TREATMENT OF REFINERY OILY SLUDGE USING ULTRASOUND, BIO-SURFACTANT, AND ADVANCED OXIDATION PROCESSES

by

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ABSTRACT

Oil refinery sludge can be generated throughout the oil production process. It consists of a large amount of petroleum hydrocarbons (PHCs) and other hazardous materials which should be disposed of appropriately. In order to find effective methods to treat the oily sludge, three different approaches were investigated in this research, including bioremediation, oil recovery, and advanced oxidation processes (AOPs). In terms of the bioremediation approach, the oily sludge was mixed with soil, and a screened bacterium strain was then introduced with the supplement of nutrients and the addition of bio-surfactant. The reduction rate of total petroleum hydrocarbons (TPH) in oily sludge spiked soil was up to 50.8% after 40 days of biodegradation. With regard to recovering oil from the oily sludge, three processes were investigated, including ultrasonic treatment alone, freeze/thaw treatment alone, and the combined ultrasonic and freeze/thaw treatment. The experimental results revealed that the combined process could achieve satisfactory performance of oil recovery. In terms of the advanced oxidation processes (AOPs), the ultrasonic treatment alone, the Fenton process alone, and the combination of ultrasound and Fenton's reagents, were examined for their abilities to reduce petroleum hydrocarbons (PHCs) content in oily sludge. The Taguchi experimental results indicated that the combination of ultrasound and Fenton reagents achieved the best effect, with the highest TPH reduction rate of 88.1% being observed in the experimental conditions.

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LIST OF ABBREVIATIONS

ANOVA	Analysis of variance
API	American Petroleum Institute
ASTM	American Society for Testing and Materials
CCME	Canadian Council of Ministers of Environment
EPA	Environmental Protection Agency
DCM	Dichloromethane
GC	Gas chromatograph
GC-FID	Gas chromatograph-Flame ionization detector
PAHs	Polycyclic aromatic hydrocarbons
PCBs	Polychlorinated biphenyls
PHCs	Petroleum hydrocarbons
TPH	Total petroleum hydrocarbons
US	Ultrasonic irradiation

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The petroleum industries can generate a great deal of oily sludge wastes during crude oil transportation, storage, and further refining processes (Adriana and Nei, 2002; Marin et al, 2006; Ramaswamy et al, 2007). Generally, the oily sludge is a complex water-in-oil (W/O) emulsion, typically consisting of 30-50 wt% of oil, 30-50 wt% of water, and 10-12 wt% of solids (Reynolds and Heuer, 1993; Ramaswamy et al, 2007). It contains a significant amount of petroleum hydrocarbons (PHCs), and many of the PHCs are of high molecular-weight alkanes, (Overcash and Pal, 1979). Due to the complex composition and the high content of PHCs, oily sludge has been known as a hazardous waste. Improper disposals could lead to environmental pollution and pose serious risk to the environment and the human health (Elektorowicz et al, 2005).

Various treatment methods, such as pyrolysis, incineration, land-filling, and land-farming (Shie et al, 2000; Che et al, 2008), have been explored to deal with the oily sludge waste. However, the treatment of oily sludge using these conventional methods is relatively time-consuming, ineffective, and expensive (Shie et al, 2000; Buyukkamaci and Kucukselek, 2007). It is thus of importance to find improved methods. Although the bioremediation technology has been widely used for the reduction of organic pollutants in soil and water, its effective application to the oily sludge treatment still needs more investigation. The biodegradation of PHCs in oily sludge could be improved by using special bacterial strains with high biodegradation capacity and by enhancing the microenvironment for bacterial activity (Banat et al, 2000; Cameotra and Singh, 2008). Effective bacterial strains could be screened and isolated from soils contaminated with PHCs for a long period. The isolated strains can then be reintroduced into the contaminated soil medium. In terms of improving the bacterial activity, adding sufficient nutrients into soils could be the foremost strategy to

stimulate bacterial growth (Cameotra and Sigh, 2008). Another improvement method is to add bio-surfactants to soil so that the solubility of hydrophobic organic pollutants can be enhanced and thus more contaminant molecules present in soil pore water can be approachable for bacteria living in soil. Consequently, the enhanced bioavailability can lead to the improved bioremediation performance.

Another method to improve the performance of conventional treatment processes is through oil recovery before disposal (Elektorowicz, et al, 2006; Zubaidy and Abouelnasr 2010). The oily sludge waste could be regarded as a valuable resource, and the oil recovery can significantly reduce the concentration of PHCs and the volume of sludge for conventional treatment. In fact, the treatment of sludge containing over 10% of oil could result in economic benefit from oil recovery (Ramaswamy, et al, 2007). Many studies have reported the recycling of oil from different oil wastes using various approaches, including solvent extraction, the use of ultrasound and microwave, and the means of freeze/thaw. However, a variety of problems are still associated with these methods, such as high cost and low recovery efficiency.

The advanced oxidation processes (AOPs) applied in wastewater treatment (Adewuyi, 2005; Pang et al, 2011) might also be plausible approaches for the treatment of oily sludge. They are chemical oxidation methods with the capability of treating many types of organic and inorganic contaminants (Adewuyi, 2005). In general, the prominent principle of AOPs is the generation of free hydroxyl radicals (•OH) which are extremely reactive species. These free radicals serve as the powerful oxidants for the destruction of contaminant molecules (Gogate et al, 2004). The use of ultrasonic and ultraviolet irradiation as well as the application of oxidation agents (e.g., hydrogen peroxide, Fenton/Fenton-like reactions, ozone)

have been investigated as viable AOPs in many studies (Gogate and Pandit, 2003; Sivasankar and Moholkar, 2009). However, the oxidation efficiency is usually limited for single AOP. In order to improve the efficiency of AOPs, many researchers have tried to develop hybrid AOPs by combining oxidation agents with ultrasonic or ultraviolet treatment. The combination of methods was proved to yield synergistic effect for the destruction of hydrophobic organic molecules (Chand et al, 2009). However, few studies have been reported to treat the oily sludge wastes using hybrid AOPs.

The objective of this study was to find effective methods for the treatment of oily sludge. The performances of three different enhanced methods were examined, including bioremediation, oil recovery, and advanced oxidation. In terms of the enhanced bioremediation method, a specific bacterial strain was isolated from soils contaminated with PHCs and was then applied to the soil remediation process, while the nutrients and bio-surfactants were added to the soil to improve bacterial activity. The Taguchi design method was applied to arrange different experiments on investigating the effects of various factors. In terms of oil recovery from oily sludge, the efficient of combing ultrasound and freeze/thaw was investigated on recovering oil from oily sludge. The impacts of several factors on the oil recovery treatment performance through the combined method were evaluated. These factors include ultrasonic power, ultrasonic treatment duration, addition of bio-surfactant, addition of salt, and the ratio of sludge to water. In terms of the investigation of advanced oxidation processes, the PHCs in oily sludge were oxidized via ultrasound, Fenton process, and the combination of ultrasound and Fenton process. A variety of factors were evaluated on the oxidation efficiency, and they include ultrasonic power, treatment duration, initial sludge concentration, and the ratio of hydrogen peroxide and ion Fe (II).

Their individual and combined effects on the reduction of PHCs in oily sludge were examined. The experimental results of these three different approaches would provide a sound basis for developing environmentally friendly and economically competitive methods for oily sludge treatment.

Chapter 2 Remediation of refinery oily sludge using isolated strain and biosurfactant¹

¹ This work was published as J. Zhang, J. B. Li, L. L. Chen, R. Thring, Remediation of refinery oily sludge using isolated strain and biosurfactant, *Proceedings of 2011 International Symposium on Water Resources and Environmental Protection (ISWREP2011)*, Xi'an, China, May 20-22, 2011, pp. 1649-1654, IEEE Press.

