



Enhanced bioremediation of oil contaminated soil by graded modified Fenton oxidation

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Abstract

Graded modified Fenton's (MF) oxidation is a strategy in which H_2O_2 is added intermittently to prevent a sharp temperature increase and undesired soil sterilization at soil circumneutral pH versus adding the same amount of H_2O_2 continuously. The primary objective of the present study was to investigate whether a mild MF pre-oxidation such as a stepwise addition of H_2O_2 can prevent sterilization and achieve a maximum degradation of tank oil in soil. Optimization experiments of graded MF oxidation were conducted using citric acid, oxalic acid and SOLV-X as iron chelators under different frequencies of H_2O_2 addition. The results indicated that the activity order of iron chelates decreased as: citric acid (51%) > SOLV-X (44%) > oxalic acid (9%), and citric acid was found to be an optimized iron chelating agent of graded MF oxidation. Three-time addition of H_2O_2 was found to be favorable and economical due to decreasing total petroleum hydrocarbon removal from three time addition (51%) to five time addition (59%). Biological experiments were conducted after graded MF oxidation of tank oil completed under optimum conditions mentioned above. After graded oxidation, substantially higher increase (31%) in microbial activity was observed with excessive H_2O_2 (1470 mmol/L, the mol ratio of $H_2O_2:Fe^{2+}$ was 210:1) than that of non-oxidized soil. Removal efficiency of tank oil was up to 93% after four weeks. Especially, the oil fraction ($C_{10}-C_{40}$) became more biodegradable after graded MF oxidation than its absence. Therefore, graded MF oxidation is a mild pretreatment to achieve an effective bioremediation of oil contaminated soil.

Key words: oil contaminated soil; graded modified Fenton's oxidation; bioremediation; citric acid; native microbial activity

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Introduction

More and more aboveground and underground storage tank systems leak nowadays, which is a pervasive universal problem in the world. The contamination of soil by leaking tank oil significantly threatens public health and environment as tank oil contains hazardous chemicals such as polyaromatic hydrocarbons (PAHs) (benzene, toluene, ethylbenzene, and naphthalene) and total petroleum hydrocarbon (TPH) (C_{10} to C_{40}) (Chen et al., 1998). The most conventional method for remediating tank oil contaminated site is excavation followed by landfilling or incineration. However, excavation/landfilling can not remove contaminants and incineration could cause a secondary pollution such as the formation of polychlorinated dibenzofurans (PCDFs) or polychlorinated dibenzo-*p*-dioxins (PCDDs). In addition, it is difficult to execute excavation for underground storage tank contaminated site. Due to the limitation of these conventional methods, various on-site and *in situ* treatment technologies are developed to

remediate contaminated sites. Among those techniques, *in situ* chemical oxidation (ISCO) with Fenton's reagent is used to remediate tank oil contamination in soil due to the following reasons: (1) transforming tank oil contaminants in the soil to carbon dioxide and water; (2) being rapid and aggressive, as well as providing residual dissolved oxygen; (3) easily combined with bioremediation (Nam et al., 2001).

The Fenton reaction was discovered by and named after H.J.H. Fenton in the late 1800s (Fenton, 1894) and further defined by Haber and Weiss (1934), who showed that the hydroxyl radical ($\cdot OH$) was the primary reactive species. The classic Fenton reaction is initiated by adding dilute hydrogen peroxide to a degassed solution of Fe(II) at acid condition, resulting in nearly stoichiometric generation of hydroxyl radicals. Modifications of the classic Fenton's reaction include using various catalysts as well as addition of excess H_2O_2 . For example, heterogeneous iron chelator (citric acid or oxalic acid) was used to enhance the catalysis of H_2O_2 at neutral pH, avoiding potential precipitation when soluble iron was used (Trye et al., 1991; Pignatello and Baehr, 1994; Ravikumar and Gurol, 1994). Moreover,

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high concentrations of hydrogen peroxide promote the reaction of H_2O_2 propagation and thereby generate significant quantities of non-hydroxyl radicals, which may be responsible for the enhanced treatment of sorbed contaminants and non-aqueous phase liquids (NAPLs) (Gates and siegrist, 1995; Watts et al., 1999).

