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Remediation of petroleum-contaminated soil after composting by sequential treatment with Fenton-like oxidation and biodegradation

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ABSTRACT

A laboratory study was conducted to enhance removal of residual contaminants after composting in a highly petroleum-contaminated soil by combining Fenton-like pretreatment with biodegradation. The contaminants were characterized by Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) during soil treatment. The optimum molar ratio of H_2O_2 and Fe^{3+} was 300/1 determined in batch experiments. At the end of Fenton-like treatment, total dichloromethane-extractable organics (TEO) decreased from 32,400 to 21,800 mg kg^{-1} soil, and the toxicity of soil was reduced greatly in the preoxidation process. A significant loss of the number of soil microorganisms was observed in the Fenton-like reaction. During the microbial treatment period, 50.6% of TEO was destroyed. Numerous varieties of polar compounds containing nitrogen and oxygen were identified by FT-ICR MS. The number of compounds containing two oxygen atoms dropped from 604 to 163 during Fenton-like oxidation, and increased again to 577 after biodegradation.

1. Introduction

Spills, leaks, and other releases of petroleum products often result in the contamination of soil and groundwater. This pollution causes significant environmental impacts and presents substantial hazards to human health.

Bioremediation of petroleum-contaminated soil is a hot topic in environmental research. This method uses microorganisms indigenous or exogenous to the contaminated sites to decompose or transform oil to materials such as water, CO_2, inorganic salts, microbial biomass, and other byproducts that may be less hazardous than the parent materials. Over the past several decades, numerous bioremediation technologies such as land farming, composting, bioventing, and bioreactor treatment have been developed (Boopathy, 2000). However, in many cases, an important fraction of pollutant and its metabolites remain in the soil over a long time period (Alexander, 1994; Devliegher and Verstraete, 1996). In some cases, microbial metabolism of contaminants may produce toxic metabolites, which can hamper subsequent biodegradation due to their toxicity that represses microbial metabolism (Boopathy, 2000; Chaillan et al., 2004). The residual levels of contamination and long-term soil toxicity may exceed the stringent cleanup standards dictated by environmental regulations and thereby limit the use of bioremediation for site clean-up (Huesemann et al., 2002).

Until now the environmental hazards assessment of remediated sites was primarily focused on on-site specific contaminants of concern (COCs). However, not all COCs may be known, and undetected metabolites or compounds may be formed during biogeochemical processes (Płaza et al., 2005). This is especially important for toxicologically relevant polycyclic aromatic hydrocarbons (PAHs), for the oxidation products of PAHs are in many cases more toxic than their parent compounds (Gibson and Subramanian, 1984).

Chemical methods have been shown to oxidize and mineralize organics. Chemical oxidation may not only destroy target compounds, but also reduce toxicity associated with formulation ingredients and active agents. It can also be an effective pretreatment step for enhancing bioremediation by reducing overall toxicity to indigenous microorganisms, allowing them to participate in the remediation process (Miller et al., 1996). The use of Fenton's reagent ($Fe^{2+} + H_2O_2$) to oxidize various compounds is one of the most studied chemical oxidation processes. It is recognized as one of the most powerful oxidizing reactions available and can be used to destroy a wide variety of biorefractory organic compounds in aqueous waste, soils, and ground water. The classical Fenton oxidation system can be modified by complexing the ferrous iron with strong ligands such as ethylenediaminetetraacetic acid, ethylene bis (oxyethylenenitrilo) tetraacetic acid, and nitrilotriacetic acid (Tachiev et al., 2000). The complex forming

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compound will keep the iron in solution and increase the reaction rate outside the ideal operating range pH for Fenton's reagent (pH 3.0–4.0). Complexed iron oxidation systems have increased the operating range of the classical Fenton system to pH of 6.0–8.5. Consequently, the modified Fenton oxidation system can be applied directly to environmental and biological systems in the neutral pH range. This precludes the requirement of pH adjustment for these systems.

In a previous work, we applied a two-liquid-phase slurry reactor using silicon oil as a solvent to degrade residual contaminants in a petroleum-contaminated soil after composting, and an obvious effect on the removal of contamination was obtained (Lu et al., 2009). Conversely, there was no reduction of soil contamination in the slurry reactor without the addition of silicon oil, due to high toxicity of metabolites to the microorganisms. Moreover, we used electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI FT-ICR MS) to preliminarily characterize polar compounds containing nitrogen and oxygen, which might not be amenable to gas chromatography/mass spectrometry (GC/MS). Despite the significant improvement in removing contamination by the use of two-liquid-phase slurry reactors, the final phase separation and solvent recycling can contribute to an increase in operational complexity of the treatment system.

In the present study, we used Fenton-like oxidation to partially destroy inhibitory compounds in the soil described above, after which the soil was remediated with microbial degradation. The efficacy of remediation was investigated by monitoring step changes in the contaminant level incorporating soil ecotoxicity testing. FT-ICR MS was used to monitor detailed compositional changes of contaminants during the remediation process.

2. Methods

2.1. Chemicals

All solvents used were of analytical or glass-distilled grade. Reagent-grade H_2O_2 (30%, w/v), $Fe_2(SO_4)_3$, H_2SO_4, iron citrate and solvents were obtained from commercial supplier (Beijing Chemical Company, China).