Abstract

A series of laboratory experiments were conducted to investigate the bioremediation of oil refinery sludge using an isolated bacterial strain and a bio-surfactant. The strain called uncultured *Luteibacter sp.* isolated from soils from a previous sludge landfarming site was used for bioaugmentation. A commercial biosurfactant of rhamnolipid (JBR 425) was used for improving the bioavailability of petroleum hydrocarbons (PHCs) to the bacteria strain. The impacts of initial total petroleum hydrocarbon (TPH) concentration, nutrient supply, and biosurfactant concentration on the remediation process were examined. The degradation efficiencies of n-alkenes between C10-C16, C16-C34 and C34-C50 were also compared. The results can provide sound scientific basis for developing cost-effective remediation methods to treat oil refinery sludge.

Key words: Oily sludge, bioremediation, biosurfactant, total petroleum hydrocarbons

1. Introduction

The petroleum industry can generate a large amount of oily sludge during production, transportation, and refining processes (Kuriakose and Manjooran, 2001; Marin et al, 2006). Due to the high content of petroleum hydrocarbons (PHCs) and complicated composition, oily sludge has been known as a hazardous and recalcitrant waste product and might cause severe environmental pollution if directly disposed into the environment (Overcash and Pal, 1979; Bhattacharyya and Shekdar, 2003). During the past years, various biological treatment approaches have been investigated to convert the toxic recalcitrant compounds into non-toxic forms by microbial consortium (Overcash and Pal, 1979). Biological treatment techniques involve two categories, including biostimulation and bioaugmentation. The bioaugmentation approach introduces microorganisms identified/screened from natural environment and enriched in laboratory condition into contaminated soil (Cameotra et al, 2008). Many studies have isolated different strains capable of degrading PHCs from oil contaminated sites. For example, Ekp et al (2008) obtained microbes from the crude oil sludge environment and found that the isolated P. aeruginosa could degrade 97.2% of the PHCs added into the medium. Cameotra et al (2008) tested the capability of one consortium of two strains (Pseudomonas aeruginosa and rhodococcus) to biodegrade hydrocarbons in sludge and they reported that 90% of the contaminants were depleted in liquid culture after 6 weeks. On the other hand, biostimulation focuses on the addition of specific nutrients or other additives as stimuli to contaminated medium in order to enhance the effectiveness of degrading pollutants by microorganisms. For example, Walworth et al (2007) focused on optimizing nutrient amendments in a sub-antarctic soil and they found that the rate of biodegradation was maximized when the nitrogen (in the form of NH₄Cl) content was 125 mg/kg.

Machin-Ramirez et al (2008) used a fertilizer solution to investigate the effect of nutrient addition on slurry-phase biodegradation of weathered oily sludge waste and 24% of PHCs biodegradation was attributed to the addition of fertilizer in the slurry. Other experiments reported a wide range of C:N and C:P ratio from 9-200 and 60-800 to enhance PHCs biodegradation (Huesemann, 1994). In general, bioaugmentation and biostimulation are used to improve the microenvironment of biodegradation. However, the efficiency of biodegradation is also usually restricted by the low bioavailability of hydrophobic organic compounds in soil. In order to enhance the solubility and desorption of PHCs entrapped in soil, chemical and biological surfactants are generally introduced for stimulation (Calvo et al, 2009). Among them, bio-surfactants produced by microorganisms have been receiving increasing interests in bioremediation studies due to their low toxicity and wide environmental compatibility (Ron and Rosenberg, 2001). Several bio-surfactants have been reported in the area of bioremediation of organic pollution in water and soil, including rhamnolipids, sophorolipids, and surfactin (Banat et al, 2000). Although many experiments have been previously carried out to investigate the bioremediation of gasoline and diesel contaminated soil, only a few works focused on oily sludge where the long carbon-chain petroleum hydrocarbons dominate (Rahman et al, 2003;Ghazali et al, 2004), especially for n-alkanes from nC20-nC50. In this study, one isolated strain from a PHCs land-farming site was applied to examine the biodegradation process of oily sludge. Taguchi experimental design (Castorena-Cortes et al, 2009) was applied to investigate the effect of initial petroleum hydrocarbon concentration, nutrient addition, and biosurfactant (JBR 425) addition on the biodegradation of long-chain hydrocarbons and to determine the optimal condition for bioremediation of oily sludge.

2. Materials and Methods

2.1. Oily sludge and soil sample

The oily sludge collected from an oil refinery plant in western Canada was stored in a capped stainless-steel bucket at 4°C. Uncontaminated soil was collected from a sampling site within a forest located near the road (close to Oskpika and Tyner Blvd) in Prince George, BC, Canada. The sampling depth was about 60 cm to 80 cm. The soil was collected with stainless steel shovel and was air dried at room temperature for 3-4 days. The soil with low concentration of petroleum hydrocarbons was passed through a # 20 sieve to remove coarse particles and was then stored in fridge at 4°C. Properties of uncontaminated soil and oily sludge were listed in Tables 2.1 and 2.2.

Properties	Percentage (% by mass)	Elements	Concentration (mg/kg)	Soil texture	
Total carbon	1.81	Ca	5900	Percentage of sand	10.9%
Inorganic carbon	0.04	Mg	6200	Percentage of silt	53.5%
Total nitrogen	0.097	Fe	28507	Percentage of clay	35.6%
Total phosphorus	0.18	Zn	161.6		
Total potassium	0.37	Cu	12.9		

Table 2.1 Summary of clean soil properties

Table 2.2 Summary of oily sludge properties

Properties	Concentration (mg/g)	Elements	Concentration
ТРН	40.99	Total carbon	86.10% (by mass)
F2 fraction	2.39	Al	27.50 mg/kg
F3 fraction	13.55	Fe	448 mg/kg
F4 fraction	67.09	Ni	11.6 mg/kg
Percentage of F4 (by mass)	61.10%	Cr	0.6 mg/kg
Percentage of F3 (by mass)	33.05%	Cd	0.043 mg/kg

2.2. Chemicals

Decane (nC10, > 99% purity, Sigma-Aldrich), hexadecane (nC16; > 99% purity, Sigma-Aldrich), tetratriacontane (nC34; > 99% Sigma-Aldrich), Pentacontane(nC50, > 99% purity, Sigma-Aldrich) were used as standard substances for GC analysis; dichloromethane (DMC) (> 99% purity, HPLC grade, Sigma-Aldrich) and cyclohexane (> 99% purity, HPLC grade, Sigma-Aldrich) were used to extract soil samples. NH₄NO₃ and KH₂PO₄ purchased from Sigma were used as nutrients for bioremediation experiments. The rhamnolipid (JBR425) bio-surfactant was purchased from Jeneil Biosurfactant Company (Saukville, WI, USA). It is a mixture of two rhamnolipids $C_{26}H_{48}O_9$ (RLL) and $C_{32}H_{58}O_{13}$ (RRLL).

2.3. Bacteria isolation and identification

The mineral salt medium (MSM) and trace element solution were used for bacterial isolation (Noordman and Janssen, 2002). MSM stock solution was prepared as following: 26.5 g /L Na₂HPO₄.12H₂O, 7 g/L KH₂PO₄, 1 g/L MgSO₄.7 H₂O and 2.5 g/L (NH₄)₂SO₄. The trace element solution was prepared as following: 2.65 g/L CaCl₂, 1 g/L FeSO₄.7H₂O, 0.05 g/L ZnSO₄.7H₂O, 0.05 g/L H₃BO₃, 0.05 g/L CoCl₂.6H₂O, 0.02 g/L MnSO₄.5H₂O, 0.015 g/L Na₂MoO₄.2H₂O, and 0.01 g/L NiCl₂.6H₂O. The pH value of MSM was adjusted to 7.3 \pm 0.1 with 1M NaOH or 1M HCl according to the background pH of samples. The MSM was sterilized by autoclaving for 30 min at 121 °C. Stock solutions of oily sludge collected from an oil refinery in western Canada were prepared in cyclohexane, and were used for providing different carbon sources for microbial growth.