The combination of modified Fenton (MF) and biological treatment processes has been a popular technology in recent years (ITRC, 2005). However, too much hydrogen peroxide retards the subsequent biological treatment and results in a poor post-biological contaminants removal because exothermic Fenton's reaction at high H_2O_2 concentration may destroy the native microbiota in the contaminated soil and even lead to undesired soil sterilization (Ferguson et al., 2004; Valderrama et al., 2009). Schrader and Hess (2004) have found a decrease in organism counts during *in situ* Fenton treatment of soils. Therefore, it is a crucial issue to find the mild MF oxidation for effective post-biological treatment.

Graded MF oxidation is a method in which stepwise additions of H_2O_2 is involved. Normally, 1/2–1/3 of H_2O_2 is applied each time, which calls for 2 or 3 additions in total. The addition method not only relieves the exothermic Fenton's reaction, but also reduces the risk of health and safety regarding explosion and the release of volatiles. In addition, it is a conventional hydrogen peroxide addition method in the field (Vitolins et al., 2003). However, graded MF chemistry has not been studied in detail. Many issues, which remain unresolved, include the optimal addition times of H_2O_2 , the optimum type of iron chelating agent, the effect of graded MF oxidation on microbial activity and the biodegradation of tank oil.

In this study, we investigated the effect of addition time frequency of H_2O_2 and type of iron chelator on oxidation of tank oil when graded MF oxidation was applied to a tank oil contaminated soil. Moreover, biological treatment was carried out before and after graded MF oxidation to investigate whether graded MF oxidation can be a mild pre-oxidation method for tank oil contaminated soil remediation.

1 Materials and methods

1.1 Chemicals

Liquid hydrogen peroxide (30%), $FeSO_4 \cdot 7H_2O$ (reagent grade), and citric acid (analytical grade), oxalic acid (analytical grade), SOLV-X (Solvay chemical GmbH, analytical grade) were used as the sources of oxidant, Fe^{2+} , and chelator, respectively. All chemicals were analytical grade and obtained from Merck, Darmstadt, Germany.

1.2 Tank oil contaminated soil

Soil samples were taken from surface layer of sandy soil contaminated by tank oil at a storage tank site (Amsterdam, the Netherlands). The contamination occurred a few months before the sampling. The samples were homogenized and graded by a 2-mm sieve, and stored in a fridge with a ventilation system without light at 4°C.

The total petroleum hydrocarbon (TPH) concentration in soil was (4840 ± 25) mg/kg dry matter (Table 1). The tank oil was characterized by the ratios of hydrocarbons with carbon numbers ranging from C_{10} to C_{40} . It is clear that a fraction with carbon number ranges from C_{10} to C_{20} took up 77.8% of the oil contaminants in this soil. The weight method was used to measure dry matter (dm) and organic matter in soil. The tank oil contaminated soil had a dry matter content of $90.6\% \pm 1.3\%$ (W/W), an organic matter content of $1.43\% \pm 0.03\%$ (W/W) and a pH of 7.86 in water (1:1).

Table 1 Physical and chemical properties of tank oil contaminants and initial concentration in used soil

Tank oil	$-\log K_{ow}^a$	$-\log S^b$	Initial concentration (mg/kg dm) ^c	Relative abundance (%)
C_{10} – C_{12}	4.64–6.00	4.83–5.64	414 (67)	8.6
C_{13} – C_{16}	6.50–9.00	5.97–6.92	1587 (16)	32.8
C_{17} – C_{20}	9.50–10.00	7.24–8.19	1762 (1)	36.4
C_{21} – C_{24}	10.50–12.00	8.52–9.45	749 (8)	15.5
C_{25} – C_{40}	12.50–21.00	9.90–14.66	326 (16)	6.7
TPH			4840 (25)	100

^a Logarithm of the octanol: water partition coefficient; ^b logarithm of solubility at 20°C; ^c values are the means of three replicate determinations (standard deviations).