2.2. Soil

The contaminated soil was a loamy sand soil, initially collected from the adjacent areas of oil wells in Dagang Oilfield (Tianjing, China, latitude 38°34′N and longitude 116°43′E). The soil had been treated using composting, and treatment details are described previously (Lu et al., 2009). Briefly, the soil was stacked with sawdust in separate piles and fertilized with a self-prepared inorganic fertilizer; the ambient temperature during treatment was 15–30 °C; a mixed culture of microorganisms isolated from petroleum-contaminated soil was used as inoculum (for more details, see Electronic Annex 1 in the online version of this article). To reduce heterogeneity, 10 kg of dry soil was mixed with tap water at a ratio of 1:1 (w/v), subsequently stirred in a mud agitator for 12 h. After homogenizing, the slurry was sieved to remove particles and sawdust larger than 0.2 mm. The slurry was dried at 40 °C for 7 days and then stored at 4 °C until used (water content less than 0.3%, w/w). The prepared soil contained (kg^{-1}) 32,400 mg total dichloromethane-extractable organics (TEO), which had a clay texture, pH of 7.8 (1:2 ratio of dry soil to distilled water).

2.3. Optimization of Fenton-like reaction

Batch experiments were performed to obtain the optimal molar ratio of hydrogen peroxide to iron. In view of the high contamination level, it cannot be expected that the Fenton oxidation treatment might be completed with one single dose of hydrogen peroxide. Hence we applied a relatively small fixed dose of hydrogen peroxide while changing the dose of iron to obtained the optimal ratio of hydrogen peroxide to iron. The experiment for each ratio tested was performed in triplicate.

In order to generate Fenton reaction at near-neutral pH, a Fenton-like reagent was developed by using iron citrate as a catalyst. Twenty grams of soil were weighed into a 250-mL Erlenmeyer flask and subsequently 59 mL of deionized water was added. The mixture was incubated for 2 h at 25 °C at 150 rpm. Subsequently, slurry received 0.1 mL of 0.9800, 0.6533, 0.4900, 0.3920, 0.3267, 0.2800, and 0.2450 M iron citrate, respectively. Slurry pH was adjusted to 6.5 with sulphuric acid. Each flask received 1 mL of H_2O_2, namely the hydrogen peroxide dose was fixed at 0.49 mol kg^{-1} soil. The molar ratio of H_2O_2/Fe^{3+} ranged from 100/1 to 400/1. The flasks were placed on a reciprocating shaker at 150 rpm for 24 h at 25 °C under dark conditions, and were kept open to prevent possible explosions due to gas accumulation.

2.4. Oxidation in bench-scale reactors

Based on the optimal molar ratio of H_2O_2/Fe^{3+}, subsequent experiments were performed in a bench-scale slurry reactor in triplicate. The reactor consisted of a 7-L round-bottom Pyrex glass vessel with an adjustable fitted cover. Several holes were drilled into the cover. The central hole in the cover accommodated a propeller blade attached to a mechanical mixer rotating at 600 rpm. One hole housed a dissolved oxygen (DO) probe and another a pH probe to allow continuous monitoring of DO and pH. The fourth hole was allowed to open to permit evacuation of the generated gas. Two sampling ports were located along the side-wall of the reactor at 5 and 30 cm from the bottom of the reactor. A hole in the bottom of the reactor was connected to an air diffuser stone and aeration was provided only in the bioslurry treatment after Fenton oxidation.

The reactor received 1.5 kg of prepared soil (32,400 mg kg^{-1} TEO), and 4425 mL of distilled water. The pH was adjusted to 6.5 with sulphuric acid and the reactor was maintained with vigorous stirring. The soil slurry, before addition of chemical reagent, was equilibrated for 2 h in the reactor. It is well documented that stepwise addition of the Fenton reagent was more effective in destroying contaminants than a single-batch addition, which avoids the competition reaction of the hydroxyl radicals and reduces foam production (Bier et al., 1999; Nam et al., 2001; Kröger and Fels, 2007). Thus, in the present study, the reagent was added in a single-batch, in four additions at 24 h intervals. Each time, the reactor received 75 mL of 30% H_2O_2 (0.49 mol kg^{-1} soil) and 7.5 mL of iron citrate solution (0.3267 M). The temperature was maintained at 25 °C in the dark during the experimental period.

2.5. Biological treatment

Following the Fenton-like pretreatment, biological treatment was carried out in the same reactor in triplicate. A mixed culture, isolated from the above contaminated soil, was used as an inoculum. Two-gram samples of soil were incubated with diesel oil in 100 mL of sterile modified Bushnell-Haas mineral solution with pH of 7.5 (Wyndham and Costerton, 1981). After 2 weeks of incubation, 10 mL of the supernatant were collected and incubated for two more weeks as described above. The consortium was inoculated into 250-mL Erlenmeyer flasks containing 100-mL Bushnell-Haas medium and 2 g of glucose, and incubated for 24 h at 30 °C on an orbital shaker (150 rpm). After harvesting by centrifugation, the cell pellet was added to the slurry to give an inoculum of 10^6 bacterial cells mL^{-1}. Timing started when the inoculation