The procedure of bacteria isolation was demonstrated in Fig 2.1 based on previous work (Chen et al, 2011). To enrich the PHCs degrading bacterium, 5 g of contaminated soil samples from one land-farming site (Fig 2.2) were added into a 250-ml conical flask with 50 ml of sterilized MSM and 5 mL of oily sludge solution after volatilization of cyclohexane in the fume hood. The flasks were shaken in a mechanical shaker (150 rpm) at room temperature ($20 \pm 2^{\circ}$ C) for two weeks as the first enrichment step. After that, the second enrichment were conducted by transferring 5 mL of the culture after 1st enrichment process to another flask containing 50 mL of sterilized MSM with the same amount of stock solution as the first enrichment (Fig 2.3). The PHCs degrading microbes in the 1st and 2nd enriched culture were determined using MSM agar plates sprayed with oily sludge as the sole carbon and energy source. After incubation on the MSM agar plates for 3-5 days at 20 ± 2°C, any visible colony growth was recorded as positive growth. Individual colony was identified by its color and morphology and further purified by streaking on nutrient agar plate. One isolated bacterium was used in this study, and it was identified as the uncultured *Luteibacter sp.*, which was used for bioremediation experiment (Fig 2.4).



Figure 2.1 Isolation procedure for PHCs degrading microorganisms



Figure 2.2 Soil contaminated with PHCs in a land-farming site



Figure 2.3 Enrichment of bacteria



Figure 2.4 Isolated strain: Luteibacter sp

2.4. Bioremediation experiment

The uncontaminated soil was autoclaved at 121 °C for 30 minutes and was then dried in an oven for 12 hours at 105°C. A certain amount of refinery oily sludge was placed into a jar with 10-20 ml of cyclohexane. The dried sterile soil was added into the jar with continuous stirring to reach a given TPH content (mg/kg). The spiked soil sample in the jar was then placed in the fume hood for 2-3 days in order to completely vaporize cyclohexane from the sample. Taguchi L-9 experimental design was applied to investigate the optimal condition of bioremediation. The initial sludge and nutrient content as well as the rhamnolipids (RL) concentration were studied with three levels (Table 2.3). The 250-ml flasks (Fig 2.5) were set up with the following treatments: (1) 25 g of spiked soil with different TPH contents; (2) inocula of *Luteibacter sp.* (OD 0.8), and (3) different nutrient solution to adjust C:N:P ratio. The flasks were sealed using rubber stoppers with two holes and aerated through a peristaltic pump for 40 days (Fig 2.7). Total petroleum hydrocarbon (TPH) concentration and PHC fractions (i.e. F2 fraction representing C10-C16, F3 fraction representing C16-C34, and F4 fraction representing C34-C50) were determined at the beginning and the end of an experiment. The experiments were conducted in triplicated. ANOVA was applied to analyze the experimental results.

2.5. Analysis of total petroleum hydrocarbon (TPH)

2 g of soil sample was added in a 40-ml vial with 10 ml of dichloromethane (DCM) and then the vial was placed on an orbital shaker for mechanical extraction at 150 rpm for 30 minutes. The extraction was conducted three times and about 30 ml of extraction solution was collected into a vial.

Test No.	TPH content (mg/kg)	Nutrients (C:N:P)	Rhamnolipid (mg/kg)
1	2297	100:10:1	40
2	2297	100:20:5	400
3	2297	100:50:10	1000
4	4674	100:10:1	400
5	4674	100:20:5	1000
6	4674	100:50:10	40
7	9690	100:10:1	1000
8	9690	100:20:5	40
9	9690	100:50:10	400

Table 2.3 Taguchi experimental design

Then the extraction solution was transferred into a glass column for cleanup. The column was packed with silica gel and anhydrous sodium sulphate and was rinsed with 20 ml of solvent (1:1 cyclohexane/DCM) before use. After the extraction solution passed through, another 20 ml of solvent (1:1 cyclohexane/DCM) was poured to elute the column. A round



Figure 2.5 A flask with soil



Figure 2.6 Setup of the bioremediation experiments

flask was placed under the column to collect the extraction after cleanup and then the extraction solution was evaporated by a rotary evaporator to reduce the volume to 1 ml. After evaporation, the residue in round flask was transferred into 2-ml sample vial with cyclohexane for GC analysis.Gas Chromatograph (Varian CP-3800) with flame ionization detector (GC-FID) was used for TPH analysis. The parameters for GC analysis were: 30-m metal column (Restek MXT-1) with 0.53 mm ID; injector temperature at 320 °C; detector temperature at 350°C; nitrogen gas as carrier gas with a constant flow at 7.5 ml/min; oven temperature starting at 40°C for 4 min, ramping to 140 °C at 10 °C /min, reaching to 340°C at 20 °C /min, and then being held at 340 °C for 11 minutes. External standard method was used to calculate TPH concentration in sample solution. The decane (C10), hexcane (C16), tetratriacontane (C34), and pentacontane (C50) were used as standard compounds to determine the TPH fractions. Fraction 1(F1) was defined as hydrocarbons before C10, fraction 2 (F2) was defined as hydrocarbons from C10 to C16, fraction 3 (F3) was the group of hydrocarbons from C16 to C34, and fraction 4 (F4) was the group of hydrocarbons from C34 to C50.

3. Results and discussion

3.1. TPH biodegradation

The TPH reduction rate and residual concentration of TPH in soil after 40-day bioremediation were shown in Fig 2.7 and Fig 2.8, respectively. The residual concentration of F2 fraction was less than 150 mg/kg for all of the treatment samples, and was not shown in Fig. 2.8. The highest (i.e. about 50.8%) and lowest (i.e. about 5.8%) TPH reduction rate was

observed with treatments L8 and L1, respectively. In terms of TPH fractions, however, treatment L1 was associated with much higher reduction rate of F3 (47.9%) and relatively no reduction of F4. For treatments L7, L8 and L9 which had the highest TPH contents (i.e. highest initial TPH concentration about 9690 mg/kg), it was observed from Fig 2.8 that the residual TPH concentration in soil samples after bioremediation was less than 6100 mg/kg with F4 fraction being less than 4600 mg/kg. As for treatments L7 and L8, the reduction rates for F2, F3, and F4 fractions were all above 30%, and the TPH reduction rate were 40.1% and 50.8%, respectively. As a result, the experimental results indicated that the isolated bacterium (uncultured *Luteibacter sp.*) was an effective bacterial strain for the biodegradation of long-chain petroleum hydrocarbons, and the combination of bioaugmentation and biostimulation was illustrated as an effective method for the remediation of oily sludge contamination. In fact, the strain of *Luteibacter sp*. was investigated for degrading PAHs with other soil bacterial strains (Cea et al, 2010).



Figure 2.7 TPH reduction rate for different treatments



Figure 2.8 TPH concentration remained in soil after bioremediation

3.2. Analysis of optimal bioremediation conditions

Signal to noise ratio (S/N ratio) analysis was applied to determine the performance of three factors on the biodegradation of TPH in oily sludge. Fig. 2.9 presents the results, and it indicates that all the three factors showed significant impacts on TPH reduction. The optimal bioremediation conditions were: initial TPH content at 9690 mg/kg (i.e. level 3), nutrient addition at the ratio of 100:50:10 (i.e. level 3) for C:N:P, and rhamnolipid addition at 400 mg/kg (i.e. level 2). Table 2.4 lists the ANOVA results, and it indicates that under the 0.05 significance level, the initial TPH content was the most significant factor to affect the bioremediation of PHCs in oily sludge, followed by rhamnolipid addition concentration (P < 0.05).