1.3 Experimental method

1.3.1 Graded MF oxidation

Graded MF oxidation tests were conducted at natural pH to optimise addition time frequency of H_2O_2 and find the best iron chelating agent. The specific procedure was as follows: (10 ± 0.01) g soil and 40 mL de-ionized water were put into 250 mL serum vial. Added 10 mL iron catalyst with pH at 7.5 of slurry. The iron catalyst was made from 6.98 mmol/L $Fe(II)$ and three iron chelating agents (179 mg of citric acid, 126 mg of oxalic acid and 10% of SOLV-X). Then, 2.5 mL of 30% H_2O_2 was applied to the slurries for each time of frequency. The H_2O_2 was added up to five equal time intervals at most in some slurries. Therefore, concentrations of H_2O_2 in the slurries ranged from 490 to 2450 mmol/L with a step of 490 mmol/L. Consequently, the mol ratio of H_2O_2 : $Fe(II)$ increased from 70:1 to 350:1 with a step of 70:1. A subsequent H_2O_2 addition was always at least 5 hr later because it was found that hydrogen peroxide was not detectable (the color of H_2O_2 test strips not changed into blue) 5 hr after MF reagent was applied to slurries. After 4 days, the samples were extracted by acetone and petroleum ether, to measure oil concentration by a gas chromatography (GC).

1.3.2 Biological treatment

Two biological treatments were carried out for pre-oxidizing and non-oxidizing soil samples in 250 mL serum vials with septum closures that allowed gas sampling possible. One microcosm contained 10 g non-oxidizing soil sample with 50 mL phosphate buffer, 6 mL macro-elements, and 0.6 mL micro-element. The other

microcosm was set up in a pre-oxidizing soil bottle after 4 days with the same nutrient. The pre-oxidized soil was prepared by oxidizing 10 g of soil with 6.98 mmol/L Fe(II) and 1470 mmol/L H₂O₂ when citric acid acted as an iron chelating agent. The third sample was sterilized with 0.5 mL of 0.2 mol/L NaN₃ as a reference.

All the samples were not inoculated. Variation of native microorganism activities was judged by the utilization of TPH. All capped serum vials were put into a rotary tumbler (22 r/min) at room temperature (20°C) in dark condition. TPH concentration in the samples were analyzed by several times within 26 days. Experiments were conducted in triplicate. During the experiments, the oxygen and carbon dioxide concentration in the headspace of the serum vials were monitored by GC. The headspace of serum vials was flushed with pressured air if the oxygen concentration dropped to below 10%.

1.4 Extraction and analysis

1.4.1 TPH analysis by GC

Acetone and water were mixed with the ratio of 4:1 (acetone/water, V/V). The mixture of 10 mL was applied to each unit soil sample (1 g). The obtained slurry was sonicated for 15 min and then shaken (175 r/min, Gerhardt Laboshaker, Germany) at room temperature for 1 hr. Subsequently, petroleum ether (25 mL) was added to the flask and shaken at room temperature for 1 hr (175 r/min, Gerhardt Laboshaker, Germany). Finally, the extraction medium was mixed with de-ionized water twice (2 × 200 mL) to separate the petroleum ether and acetone phase. The floating petroleum ether phase was transferred to the sample bottle and analyzed for oil concentration by GC.

The analysis of oil concentration (1 µL extracts) was performed on a Hewlett Packard GC system (HP 5890 Series II, USA) equipped with a WCOT fused silica column (10 m × 320 µm × 0.10 µm) with coating CP7521 SimDist (Chrompack-Varian, USA). Helium was used as carrier gas (3.5 mL/min). The GC was equipped with an FID detector. The GC was started and ended with injection of pure petroleum ether and boiling point calibration sample #1 kit (8632 mg/L) purchased from Agilent Technology. The mixture of pure *n*-alkanes by carbon numbers from 10 to 40 was made to determine the amount of specific hydrocarbon fractions.

1.4.2 O₂ and CO₂ concentration of gas analysis

Oxygen and carbon dioxide concentrations were analyzed by using an Inter-science 8340 gas chromatograph (GC) equipped with a thermal conductivity detector and Porabond column (50 m × 0.53 mm × 0.1 µm) connecting parallel with Molsieve column (30 m × 0.53 mm × 15 µm). Helium was used as the carrier gas (45 mL/min), and the oven temperature, injection temperature and thermal conductivity detector temperature were set at 40, 110, and 99°C, respectively. The GC condition was checked by the injection of standard gas. When the presenting peaks coincide with standard peaks, the gas samples could be measured.

