soil.

The physico-chemical property of extraction agents plays an important role in rendering good contact between soil and solvent phases for providing high extraction efficiency during the soil extraction process. Compared with washing by use of single agent, the combined application of surfactant and complexant can result in higher washing efficiency with less reagent consumption. Extractions of 48% and 55% were achieved for Pb and phenanthrene respectively from a historically contaminated soil, using the combination of ethylenediaminetetraacetic acid (EDTA) with polyethylene glycol dodecyl ether (Fonseca et al., 2011). EDTA was widely used for remediation of metal contaminated soils because of its high complexation ability towards heavy metals. However, EDTA has a low biodegradability and a high persistency in the soil environment (Cao et al., 2013), which limits its large-scale application. To reduce the potential environmental risk of EDTA, various easily biodegradable surfactants and chelating agents have been used and evaluated. For example, the maximum desorption rates of Pb, Cu and polychlorinated biphenyls (PCBs) were 99.8%, 85.7% and 45.7%, respectively, by addition of 10 mM S,S-ethylenediaminedisuccinic acid (EDDS) and 3000 mg/L saponin (Cao et al., 2013). Ye et al. (2014a) reported 94.3%, 93.2%, 85.8%, 93.4%, 83.2% and 97.3% removals of total PAHs, Pb, Cd, Cr, Ni and fluorine respectively from a metallurgic plant site, through three successive washing cycles using a solution composed of carboxymethyl-β-cyclodextrin (5 wt.%) plus carboxymethyl chitosan (0.5 wt.%).

Like PAHs, many HOCs can strongly adsorb to soil clay fraction and SOM. Thus, washing treatment of HOCs-polluted sites could result in higher pollutant residue levels and higher operation/reagent costs through conventional washing process (Son et al., 2011). In comparison to mechanical agitation, ultrasound irradiation is a more effective method for enhancing desorption of adsorbed substances from solid phase to solution phase. Washing/leaching assisted by ultrasound wave can achieve higher removal efficiency with less time compared with mechanically stirring, through violent actions including microjet, microstreaming, oscillating cavitational bubbles, and shock waves (Abramov et al., 2009). Recently, some scholars demonstrated the ultrasound-enhanced release of different types of pollutants from soil such as dichlorodiphenyl-trichloroethane (Thangavadivel et al., 2011), PAHs/heavy metals (Wen et al., 2012; Sun et al., 2013), and petroleum hydrocarbons (Abramov et al., 2009; Son et al., 2011). The addition of solubilizing agents, such as surfactants, can enhance this process even more by complexating the released pollutants and keeping them in solution. The integration of ultrasound in soil washing can improve available techniques to clean soil physico-chemically (Thangavadivel et al., 2011). Despite several promising publications, however, the overall research regarding this technique to promote the remediation of organic-metal co-contaminated soil is rather limited.

Therefore, the current study investigated the potential of a combined technique on remediation of an actual soil co-contaminated with PAHs and heavy metals through lab-scale experiments. The soil samples were first washed with EDDS and methyl-β-cyclodextrin (MCD) solutions to remove most of PAHs and heavy metals under ultrasound-assisted conditions. Then the soil was inoculated with a specific PAH-degrading microflora to biodegrade soil-bound PAHs residues. The effects of certain factors on the removal efficiency were examined.

2. Materials and methods

2.1. Chemicals

The following chemicals were purchased from Sigma–Aldrich, St. Louis, MO, USA: a standard mixture of 16 priority PAHs; deuterated surrogate standards (1-methylnaphthalene-d8, fluorene-d10, anthracene-d10, pyrene-d10, p-terphenyl-d14, benzo[a]pyrene-d12, and benzo(g,h,i) perylene-d12); internal standards (hexamethyl benzene and perylene-d12); [9-^{14}C]-phenanthrene (13.1 mCi/mmol), [3-^{14}C]-fluoranthene (45.0 mCi/mmol), [1,2,3,4,4a,9a-^{14}C]-anthracene (20.6 mCi/mmol), and [4,5,9,10-^{14}C]-pyrene (58.7 mCi/mmol); all of them with a purity > 98%. All solvents used were of HPLC grade. Deionized water (>18 MΩ) was used for all experiments. EDDS and MCD (purity > 98%) were purchased from Ziyi Reagent Factory (Shanghai, China), and used without further purification. All other chemicals and reagents used were of analytical-reagent grade or higher purity.

2.2. MGP site soil

The co-contaminated soil used in this study was collected from a former MGP site in Jiangsu, China. The site was used for more than 30 years but is now no longer used. For sampling, the top 15–cm soil was removed and the remaining soil (15–50 cm) was collected. The soil was air-dried and sieved through a 2-mm mesh sieve, homogenized by hand with a shovel, and then stored at 4 °C in the dark until used. The main physicochemical and microbiological properties of the soil sample studied are summarized in Table 1. The basic soil properties were measured according to standard methods (Lu, 1999). Concentrations of Pb, Cd and PAHs exceed the limit of Chinese soil quality standard (China EPA, 2008).

2.3. Soil washing

Batch experiments were carried out to evaluate the extraction of PAHs and heavy metals under different operational conditions. For this, 100 g soil sample was placed in a 2-L glass flask with a Teflon-lined cap, to which 1-L of different washing solutions were added at three different soil:solution ratios (1:2, 1:5 and 1:10). Different concentrations of EDDS, MCD and their combinations were tested. Three treatments were tested, including mechanical stirring (at 150 rpm), ultrasound agitation (at 20 kHz and 50 W), and their combination. Ultrasound treatment was conducted in a KQ-500 B ultrasonic device (Kunshan Ultrasound Instrument Company, China). At regular intervals, three replicate flasks were sacrificed per experimental run, and the suspensions were centrifuged at 10,250 × g for 10 min. The supernatants and soil residues were separately collected for analysis. A blank test was properly performed using deionized water. Successive washings of four cycles were examined to evaluate removal efficiency base on the optimum conditions obtained through above described experiments. The pH was monitored in all experimental sets. All soil washing experiments were performed in triplicate at room temperature.