Factor	Square	MS*	df	F value	P value
Initial TPH	0.0885	0.0443	2	45.7925	0.0002
Nutrient addition	0.0165	0.0082	2	4.2553	0.0707
Rhamnolipid addition	0.0260	0.0130	2	6.7250	0.0294

Table 2.4 ANOVA for bioremediation of TPH

(MS: means of squares)

Fig. 2.10 presents the S/N ratio analysis results in terms of F3 reduction after bioremediation, and it indicates that the optimal condition for F3 degradation was: initial TPH content at 2297 mg/kg (i.e. level 1), nutrient addition at the ratio of 100:25:5 (i.e. level 2), and rhamnolipid content at 400 mg/kg (i.e. level 2). Table 2.5 lists the ANOVA results for F3 reduction, and it indicates that under the significance level of 0.05, there was no significant difference among all the three factors. In terms of F4 fraction reduction, Fig. 2.11 and Table 2.6 present the S/N ratio analysis and ANOVA results, respectively, and the optimal condition for F4 degradation was: initial TPH content at 9690 mg/kg (i.e. level 3), nutrient addition at the ratio of 100:50:10 (i.e. level 3), and rhamnolipid content at 1000 mg/kg (i.e. level 3).

However, the S/N ratio at 400 mg/kg of rhamnolipid was close to that at 1000 mg/kg, indicating that further increase of rhamnolipid concentration above 400 mg/kg did not effectively contribute to the increase of F4 reduction. ANOVA results in Table 2.6 indicate that the initial TPH content was the most significant factor (P<0.05), followed by rhamnolipid concentration and nutrient addition, in terms of the degradation of F4 fraction in oily sludge.



Figure 2.9 Effect of independent factors on TPH reduction



Figure 2.10 Effect of independent factors on F3 fraction reduction

Table 2.5 ANOVA for F3 fraction degradation

Factor	Square	MS*	df	F value	P value
Initial TPH	0.5236	0.2618	2	1.1795	0.370
Nutrient addition	0.4736	0.2368	2	1.0667	0.407
Rham addition	0.4792	0.2396	2	1.0794	0.398

(MS: means of squares)

Factor	Square	MS*	df	F value	P value
Initial TPH	0.1512	0.0756	2	77.6373	0.0001
Nutrient addition	0.0251	0.0125	2	12.8806	0.0067
Rham addition	0.0301	0.0151	2	15.4707	0.0043

Table 2.6 ANOVA for F4 fraction degradation

(MS: means of squares)

The initial TPH concentration in soil was found as a significant factor influencing the bioremediation efficiency by *Luteibacter sp.* The degradation of F3 fraction at low initial TPH content (i.e. level 1) in soil was better than those at higher initial TPH contents (i.e. levels 2 and 3) as shown in Fig. 2.10. However, the best biodegradation of F4 fraction was achieved for the treatments with the highest initial TPH content as shown in Fig. 2.11. It was also observed from Fig. 2.7 that the reduction of F3 fraction was higher than that of F4 among all the treatments at low initial TPH content (i.e. treatments L1-L6), but was lower for treatments at high initial TPH content (i.e. treatments L7-L9).

Fig. 2.12 presents the PHCs fraction distribution before and after bioremediation, and it was observed that the proportion of F3 in TPH was reduced from 16.0% to 8.8%, indicating that the isolated bacterial strain (*Luteibacter sp.*) preferred to use hydrocarbons in the F3 group as its carbon and energy sources for growth rather than those heavier components such as F4 (C34-C50). Also, the petroleum hydrocarbon compounds in the F4 group are more

hydrophobic and more strongly attached to soil particles, and hardly released into the water phase. In terms of PHCs fraction distribution at higher initial TPH content, the F4 fraction in TPH was decreased while the F3 fraction was increased. For example, the F4 fraction accounted for 80.2% of TPH before bioremediation, but it was decreased to 75.7% for treatment L8. On the contrary, F3 fraction in TPH was increased from 18.1% to 22.2%. Previous studies reported that long-chain alkane could be monooxidized or cooxidized during microbial growth (Kester and Foster, 1963). As a result, some intermediate hydrocarbons were generated during the degradation of compounds in the F4 group by bacterial strain, and these intermediate products might contribute to the increase of F3 fraction in TPH.



Figure 2.11 Effect of independent factors on F4 fraction reduction

Previous studies (Franzetti and Caredda, 2009) reported that the biodegradation performance of bacteria could be enhanced when the ratio of carbon, nitrogen and phosphorus element (C:N:P) was appropriately adjusted, but could be inhibited when
excessive amount of nutrients was added. In this study, such negative effect of nutrient addition was not observed on the degradation of TPH and F4 fraction, but it was observed on F3 fraction reduction. The F4 group was a dominant long-chain hydrocarbon fraction in oily sludge used in this study, and therefore its degradation by uncultured *Luteibacter sp.* might need a relatively higher concentration of nutrient addition to the soil medium as compared with that for shorter carbon-chain compound.



Figure 2.12 TPH fraction distribution before and after bioremediation: "Be"- before bioremediation and "Af"- after bioremediation

The addition of rhamnolipids could also aid bioremediation due to its capability to enhance PHC's solubility and to improve the desorption of PHCs entrapped in soil. However, the concentration of bio-surfactant added into soil for stimulation was different among various research studies. Rahman et al (2003) reported positive effect on n-alkanes biodegradation with adding 4 mg of rhamnolipid to 100 g soil. During the bioremediation process, rhamnolipids molecules could also be adsorbed onto soil particles and the amount of rhamnolipids soluble in soil water phase could be decreased, and part of rhamnolipid molecules might not work to enhance bioremediation. Therefore, a high concentration of rhamnolipids (above critical micelle concentration) might be needed to add into soil for biostimulation. In this study, the concentration of rhamnolipids added to soil was set at 40, 400, and 1000 mg/kg, respectively. When the concentration of rhamnolipids was at higher level (i.e. 400 and 1000 mg/kg), the reduction efficiency was better for F4 group and 400 mg/kg was the optimum for F3 group degradation.

4. Conclusion

The bioremediation of refinery oily sludge using a bio-surfactant (rhamnolipids) and a bacterium strain called uncultured *Luteibacter sp.* isolated from an oily sludge landfarming site was investigated in this study. The Taguchi experimental design method was used to investigate the impacts of initial TPH content in soil/sludge mixture, nutrient and bio-surfactant on the PHCs degradation. The experimental results indicated that the optimal bioremediation condition for TPH reduction was: initial TPH content at 9690 mg/kg, nutrient addition at the ratio of 100:50:10 for C:N:P, and rhamnolipid addition at 400 mg/kg. A TPH reduction of up to 50.8% was observed after 40-day bioremediation of oily sludge. The results also indicated that the degradation of F3 fraction at low initial TPH content was better than those at higher initial TPH contents, while the best biodegradation of F4 fraction was achieved for the treatments with the highest initial TPH content. The results indicated that the isolated bacterium was effective for degrading long-chain PHCs.

Chapter 3 Oil recovery from refinery oily sludge via ultrasound and freeze/thaw²

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Abstract

The effective disposal of oily sludge generated from the petroleum industry has received increasing concerns, and oil recovery from such waste was considered as one feasible option. In this study, three different approaches for oil recovery were investigated, including ultrasonic treatment alone, freeze/thaw alone and combined ultrasonic and freeze/thaw treatment. The results revealed that the combined process could achieve satisfactory performance by considering the oil recovery rate and the total petroleum hydrocarbon (TPH) concentrations in the recovered oil and wastewater. The individual impacts of five different factors on the combined process were further examined, including ultrasonic power, ultrasonic treatment duration, sludge/water ratio in the slurry, as well as bio-surfactant (rhamnolipids) and salt (NaCl) concentrations. An oil recovery rate of up to 80.0% was observed with an ultrasonic power of 66 W and ultrasonic treatment duration of 10 min when the sludge/water ratio was 1:2 without the addition of bio-surfactant and salt. The examination of individual factors revealed that the addition of low concentration of rhamnolipids (<100 mg/L) and salt (<1%) to the sludge could help improve the oil recovery from the combined treatment process. The experimental results also indicated that ultrasound and freeze/thaw could promote the efficiency of each other, and the main mechanism of oil recovery enhancement using ultrasound was through enhanced desorption of petroleum hydrocarbons (PHCs) from solid particles.