The volume of headspace in the serum vials was de-

termined by subtracting the mass of the microcosm. The molar quantity of O₂ or CO₂ in the microcosms was determined by the headspace volume and O₂ or CO₂ concentration.

2 Results

2.1 Graded MF oxidation optimization

2.1.1 Soluble iron concentration

Under acidic conditions (pH 3–5), Fe²⁺ dissociates H₂O₂, which forms unstable and highly reactive hydroxyl radicals (-OH) that actively mineralize organic contaminants into CO₂, water, and inorganic salts (Walling, 1975; Sun and Pignatello, 1992). The Fe²⁺ is then catalytically regenerated by the reaction of Fe³⁺ and H₂O₂. However, under neutral conditions (pH 7.5), the iron catalyst precipitates as Fe(OH)₃. In addition, instead of generating the hydroxyl radical, the H₂O₂ decomposes into oxygen, water, and heat, which can create a hazardous operation condition. Therefore, it is critical to keep iron soluble by the addition of iron chelating agents to achieve optimum and safe decontamination. In our experiments, citric acid, oxalic acid and SOLV-X were added to increase the iron solubility.

The total soluble iron concentration was measured using Quantofix test-strips (MACHERY-NAGEL GmbH, Germany) after each addition of H₂O₂ to investigate the effect of different iron chelators on iron solubility (Table 2). The results showed that soluble iron concentration maintained at 390 mg/L in the citric acid-MF system before the third addition of H₂O₂. However, the soluble iron concentration decreased from 390 to 200 mg/L in the oxalic acid-MF system after the first addition. The soluble iron concentration decreased from 390 to 150 mg/L in SOLV-X-MF system after the second addition. Therefore, the ability of the iron chelates to keep iron soluble decreases in the following order: citric acid > SOLV-X > oxalic acid. The results indicate that citric acid may contain a high density of functional groups, which can conjugate metal ions to form soluble iron complexes and by this way act as an iron source (Lindsey and Tarr, 2000). According to Table 1, citric acid is an optimum iron chelating agent for graded MF oxidation.

2.1.2 Tank oil oxidation

The results of tank oil oxidation in different chelating agent systems are illustrated in Table 3. According to Table 3, the extent of tank oil removal efficiency depends

Table 2 Iron concentration after graded MF oxidation

Addition of 1.5% H ₂ O ₂	Soluble iron concentration (Fe ²⁺ and Fe ³⁺ , mg/L)		
	Citric acid	Oxalic acid	SOLV-X
0 dose	390	390	390
1st dose	390	200	390
2nd dose	390	200	150
3rd dose	100	25	10
4th dose	10	na	na
5th dose	0	na	na

na: not assayable.

Table 3 Tank oil concentration after graded MF oxidation

Addition of 1.5% H ₂ O ₂	TPH concentration (mg/kg)			TPH removal efficiency (%)		
	Citric acid	Oxalic acid	SOLV-X	Citric acid	Oxalic acid	SOLV-X
1st dose	3159 (179)	4400 (194)	3982 (199)	35	9	18
2nd dose	3075 (167)	4403 (83)	3981 (142)	36	9	18
3rd dose	2367 (116)	4401 (181)	2974 (162)	51	9	44
4th dose	2219 (152)	na	na	54	na	na
5th dose	1987 (133)	na	na	59	na	na

Values are the means of three replicate determinations (standard deviations); na: not assayable.

on the type of iron chelating agent. Citric acid MF reagent effectively removed tank oil (> 50%) by three times addition of H₂O₂. The poor oil removal (9%) was observed in the oxalic acid system due to soluble iron concentration decreasing from 390 to 200 mg/L after the second addition of H₂O₂. The activity order of iron chelates in terms of TPH oxidation was citric acid (59%) > SOLV-X (44%) > oxalic acid (9%) (Table 3).

However, the order is opposite to the results while 2,4-D and chlorinated ethylenes were transformed (Sun and Pignatello, 1992; Seol and Javandel, 2008). Possible explanations for this inverse order could be the difference of hydrophobicity of contaminants. Comparing the hydrophobicity, *n*-alkane is much more hydrophobic than 2,4-D and chlorinated ethylenes. The minus log octanol–water partition coefficient ($-\log K_{ow}$) of chlorinated ethylenes is 1.82 and the corresponding minus $\log K_{ow}$ of 2,4-D is 2.81 (Quan et al., 2003). While as can be seen in Table 1, the minus $\log K_{ow}$ of decanol (C₁₂) and hexadecane (C₁₆) are 6.00 and 9.00, respectively.

