Remediation of Diesel-contaminated Soil by Bioventing and Composting Technology

Lihua Mao
School of Environmental Science and Engineering
Shandong University
School of Resources and Environment
University of Jinan
Jinan, China
e-mail: stu_maolh@ujn.edu.cn

Qinyan Yue
School of Environmental Science and Engineering
Shandong University
Jinan, China
e-mail: qinyanyue@sdu.edu.cn

Abstract—Bioventing and microbe composting methods were used in the laboratory to simulate the remediation of the diesel-contaminated soil. Consequently the contaminants removal paths and mechanism were discussed. The results showed that these two methods were effective in the remediation process. After 45 days, over 64% diesel was removed from the soil given the original oil content at 5.00×10⁻⁵ mg·kg⁻¹. The rate constant of biodegradation and half life was 0.0384 d⁻¹ and 18.05 d, respectively. Biodegradation was the main way of contaminant removal. Volatilization loss of diesel oil was less than 2.5% of initial diesel oil content. Among the three ratio of contaminated soil to sewage sludge (dry weight) with the ratio of 8:2, 7:3 and 5:5 respectively, the highest removal of diesel oil was observed in the ratio of 7:3, in which the removal of complete biodegradation reached to 73.59% of the total removal.

Keywords—biodegradation; diesel-contaminated soil; composting; sewage sludge; bioventing

I. INTRODUCTION

Soil contamination of petroleum is a common and severe problem in the world nowadays. The technology of the remediation of the petroleum-contaminated soil has been a research focus of the academia, and to seek some effective and economical and simple methods to solve this problem is the common goal of all the researchers.

Composting technology has been widely used in remediation of organic contaminated soils in the past a few years. At present, some contaminants can be disposed of including petroleum hydrocarbon, dynamite, chlorophenol, pesticide, PAHs etc [1]. Effective bioremediation of petroleum-contaminated soil by composting technology has been proved by some research. Jorgensen (2000) studied the remediation of oil-contaminated soil with composting through adding wood chips, fungi and suitable nutrient of nitrogen, phosphorus and Potassium. About 70% of the initial oil content removal is reported after 5 months [2]. Wan Namkoong (2002) studied the bioremediation of diesel-contaminated soil with composting through adding sewage sludge and compost respectively. Degradation rates of total petroleum hydrocarbons (TPH) are over 95% [3]. Van Gestel (2003) studied the bioremediation of diesel-contaminated soil by composting with biowaste (vegetable, fruit and garden waste). 85% of the initial oil content removal is reported after 12 weeks [4]. But there is no further research on the appropriate mix ratio or the compost supplement for enhancing oil degradation during contaminated soil composting until now. Target contaminant of this research is diesel oil, which is widely used nowadays. Bioventing and composting methods were used to simulate the remediation of the diesel oil-contaminated soil. Consequently the contaminants removal paths and mechanism were discussed.

II. MATERIALS AND METHODS

A. Materials

The main materials used for this research include diesel oil, soil, and sewage sludge. Target contaminant of this research was diesel oil (-20⁰), which was obtained from a gas-station of Beijing city. The soil was collected from the top 20 cm of the soil surface in the campus of China University of Geosciences (Beijing). The soil was air-dried and sieved to pass a 2-mm sieve. Sewage sludge was obtained form Beijing Gaobeidian sewage treatment factory. Table 1 shows characteristics of soil and compost used for this research. As shown in table 1, Sewage sludge contains significantly large amount of effective nitrogen and effective phosphorus and microorganism compared with the soil. These analyses indicate that sewage sludge can be added as nourishment for composting of soil. In addition, the adding of sewage sludge can increase the microorganism density and activity of soil.

B. Experimental apparatus

Experimental apparatus used for this research consisted of a compost reactor, two CO₂ removal traps, a humidifier, and a trap for collecting CO₂ evolved from biodegradation (Fig. 1). Carbon dioxide-removed and humidified air was entered into the compost reactor (air-tight organic-glass vessel) through a cribriform plate. This cribriform plate was covered with 5-mm diameter glass beads, which were used to supply air evenly and efficiently and to prevent the cribriform plate from clogging with fine particles. Volatile organic compounds (VOC) from the reactor were collected using a glass tube containing 150 mg of charcoal (coconut activated carbon), which has high adsorption capacity for VOC (Wan Namkoong). Sampling time was regulated to avoid breakthrough of charcoal. Evolved CO₂ was continuously trapped in a solution of 4N NaOH.
C. Experimental conditions

This research was conducted under the room temperature condition (the room temperature was about 15℃±3℃ during the experiment period. Target contaminant of this research was diesel oil, which was spiked at 5×10^3 mg/kg sample on a dry basis. An aeration rate of 200 ml/min was introduced into the reactor. The ratios of contaminated soil to sewage sludge were 8:2, 7:3, and 5:5 as dry weight basis (Table 2). To investigate the degradation rate of diesel oil in soil alone, a soil-only experiment was carried out as control run. Also a biocide control experiment by addition of NaN₃ of 2,000 mg/kg was also carried out to discriminate abiotic degradation portion from total degradation portion (Table 2).