Key Words: Oily sludge, Ultrasound, Petroleum hydrocarbons, Freeze/thaw, Oil recovery

1. Introduction

The effective disposal of oily sludge wastes generated from petroleum industry during crude oil transportation, storage and refinery process is a worldwide problem. Generally the oily sludge is a complex of water-in-oil (W/O) emulsion, typically including 30-50% of oil, 30-50% of water and 10-12% of solids by mass (Ramaswamy et al, 2007; Reynolds and Heuer, 1993). Due to the existence of high concentration of petroleum hydrocarbons (PHCs), oily sludge is considered to be hazardous to environments and human health, thus requiring effective remediation (Ferrari et al, 1996). However, the emulsion and high PHC concentration could make the conventional sludge treatment process (i.e. landfarming, landfilling, incineration) to be time-consuming, ineffective and expensive (Shie et al, 2000; Buyukkamaci and Kucukselek, 2007). Given the high oil concentration in oily sludge, oil recovery before disposal would be considered as one feasible method to improve the performance of those conventional treatment processes (Elektorowicz and Habibi 2005; Zubaidy and Abouelnasr, 2010). In fact, the treatment of sludge containing over 10% of oil could result in economic benefit from oil recovery (Ramaswamy et al, 2007). The oil recovery would significantly reduce the PHC concentration and the volume of sludge for further treatment, thus the efficiency of conventional process such as land-farming could be improved through significantly reducing soil/sludge mixing ratio in landfarm and providing a PHC concentration non-toxic to microorganisms.

Solvent extraction has been applied to recover oil from waste oily sludge. For example, Zubaidy and Aouelnasr (2010) applied methyl ethyl ketone (MEK) and LPG condensate (LPGC) for oil recovery from sludge generated from the storage of crude petroleum, and found that these two solvents could achieve an oil recovery of 39% and 32%, respectively, when using the optimal 4:1 solvent-to-sludge ratio; Avila-Chavez et al. (2007) used the supercritical fluid extraction apparatus to investigate the extraction of hydrocarbons from a crude oil tank bottom sludge with supercritical ethane at varying pressure and temperature conditions, and an extraction yield of up to 58.5% was obtained; Taiwo and Otolorin (2009) reported an oil recovery of about 67.5% from the accumulated sludge in oil storage facilities by using hexane and xylene extraction. Although being applied to a number of oil recovery studies, the solvent extraction method is still associated with relatively lower oil recovery efficiency and requires the use of massive volume of solvents which may then restrict its application (Zubaidy and Abouelnasr, 2010). In addition to solvent extraction, a number of other studies have been reported to focus on physical approaches for oil recovery, including air flotation, thermal desorption, sonication, electrical and microwave heating (Eelktorowicz et al, 2006; Ramaswamy et al, 2007; Nour et al, 2010; Xu et al 2009). Among these methods, ultrasonic irradiation has been proved as an effective treatment of removing adsorbed materials from solid particles, solid/liquid separation in high-concentration suspensions (i.e. dewatering of biological sludge), and decreasing the stability of water/oil emulsion (Newman et al, 1997; Kim and Wang et al 2003; Dewil et al 2006; Ye et al, 2008). The cavitation collapse due to ultrasound can not only affect the surface of solid particles but also penetrate into the soil matrix, and could thus improve the separation of oil from soils and slurries (Kim and Wang, 2003, Abramov et al, 2009). A number of ultrasonic factors such as ultrasonic power and treatment time were found to affect the separation efficiency, while some experiments also indicated that the addition of alkaline reagents or sodium salts could enhance the separation (Collings et al 2006; Abramov et al, 2009). In spite of the successful application to many engineering fields, few studies were reported to apply ultrasound for oil

removal or recovery from oily sludge.

In order to effectively recover oil from the sludge, the emulsions need to be broken down. Freeze/thaw (F/T) used for sewage sludge dewatering in cold regions has been reported as one effective and feasible method for demulsification in recent years (Jean et al, 1999; Chen and He, 2003; Rajakovic and Skala, 2006). For example, Lin and He (2007) applied the freeze/thaw treatment method to break the water/oil emulsions with loosely packed droplets that were produced from oils, and the volume expansion of water turning to ice and interfacial tension of oil-water interface were determined as the main driving forces of demulsification. A number of factors such as freezing and thawing temperature as well as freezing time were found to affect the performance of this method (Chen and He. 2003: Lin and He, 2007), and some other parameters such as components in aqueous phase (salts, surfactants) were also reported to affect the demulsification process (Ghosh and Coupland, 2008). In general, ultrasonic and freeze/thaw treatment processes represent simple but effective methods for demulsification. It is recognized that the combination of alternative demulsification methods maybe more effective than individual method (Rajakovic and Skala, 2006). However, there have been very few studies into combining ultrasound with freeze/thaw for increasing the water/oil separation of oily sludge.

The objective of this study is then to evaluate the oil recovery efficiency of the combined ultrasonic and freeze/thaw approach for oily sludge treatment, and several factors including ultrasonic power, ultrasonic treatment duration, addition of bio-surfactant, addition of salt as well as sludge to water ratio were investigated for their effects on the treatment performance. The results would provide a sound basis for developing environmentally friendly and economically competitive methods for oily sludge treatment.

2. Materials and methods

2.1. Oily sludge

The oily sludge (Fig 3.1) used in the experiments was collected from a crude oil tank bottom in an oil refinery plant in western Canada and it is stored in a capped stainless-steel bucket which was put in darkness at 4°C. The sludge was very sticky, and its characteristics are listed in Table 3.1. The total petroleum hydrocarbon (TPH) concentration in sludge was analyzed based on the sample extraction process which will be described in Section 2.5. The metal elements were measured using Inductively Coupled Plasma (ICP) analysis based on the method given in ASTM D5185 (2009), the water content was analyzed based on the ASTM D1744 method (1992), and the solid content was calculated based on the measured TPH and water contents.



Figure 3.1 Oily sludge sample

Parameter	Concentration	Parameter	Concentration	
TPH (by mass)	61%	Barium(mg/kg)	2,136	
Water content (by mass)	24%	Iron (mg/kg)	6,339	
Solid content (by mass)	15%	Zinc (mg/kg)	209	
Sodium (mg/kg)	76	Copper (mg/kg)	43	
Potassium (mg/kg)	423	Lead (mg/kg)	19	
Magnesium (mg/kg)	432	Chromium (mg/kg)	11	
Aluminum (mg/kg)	999	Nickel (mg/kg)	9	
Calcium (mg/kg)	1,145			

Table 3.1 Characteristics of the oily sludge

2.2. Chemicals and Bio-surfactant

Hexadecane (nC16; >99% pure), Nonadecane (nC19; >99% pure), Tetratracon (nC34; >99% pure), and pentacontane (C50) were purchased from Sigma and used as standard compounds for PHCs analysis. Rhamnolipid (JBR-425) purchased from Jeneil Bio-surfactant Co. (LLC, USA) was used as the bio-surfactant. It is a 25% aqueous solution mixed with two rhamnolipids: $C_{26}H_{48}O_9$ and $C_{32}H_{58}O_{13}$. FeSO₄·7H₂O.

The dichloromethane (DCM) (>99%, HPLC) and cyclohexane (>99%, HPLC) were used as solvents for sample extraction. The toluene (>99%, HPLC) was used as solvent to dilute extraction samples for GC analysis. Silica gel (purchased from Sigma) activated at 105 °C for 12 h was used to clean up extraction solution, and anhydrous sodium sulfate dried at 400 °C for 12 h was used to absorb water in the extraction solution.