Oxalic acid chelating iron catalyzes H₂O₂ more actively by producing hydroxyl radical than citric acid due to lower stability constants ($\log K$ of oxalic acid is 9.4 and $\log K$ of citric acid is 11.85) (Seol and Javandel, 2008). However, TPH characterized by strong hydrophobicity absorbed on soil, retarded the oxidation of TPH by hydroxyl radical. In contrast, the stable citric acid iron catalyst resulted in slow decomposition of H₂O₂, which may also stabilize hydrogen peroxide in the presence of subsurface solids. A series of propagation reactions occur, which produce the nucleophile radicals (Quan et al., 2003). One or more of nucleophile radicals had enhanced the desorption of strong hydrophobic TPH and resulted in the significant removal of TPH in citric-acid MF system.

The results indicate that the oxidation of tank oil by graded MF depends on the soluble iron amount. Citric acid was an optimized iron chelating agent. Maximum TPH removal efficiency was 59% and could be achieved in the citric acid-MF system after 5-time addition of H₂O₂. However, 3-time addition of H₂O₂ was favorable and economical due to lower increase of TPH removal between 3-time addition (51%) and 5-time addition (59%) in the citric acid-MF system (Table 3).

2.2 Biological treatment after graded MF oxidation

In order to investigate the effect of graded MF oxidation on the biodegradation of tank oil and native microbial activity, biological treatments were conducted after graded MF oxidation without inoculation. Graded MF oxidation

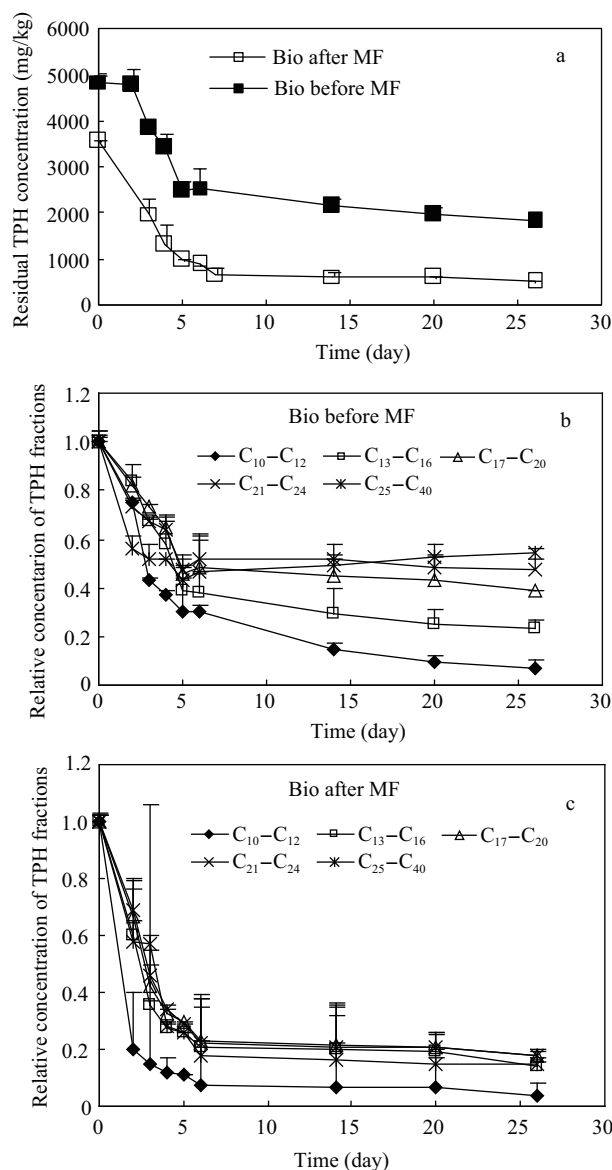


Fig. 1 Residual concentrations of total petroleum hydrocarbon (TPH) (a) and fractions (b, c) in biological treatment before or after graded MF oxidation.

was conducted under optimum conditions described above.