D. Analysis

Samples for GC analysis were prepared by 2h extraction at 200 rpm on a shaker. The ratio of sample to solvent (dichloromethane) was 1:5. Extraction recovery efficiency of oil by this procedure was 91.0% on average. A 1 ml extract was injected into a gas chromatograph (Agilent 6820). Measured compounds include isooctane (C₈), 1,2,4-tri-metho-benzene (C₉), normal alkanes including C₁₀, C₁₂, C₁₆, C₁₈, C₂₂, C₂₈. The initial temperature was kept at 45℃ for 1 min. Temperature was increased at 5℃/min to 100℃and maintained for 1 min, and then temperature was increased at 8℃/min to 275℃and maintained for 1 min, and then temperature was increased at 10℃/min to 310℃ and maintained for 5 min, and then temperature was increased at 20℃/min to final temperature of 320℃ and maintained for 5 min in order to ensure that the column was clean. The injection port and detector temperatures were 250℃ and 300℃, respectively. Hydrogen gas and air flow rates for the flame ionization detector were 30 ml/min and 330 ml/min, respectively. Nitrogen carrier gas was delivered at a rate of 30 ml/min. Carbon dioxide evolved by biological reaction was collected in 4 N NaOH as proposed by Stotzky (1979) [5]. An excess of barium chloride (3N BaCl₂) was added to precipitate the carbonate as BaCO₃. After adding a few drops of phenolphthalein indicator, the samples were titrated with 1N HCl. Carbon dioxide-uncollected NaOH was titrated as blank.

III. RESULTS AND DISCUSSION

A. Oil content and removal changing with time in the contaminated soil

Diesel oil content changing with time in the contaminated soil are presented in figure 2. In all experiments, Diesel oil content declined after 45 days, and the removal rate were raised simultaneity. Compared to column 1 and column 2, remarkable changes were found in column 3, column 4 and column 5, and the oil removal rate reached to 64.77% 64.62% 78.43% respectively. Rapid degradation of diesel oil was observed in the early stage (within 15 days) in all experiments, but especially in the sewage sludge amendment experiments. Residual diesel oil was degraded slowly compared with the early stage. Difference in diesel oil degradation rate depending on time was due to the rapid degradation of n-alkanes in diesel oil at the early stage. Heavier molecular weight compounds are more resistant to degradation resulting in a decrease in biodegradation rate (van Zyl and Lorenzen, 1999) [6]. In addition, rapid degradation may be restricted by the nutrient content in compost materials, with the nutrients consumed during the degradation.

Oil contaminants were removed by volatilization and biodegradation during the remediation process. Biodegradation including complete and incomplete biodegradation was the main removal path. The final products of the complete biodegradation are CO₂ and H₂O which are nontoxic. However, the middle products of the incomplete which might be toxic would become residad and keep up in soil. We can judge the degree of the contaminant removal by calculating the volatilization, complete and incomplete biodegradation proportion in the total removal rate, which is an important criterion to assess the remediation effect.

B. Diesel oil removal through the volatilization

Volatile constituents of diesel oil volatilized continuously with the aeration and the biodegradation. Volatile consist with the volatile constituents of original diesel oil and the volatile constituents of biodegradation products. As shown in figure 3, accumulated removal quantity of diesel oil through the volatilization in all experiments ranged from 1.08% to 2.46%, which was was consistent with the result of Wan Namkoong (2002). Compared to the total removal rate, volatilization loss was very little.

C. Diesel oil complete biodegradation and the CO₂ evolved

As shown in figure 4, a part of oil contaminants were degraded completely in all experiments because of the evolved CO₂ in all columns. There was CO₂ produced in column 1. This indicted that there were live microbe in column 1 because the experiments were not carried out under a sterile operating area, thus a part of crude oil in column 1 was also biodegraded. This was the reason that the total removal rate was inconsistent with the volatilization loss. Accumulation of produced CO₂ through biodegradation in column 3, column 4 and column 5 were more than that produced in column 2, especially in column 4.

We can calculate the oil content that degraded completely according to the accumulation of produced CO₂ through biodegradation, and calculate the complete biodegradation rate of oil consequently (Jia Jianli, 2005) [7]. As shown in figure 5, the complete biodegradation rate of diesel oil in column 4 reached to 47.55%, which was the highest in all the columns. This confirmed the advance of the sewage sludge that added to the complete biodegradation of diesel oil on one hand. On the other hand, it indicated that excessive sewage sludge could not result in the increase of the diesel oil that biodegraded completely. There was an appropriate mixed ratio of contaminated soil and sewage sludge in composting process. Thomas et al. (1992) suggested that the addition of organic amendments could increase the degradation.
rate of target contaminants, but might inhibit degradation the rate when an excessive amount of organic amendment was added [8].