2.3. Experiments on oil recovery using three different processes

The experiments were conducted to compare the efficiencies of oil recovery from refinery sludge by using three different treatment processes, including ultrasonic treatment alone (US), freeze/thaw alone (F/T), as well as the combined ultrasonic and freeze/that treatment (US + F/T). In terms of ultrasonic treatment alone, 10 g of oily sludge was placed inside a 120 ml beaker which contained 40 ml of deionized water, and was then treated by placing the 0.5 in. diameter titanium sonic probe into the center of the sample. The sonic probe was operated by a 20 kHz Misonix Sonicator 3000 generator. The treatment was conducted at a working power of 66 W for 10 min. Figs. 3.2 and 3.3 illustrate the ultrasonic treatment system.



Figure 3.2 Ultrasonic treatment system

After ultrasonic treatment, the treated sample was observed to have a reduced viscosity than the original sludge and was transferred into a 50-ml centrifuge tube. The sample was then centrifuged for 15 min at 5000 rpm. The oil and aqueous phases after centrifugation were then separated using a separation funnel. The mass of oil layer separated was then measured and considered as the oil recovery. The total petroleum hydrocarbon (TPH) concentrations in the separated oil layer and aqueous phase were also analyzed.



Figure 3.3 Ultrasonic treatment for oil recovery

In terms of freeze/thaw treatment alone, 10 g of oily sludge was put into a 50-ml centrifuge tube with 40 ml of DI water and was frozen within a freezer under $-20 \circ$ C for 12 h. The frozen sample was then thawed at an ambient temperature of 24 °C. After thawing, the sample in the tube was centrifuged for 15 min at 5000 rpm. The oil and aqueous phases after centrifugation were separated using a separation funnel, and the mass of oil layer separated from the sample as well as the TPH concentrations in oil layer and aqueous phase were then measured.

In terms of the combined ultrasonic and freeze/thaw treatment process, 10 g of oily sludge was put into a 120 ml beaker with 40 ml of deionized water, and was then treated by

ultrasound at 66 W for 10 min. After ultrasonic treatment, the sample was transferred to a 50-ml centrifuge tube and was centrifuged for 15 min at 5000 rpm. After centrifugation, the sample in the tube went through the freeze/thaw process, and the remaining treatment procedures were the same as those for the freeze/thaw treatment alone.

2.4. Experiments on factors affecting the combined treatment process

The individual impacts of five different factors on the oil recovery rate from the combined ultrasonic and freeze/thaw treatment process were further examined to better understand this process and provide useful information for its effective operation. Five factors were selected, including ultrasonic power, ultrasonic treatment duration, sludge/water mixing ratio, bio-surfactant concentration, and salt (NaCl) concentration. Table 3.2 summarizes the corresponding levels of the experimental factors, while the interaction effects of different factors were not investigated in this study. In terms of ultrasonic power, experiments were conducted at four levels from 21 to 66 W with an ultrasonic treatment duration of 10 min (i.e. the maximum treatment duration level in this study) and a sludge/water ratio of 1:4 (i.e. the medium mixing ratio level selected in this study), without the addition of bio-surfactant and salt. In terms of ultrasonic treatment duration, four levels (0.5, 1, 5 and 10 min) were examined at the ultrasonic power of 66 W (i.e. the maximum power level selected in this study) and sludge/water ratio of 1:4 without the addition of bio-surfactant and salt. In terms of other factors, four different sludge/water mixing ratios from 1:8 to 1:1 as well as five different levels of bio-surfactant concentration (from 0 to 700 mg/L) and salt concentration (from 0 to 5.0% by mass) were investigated at the ultrasonic power of 66 W and 10 min of treatment time. For the examination of sludge/water ratio, no

rhamnolipids and salt were added to the sludge slurry system; for the examination of bio-surfactant concentration, a sludge/water ratio of 1:4 was maintained without the addition of salt, and for the examination of salt concentration, a sludge/water ratio of 1:4 was applied without the addition of rhamnolipids. The experimental procedures for each factor's examination were the same as described before.

Influencing factors	Level descriptions	
Ultrasonic power (W)	21, 33, 48, 66	
Ultrasonic duration (min)	0.5, 1, 5, 10	
Sludge/water ratio	1:8, 1:4, 1:2, 1:1	
Rhamnolipids concentration (mg/L)	0, 40, 100, 400, 700	
NaCl concentration (% by mass)	0, 0.3, 1.0, 3.0, 5.0	

Table 3.2 Influencing factors and their corresponding levels

2.5. Sample extraction and analysis

2.5.1. TPH concentration in the recovered oil layer

1 g of the recovered oil layer sample was dissolved with 20 ml of solvent (cyclohexane) in a 40-ml vial and then the vial was placed on an orbital shaker for mechanical extraction at 150 rpm for 1 h. After shaking, the extraction solution was transferred into a glass column for cleanup to remove moisture, particulate, and unwanted polar organic compounds (CCME, 2001). The column was packed with silica gel and anhydrous sodium sulfate and rinsed with 20 ml of solvent (1:1 cyclohexane/DCM) before use. After the extraction solution passed through, another 20 ml of solvent (1:1 cyclohexane/DCM) was poured to elute the column. A round flask with mass of M_0 (mg) was put under the column to collect the extraction solution after cleanup, and then the extraction solution in the flask was evaporated using a rotary evaporator (Fig 3.4) to remove the solvent contained in the extraction solution.



Figure 3.4 Evaporation of extraction solution

After evaporation, the round flask (Fig. 3.5) with residue was put in the fume hood for 30 min at room temperature and only petroleum hydrocarbons (PHCs) were left in the flask (CCME, 2001). The mass of the flask containing PHCs was then measured as M_T (mg). Consequently, the concentration of TPH in the recovered oil can be calculated by Eq. (1). Similarly, TPH concentration in the original sludge can also be obtained.

$$C = \frac{M_T - M_0}{M} \tag{1}$$

where M is the mass of oil layer sample or original sludge sample used for extraction analysis (g), M_0 is the mass of a round flask and C is the TPH concentration in oil layer or original sludge (mg/g).



Figure 3.5 Round flask with residual after evaporation

The oil recovery was defined as the ratio of the mass of PHCs in the recovered oil to the mass of PHCs in the original sludge sample, and can be obtained using Eq. (2):

$$R = \frac{C_{oil-layer} \times M_{oil-layer}}{C_{sludge} \times M_{sludge}} \times 100\%$$
⁽²⁾

where R is oil recovery (%), $C_{oil-layer}$ and C_{sludge} are TPH concentrations (mg/g) in the recovered oil layer and original sludge, respectively, $M_{oil-layer}$ (g) is the total mass of recovered oil layer from separation, and M_{sludge} (g) is the mass of oily sludge used for each experimental treatment.

2.5.2. TPH concentration in separated aqueous phase

The separated aqueous phase (Fig 3.6) from the sample after oil recovery treatment consists of petroleum hydrocarbons and could be considered as wastewater, and the TPH

concentration in such aqueous phase should also be analyzed. This was completed using about 40 ml of aqueous phase water through liquid–liquid extraction with 15 ml of cyclohexane for three times (SW-846 EPA, 1993).



Figure 3.6 Aqueous sample after oil recovery

About 45 ml of extraction solution was collected and then cleaned up through a glass column packed with silica gel and anhydrous sodium sulfate as described above. The remaining procedures were the same with that for measuring TPH in oil layer. As a result, TPH concentration in the aqueous phase C_{water} (mg/L) was obtained using Eq. (3):

$$C_{water} = \frac{M_T - M_0}{V}$$
(3)

where V is the volume of aqueous phase used for sample extraction (L).