2.2.1 Biodegradation of TPH after graded MF oxidation

An increase in overall extent of TPH biodegradation after graded MF oxidation was observed. TPH removal efficiency increased from 62% (before graded MF oxidation) to 93% (after graded MF oxidation) on day 26 (Fig. 1a). Residual tank oil was 490 mg/kg for pre-oxidation sample

while considerable tank oil (1815 mg/kg) still remained in non-oxidized samples. Residual tank oil load was three times lower in the pre-oxidation samples than that in the non-oxidation samples. In addition, a 23% increase of biodegradation in TPH was observed after graded MF pre-oxidation treatment. It is concluded that the combined chemical and biological treatment was more effective in PAHs contaminated soil than either treatment alone, and at least a 20%–30% increase of biodegradation in PAH was observed after Fenton's like pre-oxidation treatment (Nam et al., 2001; Valderrama et al., 2009). Therefore, an appropriate chemical oxidation pre-treatment is extremely beneficial for post-biological treatment because it not only reduces the pollution load at the same time, but also enhances the bioavailability of hydrophobic oil. From Fig. 1, it is obvious that combined graded MF oxidation and biological treatment was more efficient in tank oil elimination in contaminated soil than either treatment alone.

Figure 1b, c presents the concentration variation of specific hydrocarbon fractions. Tank oil may contain thousands of components. The commonest aliphatic components are *n*-alkanes and with carbon numbers between 10 and 40 or more. As can be seen in Fig. 1b, the smallest molecule cluster (C_{10} – C_{12}) was degraded with the rapidest rate due to its easiness for diffusing the cell membrane (Morgan and Watkinson, 1989). The relative concentration of the longer-chain molecules (C_{13} – C_{40}) reached a stable level within 6 days. Moreover, the relative concentration of hydrocarbons increased as carbon number increased. These results showed that small molecules (C_{10} – C_{12}) were generally rapidly metabolized, and long-chain hydrocarbon molecules (C_{13} – C_{40}) entered the cell membrane with more resistance due to high minus $\log K_{ow}$. However, C_{13} – C_{40} were easily adsorbed on hydrophobic soil particles, which reduced the bioavailability in weathered soil (Morgan and Watkinson, 1989). In contrast, as observed in Fig. 1c, the relative concentration of C_{13} – C_{40} is reduced to a large extent (30%) after biodegradation which followed graded MF oxidation treatment. A possible explanation is that after MF oxidation long-chain hydrocarbons were available and easily had access to microbial membrane because non-radical and nucleophilic species generated during MF reaction enhanced desorption of long-chain hydrocarbons (Corbin et al., 2007). In addition, part of soil organic matter (SOM) in soil can be oxidized by MF reagents (Yeh et al., 2002) and resulted in altered binding positions of heavy oil sorbed in SOM. Therefore, graded MF oxidation enhanced bioavailability of C_{13} – C_{40} .

2.2.2 Microbial activity after graded MF oxidation

The cumulative of O_2 consumption and CO_2 production of soil samples during the whole period are presented in Fig. 2a, b. The phenomenon of significant suppression of indigenous microorganisms' activity after graded MF oxidation was not observed, comparing to the control series sterilized by NaN_3 . In contrast, oxygen consumption and carbon dioxide production were more significant after MF oxidation. Total cumulative CO_2 amount of pre-oxidized soil sample was 1.66 mmol during 26-day's biological