D. Diesel oil removal paths and mechanism discussion

Diesel oil was removed by volatilization, complete biodegradation and incomplete biodegradation during the remediation process as discussed. As shown in figure 6, biodegradation was the main way of the diesel oil removal. The complete biodegradation rates in column 3, column 4, and column 5 were 29.47%, 47.55%, 31.32%, and the complete biodegradation rates were 45.51%, 73.59% and 39.93% of the total removal, respectively. However, the complete biodegradation rate in column 2 was only 9.93%, which was only 20.03% of the total removal. Diesel oil was degraded much more completely when contaminated soil mixed with sewage sludge on dry weight basis at the ratio 7:3. Therefore, the appropriate mixed ratio of contaminated soil to sewage sludge on dry weight basis was 7:3 in this experiment.

E. Half life of crude oil degradation

The correlation coefficients for the kinetic models indicated that the commonly used first order model describes the degradation of diesel oil with high correlation coefficients (Table ). The first order kinetic model was linearly regressed with relationship between operational period and natural log value of diesel oil content [9]. The first order degradation rate constants also indicated that active degradation of diesel oil occurred in column 3 (K = 0.0244d^-1), column 4 (K = 0.0205d^-1), and column 5 (K = 0.0384d^-1), and half life of degradation were 28.41d, 33.81d and 18.05d, respectively. However, the first order degradation rate of crude oil was 0.0153d^-1, and the half life of degradation was 45.30d in column 2.

IV. CONCLUSIONS

Conclusions found from this research are as follows:

A. Bioventing and composting method was effective in the remediation of the diesel oil-contaminated soil. After 45 days, over 64% crude oil was removed from the soil given the original oil content at 5.00×10^5 mg·kg^-1. The highest constant of biodegradation and half life was 0.0384d^-1 and 18.05d, respectively.

B. Biodegradation was the main way of contaminant removal. Volatilization loss was less than 2.5% of initial diesel oil content.

C. Among the three ratio of 8:2, 7:3and 5:5 of contaminated soil to sewage sludge (dry weight), the highest removal of diesel oil was observed in the ratio of 7:3, in which the removal of complete biodegradation reached to 74% of the total removal.

D. Sewage sludge was a kind of appropriate composting material for diesel oil-contaminated soils bioremediation.

ACKNOWLEDGMENT

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REFERENCES


TABLE I. CHARACTERISTICS OF SOIL AND SEWAGE SLUDGE

<table>
<thead>
<tr>
<th>material</th>
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<th>sewage sludge</th>
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<td>Water content (%)</td>
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<td>81.59</td>
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<tr>
<td>pH</td>
<td>8.4</td>
<td>7.6</td>
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<tr>
<td>Effective nitrogen (mg·kg^-1)</td>
<td>17.77</td>
<td>410.31</td>
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<tr>
<td>Effective phosphorus (mg·kg^-1)</td>
<td>12.40</td>
<td>42.39</td>
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<tr>
<td>Amount of microorganism (×10^6 CFU/g)</td>
<td>0.5</td>
<td>570</td>
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<tr>
<td>Activity of microorganism (abs·g^-1·h^-1)</td>
<td>0.28</td>
<td>3.18</td>
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TABLE II. COLUMNS ASSEMBLED IN THE EXPERIMENT

<table>
<thead>
<tr>
<th>Columns</th>
<th>Compost materials</th>
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<tbody>
<tr>
<td>Column 1</td>
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<td>—</td>
</tr>
<tr>
<td>Column 2</td>
<td>contaminated soil</td>
<td>2</td>
<td>—</td>
</tr>
<tr>
<td>Column 3</td>
<td>contaminated soil, sewage sludge</td>
<td>2</td>
<td>—</td>
</tr>
<tr>
<td>Column 4</td>
<td>contaminated soil, sewage sludge</td>
<td>2</td>
<td>—</td>
</tr>
<tr>
<td>Column 5</td>
<td>contaminated soil, sewage sludge</td>
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TABLE III. RATE CONSTANT OF BIODEGRADATION AND HALF LIFE

<table>
<thead>
<tr>
<th>Columns</th>
<th>K/(d⁻¹)</th>
<th>R²</th>
<th>t₁/₂/d</th>
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<tr>
<td>Column 2</td>
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<td>0.992</td>
<td>39.84</td>
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<tr>
<td>Column 3</td>
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<td>0.996</td>
<td>25.48</td>
</tr>
<tr>
<td>Column 4</td>
<td>0.0285</td>
<td>0.984</td>
<td>24.32</td>
</tr>
<tr>
<td>Column 5</td>
<td>0.0476</td>
<td>0.978</td>
<td>14.56</td>
</tr>
</tbody>
</table>

Figure 1. Sketch of experimental device

Figure 2. Oil removal changing with time in the contaminated soil

Figure 3. Accumulated removal quantity of diesel oil through the volatilization

Figure 4. Accumulation of produced CO₂ through complete biodegradation

Figure 5. Accumulation of removal of diesel oil through complete biodegradation

Figure 6. Comparison of oil removal rates through different paths