2.5.3. PHCs analysis

After evaporation using a rotary evaporator, petroleum hydrocarbons in the round flask were transferred into a 15-ml sample vial by using cyclohexane, and 2 ml of solution in the

vial was then sent for the analysis of PHCs using a Varian CP-3800 Gas Chromatograph with flame ionization (GC-FID) (Fig 3.7).



Figure 3.7 Samples for GC analysis

External standard method was used for identification. The decane (C10), hexadecane (C16), tetratriacontane (C34), and pentacontane (C50) were used as external standards to determine the concentration of PHCs and TPHs fractions (CCME, 2001), where fractions F1, F2, F3 and F4 were defined as the group of hydrocarbons from C6 to C10, C10 to C16, C16 to C34, and C34 to C50, respectively. The GC analysis conditions were: ZB-capillary column (Phenomenex Torrance, CA) with 30 m \times 0.25 mm ID (inner diameter) and 0.25-µm film thickness; inject volume of 1 µL; injector and detector (FID) temperatures at 320 °C; carrier gas (helium) at a constant flow rate of 1.5 mL/min during analysis. The splitless injection mode was performed on the 1079 PTV injector and after 0.7 min the split mode was activated at split ratio of 10:1. The capillary column temperature program was initially held at 50°C for 1 min, then ramped at 15.0 °C/min to 110 °C and further increased at 10.0 °C/min to 300°C and then held for 11 min. The total running time for a sample was 45 minute.

3. Results and discussion

3.1. Comparison of methods

The experimental results of using different oil recovery methods are summarized in Table 3.3, and it was indicated that F/T method alone worked more effectively in terms of the oil recovery rate (with an oil recovery of 65.7%) than the two other method (Fig. 3.8). It is recognized that the water/oil emulsion is stabilized by the existence of an emulsifying film consisting of surfactant molecules which could prevent water droplets from contacting each other (Chen and He, 2003). During the freezing of water droplets, some surfactant molecules that form the water-in-oil emulsion would be expelled from the ice lattices at the oil-water interface and diffuse into the oil phase, and during thawing process more surfactant molecules could be diffused away from the interface, leading to the lack of surfactant molecules on the emulsifying film. Thus the water droplets could coalesce and form larger water droplets which facilitate the water/oil separation, while some surfactants may form micelles inside the water droplets with trace amount of oil (Chen and He, 2003; Lin and He, 2007). It was found from the experiments that ultrasonic treatment alone was associated with the lowest oil recovery (i.e. 58.9%), while the combination of ultrasound and freeze/thaw achieved an oil recovery of 64.2% which was close to that for F/T alone. This may indicate that ultrasound alone could not effectively break the emulsifying film of surfactant molecules.

However, ultrasound alone achieved the highest TPH concentration in the recovered oil layer (i.e. highest purity) (Fig. 3.9a). The TPH concentration in the recovered oil was 625 mg/g for F/T, 933 mg/g for US, and 851 mg/g for US + F/T, while the TPH concentration in

the original oily sludge was 610 mg/g. As a result, the recovered oil from ultrasonic treatment alone contained 93.3% of TPH. In fact, for a multiphase system when solid phase exists, petroleum hydrocarbon molecules are either strongly adsorbed onto the surface of solid particles or trapped inside the sediment matrix, and this would prevent the separation of oil from the multiphase system. Previous studies (Feng and Aldrich, 2000; Breitbach et al, 2003; Hamdaoui et al, 2005) proved that ultrasound could effectively promote the desorption of

Table 3.3 Summary of oil recovery results using different methods.

Method	Mass of recovered oil layer (g)	TPH concentration in recovered oil layer (mg/g)	TPH recovery rate (%)	TPH concentration in wastewater (mg/L)
F/T method	6.41	625	65.7%	< 25
US method	3.84	933	58.9%	1550
US+ F/T method	4.60	851	64.2%	200
TPH in original slu	idge (mg/g)	610		



Figure 3.8 Oil recoveries for different treatment methods (error bar represents standard deviation)



Figure 3.9 TPH concentrations in separated oil layer (a) and water (b) (error bar represents standard deviation).

organic compounds. Due to ultrasonic irradiation in liquid media, micro-bubbles could form and then collapse or implode when they reach some critical size (Hamdaoui et al, 2007), leading to localized high pressure and temperature shockwave. The collapse or implosion occurring in the vicinity of particle surface would release the adsorbed or trapped organic compound molecules from the solid particles or sediment matrix into the solution. Moreover, the collapse can bring high-speed liquid micro-jets with strong shear force which can then break the aggregates of solid particles and result in the detachment of oil and water from the solid particles (Feng and Aldrich, 2000; Mason, 2007). Consequently, ultrasound could considerably enhance the separation of oil from solid phase and more adsorbed or trapped oil could enter the oil layer after oil/water separation. The experimental results in this study indicated that freeze/thaw alone was not effective for desorption. Although it obtained the highest oil recovery, the concentration of TPH in the recovered oil was the lowest (i.e. 62.5%). Through application of ultrasound, the TPH concentration in the recovered oil for combined US + F/T process increased significantly from 62.5% to 85.1% which was close to that for ultrasonic treatment alone (i.e. 93.3%).

The TPH concentrations in aqueous phase after water/oil separation for different treatment methods are presented in Fig. 3.9 b. It was found that for ultrasonic treatment alone, the separated aqueous phase contained very high concentration of TPH (1550 mg/L). Such high concentration may result in high cost for further treatment of the wastewater after oil recovery. In contrast, freeze/thaw treatment alone was associated with the lowest TPH concentration in wastewater (i.e. less than 25 mg/L). The application of ultrasound could promote the desorption of adsorbed or trapped PHCs and then effectively release them to the solution, while freeze/thaw was not effective in promoting the desorption. In fact, for the samples treated by freeze/thaw alone, it was observed in the experiments that the solid particles were hardly separated and settled in the bottom of the tube. Thus the recovered oil (i.e. 62.5%) was close to that in the original sludge (i.e. 61%). The observed sludge settleability after freeze/thaw treatment in this study was not in agreement with previous study conducted by Jean et al. (1999) who used freeze/thaw to treat the oily sludge samples taken from the dissolved air flotation (DAF) unit of a wastewater treatment plant. The crude

oil tank bottom sludge used in this study contained more solid content (i.e. 15%) than the DAF sludge (i.e. 7.8%), and this emulsion had an oil/solid ratio of about 4.0 (Table 3.2). The oil recovery from sludge requires not only the separation of oil from water but also the detachment of oil molecules from solids. It was suggested that the F/T method was effective to drive hydrocarbon molecules away from water to form free oil layer (Chen and He, 2003). However, as described before, the F/T method could not provide a strong driving force to remove the adsorbed oil to the aqueous phase from solid particles within the crude oil tank bottom sludge.

For samples treated by ultrasound or combined ultrasound and freeze/thaw, it was observed in the experiments that the solid particles were significantly separated from aqueous phases and settled in the bottom of the tube, and this indicates that ultrasound could enhance the settling of solid particles. As a result, the recovered oil for ultrasound alone and combined ultrasound and freeze/thaw contained much less solids but with much higher TPH (i.e. 93.3% and 85.1%) as compared with that for freeze/thaw alone. Due to ultrasonic irradiation, some desorbed PHCs from solids also entered the aqueous phase, but with the effect of freeze/thaw, some hydrocarbon molecules could be expelled from the expansion of water droplets turning into ice and then enter the oil phase. As a result, it was observed that the TPH concentration in the separated aqueous phase for combined ultrasound and freeze/thaw was much lower (i.e. 200 mg/L) than that for ultrasound alone (i.e. 1550 mg/L) but higher than that for freeze/thaw alone (i.e. <25 mg/L). This was in agreement with previous studies that F/T method was effective for separating oil from the aqueous phase (Chen and He, 2003; Jean et al, 1999). As described above, the combined process brought higher oil recovery than that for the ultrasonic treatment alone, and much higher TPH concentration in the recovered oil layer

than that for the F/T method. Consequently, the combined ultrasonic and freeze/thaw treatment was identified in this study as more effective than the other two methods and was further examined for oil recovery from the refinery crude oil tank bottom sludge.