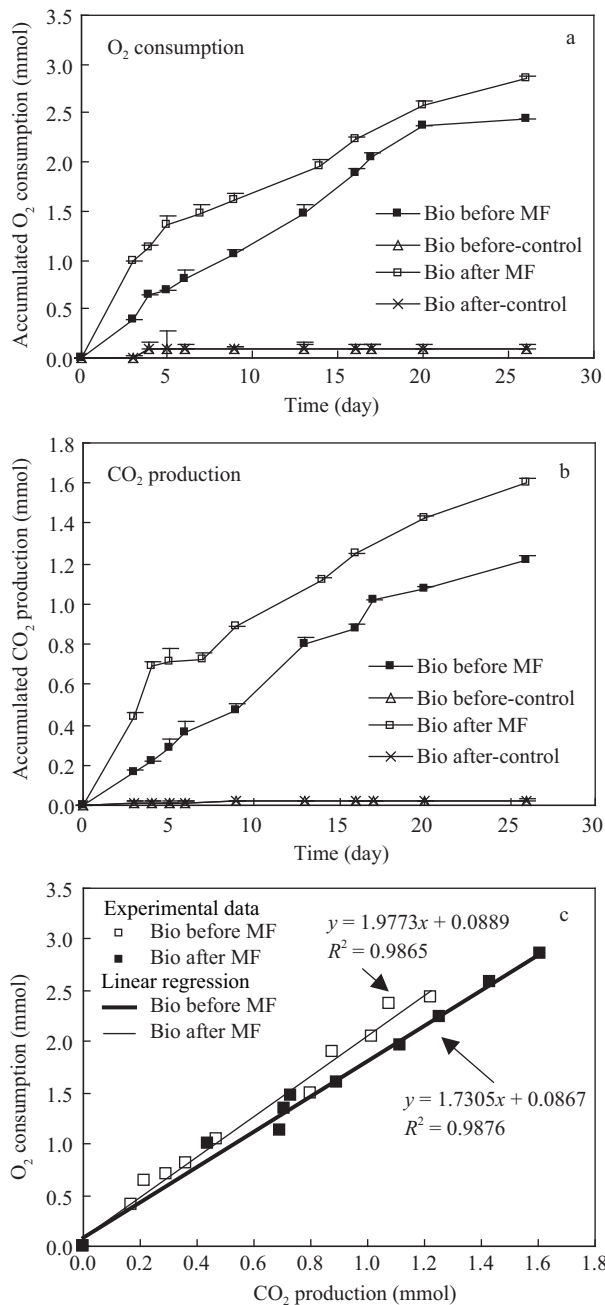


Fig. 2 Accumulated O_2 consumption and CO_2 production in biological microcosms.

treatment, which was 1.3 folds larger than that of the non-oxidized soil sample. Moreover, in the initial five days, high rate of oxygen consumption indicated that microbial activity increased to a great extent after graded MF oxidation.

The cumulative of O_2 consumption and CO_2 production of soils can be used to determine the ratio of mol O_2 consumption per mol CO_2 evolution. For example, glucose is completely mineralized according to the following equation: $C_nH_{2n}O_n + nO_2 \rightarrow nCO_2 + nH_2O$, the ratio of O_2 consumption versus CO_2 production is equal to 1. Petroleum hydrocarbon is mineralized according to the following equation $CH_{1.8} + 1.45O_2 \rightarrow CO_2 + 0.9H_2O$, the same ratio is 1.45.

The biomass yield is neglected in this equation. SOM is mineralized according to equation $\text{CH}_{5/9}\text{O}_{10/9} + \text{O}_2 \rightarrow \text{CO}_2 + 5/9 \text{H}_2\text{O}$. Therefore, the consumption of 1 mol O_2 is accompanied by 1 mol CO_2 production. As the ratio is smaller than 1.45, CO_2 may derive from part of SOM other than petroleum hydrocarbon.

Figure 2c presents the linear regressions of O_2 consumption and CO_2 production of soils. The ratio of mol O_2 consumption per mol CO_2 evolution in both soils were higher than 1.45. This may be explained as follows: tank oil was not easily utilized by microorganism as the mineralized TPH may not be fully oxidized to CO_2 ; SOM was hardly oxidized while stepwise addition of H_2O_2 was applied. It coincided with the results of SOM as only 5% SOM was oxidized after the third time addition of H_2O_2 . In addition, chemically oxidized soils consumed 1.731 mol O_2 per mol CO_2 production, and this value was smaller than that of non-oxidized soils (1.977). This indicated that the microbial activity increased after graded MF oxidation because TPH was more biodegradable.

In summary, multiple dosing graded MF pre-oxidation treatment did not reduce indigenous microorganism activity. On the contrary, substantial increase in microbial activity was observed for the subsequent biological treatment of the multiple dosing graded MF pre-oxidation because oxygen consumption and carbon dioxide were higher than that of biological treatment alone. In addition, MF oxidation enhanced the bioavailability of longer-chain molecules $\text{C}_{13}\text{--}\text{C}_{40}$ as the hydrophobic hydrocarbon may be easily desorbed after MF oxidation.

3 Discussion

The combined chemical and biological treatment is a promising technology for remediation of contaminated soil and has been studied extensively in recent years. Valderrama et al. (2009) proposed that the feasibility of integrated MF oxidation and biological treatment depends on MF pre-oxidation step in creosote contaminated soil because excessive hydrogen peroxide results in a poor biological removal. They reported that total PAH removal efficiency of post biological treatment decreased from 45% to 9% as the mole ratio of $\text{H}_2\text{O}_2:\text{Fe}^{2+}$ increased from 10:1 to 40:1. Meanwhile, as the molar ratio of $\text{H}_2\text{O}_2:\text{Fe}^{2+}$ increased to 60:1, no further decrease was observed. These results indicate that excessive of H_2O_2 resulted in a poor post-biological removal because the exothermic reaction can lead to a significant increase in soil temperature, which leads to undesired soil sterilization (Mecozi et al., 2006). The primary objective of the present study was to show whether a mild MF pre-oxidation such as a stepwise addition of H_2O_2 can prevent sterilization and achieve a maximum degradation of tank oil in soil. As we expected, multiple dosing citric acid MF pre-oxidation treatment with 1470 mmol/L H_2O_2 (the mol ratio of $\text{H}_2\text{O}_2:\text{Fe}^{2+}$ is 210:1) did not reduce indigenous microorganism activity. On the contrary, substantial increases in microbial activity were conducive to 93% removal of TPH after 4 weeks of the subsequent biological treatment after graded MF

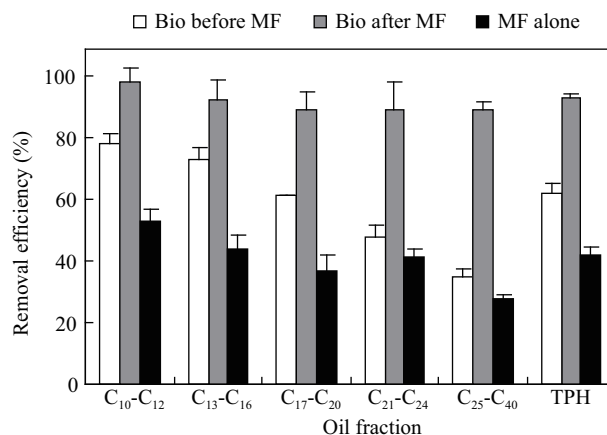


Fig. 3 Removal efficiency of tank oil using three treatments.

pre-oxidation. In our experiment, a 31% increase in tank oil was observed when a mild graded MF oxidation was conducted before biological treatment (Fig. 3). In addition, all oil fractions ($\text{C}_{10}\text{--}\text{C}_{40}$) became more biodegradable after graded MF oxidation. This denotes that the graded MF oxidation is a mild pre-treatment for achieving more effective bioremediation.

In addition, no sign of gas accumulation or solid precipitation was observed in the citric acid-MF batches, which suggests that citric acid addition alleviated the adverse impacts that occurs during traditional Fenton's oxidation. The similar observation was reported in literature (Seol and Javandel, 2008). On the other hand, in this study, 50 mL water and 10 g dry soil was applied in MF batches. A large water to soil ratio may alleviate the exothermic effects. Further study of various ratios of water to soil MF oxidation should be carried out to find the reason in detail.

4 Conclusions

In citric acid MF system, the removal efficiency of tank oil achieved over 50%, while the corresponding removal efficiency in SOLV-X system was 44%. The removal capacity of oxalic acid MF reagent was only 9%. Therefore, citric acid is the most effective iron chelator for stepwise MF oxidation of tank oil. It was also found that the biological removal of tank oil after graded MF oxidation was up to 93% after 4 weeks, with a 31% increase comparing to non-oxidized soil. Especially, a fraction of oil ($\text{C}_{10}\text{--}\text{C}_{40}$) became more biodegradable after graded MF oxidation. Therefore, graded MF oxidation is a mild pre-treatment method to obtain more effective bioremediation for oil contaminated soil.

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