3.2. Effects of different factors on the combined treatment process

3.2.1. Effects of ultrasonic power and treatment duration

In terms of the combined ultrasonic and freeze/thaw treatment process, Figs. 3.10 and 3.11 present the oil recovery results under the impacts of ultrasonic power and treatment duration. It was observed from Fig. 3.10 that the oil recovery of the combined process could be improved by increasing ultrasonic power at low level. For example, the recovery rate was increased from 57.7% at ultrasonic power of 21 W to 63.6% at 33 W. However, further increase in ultrasonic power at level above 33 W was not associated with significant enhancement of oil recovery. The oil recovery was only increased to 64.1% at ultrasonic power of 66 W. Similar results of the limitation of ultrasonic power have also been reported in many studies in other areas (Feng and Aldrich, 2000; Mason and Lorimer, 2002). It has been reported that the phenomena of ultrasonic cavitation could play a significant role in enhancing the desorption of adsorbed molecules, and the effect of cavitation depends on the size of bubbles while more energy could be stored within the bigger bubbles (Breitbach et al, 2003). In this study, the low frequency of ultrasound (20 kHz) was applied. In order to produce shockwave and high speed microjets, implosion radius of bubbles is around 170 µm at 20 kHz (Schueller and Yang, 2001). However, bubbles with radius at a few microns usually become unstable and collapse at such ultrasonic frequency, leading to the rare existence of larger bubbles. Thus the inhibition on the size of cavitation microbubbles could be attributed to no further significant increase of oil recovery rate even though the ultrasonic power was increased from 33 W to 66 W.



Figure 3.10 Oil recovery versus ultrasonic power for the combined process (error bar represents standard deviation) (experimental condition: ultrasonic treatment duration of 10 min, sludge/water ratio of 1:4, without the addition of rhamnolipids and NaCl).

In terms of the impact of ultrasonic treatment duration, it can be found from Fig. 3.11 that the oil recovery was increased to 64.2% within 1 min of ultrasonic treatment followed by freeze/thaw. No further significant increase of oil recovery was observed when ultrasonic irradiation was increased to 10 min. The oil recovery was 64.1% when the treatment duration was 10 min which was close to that at 1 min of treatment. This may be explained by the fact that when adsorbed organic molecules were desorbed from solid particles into aqueous phase even through long duration of ultrasonic treatment re-adsorption might happen in the system during freeze/thaw process and would thus compromise the effect of ultrasonic desorption (Feng and Aldrich, 2000).



Figure 3.11 Oil recovery versus ultrasonic treatment duration for the combined process (error bar represents standard deviation) (experimental condition: ultrasonic treatment power of 66 W, sludge/water ratio of 1:4, without the addition of rhamnolipids and NaCl).

3.2.2. Effects of sludge/water ratio

Fig 3.12 presents the oil recoveries at different sludge/water ratios for the combined treatment process. It can be observed that oil recovery was increased from 41.9% to 80.0% as the slurry content was increased from sludge/water ratio of 1:8 to 1:2 and then slightly dropped to 72.2% at sludge/water ratio of 1:1. The increase of sludge content in the slurry system could result in more oil recovery. However, further increase of sludge content when the sludge/water ratio was above 1:2 could result in increased viscosity of the slurry which then could impede the formation and collapse of cavitation bubbles. As a result, the effect of sonication was weakened and oil recovery rate was decreased when the sludge content was too high in the slurry. Similar phenomena was also reported by Feng and Aldrich (2000) who used ultrasonic irradiation to remove diesel from solid in slurry state, and they indicated that the increase of solid concentration above 50% significantly inhibited cavitation process in

oily sand-water system. In terms of the TPH concentration in the recovered oil, it was observed to be 658, 846, 851, and 659 mg/g for the sludge/water ratios of 1:1, 1:2, 1:4 and 1:8, respectively. The TPH concentration in the recovered oil for sludge/water ratio of 1:2 was close to that for sludge/water ratio of 1:4. Consequently, by considering oil recovery and the quality of the recovered oil, the effective sludge/water ratio was 1:2 when using the combined treatment process.



Figure 3.12 Oil recovery versus sludge/water ratio for the combined process (error bar represents standard deviation) (experimental condition: ultrasonic power of 66 W, ultrasonic treatment duration of 10 min, without the addition of rhamnolipids and NaCl).

3.2.3. Effects of bio-surfactant (rhamnolipids)

The effect of rhamnolipid addition to the oily sludge slurry system on the combined treatment process is shown in Fig. 3.13. It can be found that the oil recovery was increased from 64.1% to 73.2% as the concentration of rhamnolipids in water was increased from 0 to 100 mg/L. However, the oil recovery dropped to 61.8% and 62.5% at rhamnolipids

concentration of 400 and 1000 mg/L, respectively.



Figure 3.13 Oil recovery versus bio-surfactant concentration for the combined process (error bar represents standard deviation) (experimental condition: ultrasonic power of 66 W, ultrasonic treatment duration of 10 min, sludge/water ratio of 1:4, without the addition of NaCl).

Rhamnolipids are a class of glycolipid bio-surfactants usually produced by specific bacterial strains (Mulligan, 2005), and the critical micelle concentration (CMC) has been reported between 10 and 230 mg/L (Nitschke et al, 2005). The addition of rhamnolipids into the oily sludge slurry samples could affect the adsorption energy of petroleum hydrocarbons with solid particles and lower the energy required for desorption, and thus the organic compounds could be easily removed at the same ultrasonic power application. Furthermore, the presence of surfactant could lower the surface tension and affect the formation and collapse of ultrasonic cavitation bubbles. Therefore, an apparent increase of oil recovery was observed with addition of rhamnolipids up to 100 mg/L. However, when the adsorbed hydrocarbon molecules was continuously removed from solid particles by ultrasonic irradiation, the free sites on solid particle surface could allow for the adsorption of

bio-surfactants if there were a large amount of rhamnolipids in the oil/solids/water multiphase system. The ultrasonic cavitation would also exert an effect on the adsorption and desorption of rhamnolipids, and thus not all of the ultrasonic energy introduced into the system was used to remove oil from solid particles. As a result, the oil recovery rate dropped when the rhamnolipid concentration was above 100 mg/L.

3.2.4. Effects of salt addition (sodium chloride)

Fig. 3.14 presents the effect of sodium chloride (NaCl) concentration on the combined treatment process. It was found that the oil recovery was increased from 64.1% to 74.2% as the addition of NaCl was increased from 0 to 1%. As the salt concentration was further increasing, the oil recovery started decreasing and dropped to 59.0% when the NaCl concentration was 5%. Thus the low salinity showed a positive impact while the high salinity illustrated a negative impact on oil recovery from oily sludge.

Low salinity brine injection has been studied for oil recovery and it has been reported that the presence of ions would affect the adsorption of oil onto clay or mineral layers (Cissokho et al, 2009; Lager et al, 2006). Abramov et al. (2009) indicated that the addition of Na⁺ helped to break the bond between oil and sand soils by increasing the negative charges on the soil surfaces. In addition, the presence of NaCl could also enhance cavitation bubble implosion and thus enhance the sonic power intensity (Suri et al, 2010). As a result, the addition of salt could introduce a positive effect on oil recovery using the combined treatment process. However, excessive amount of NaCl (i.e. above 1%) in the sludge slurry system could reduce the concentration of PHCs in the aqueous phase and lead to a negative impact on the desorption of PHCs from solid particles by ultrasound (Dukkanci and Gunduz, 2006). Therefore, the effective salinity was found to be about 1% for oil recovery from oily sludge.



Figure 3.14 Oil recovery versus NaCl concentration for the combined process (error bar represents standard deviation) (experimental condition: ultrasonic power of 66 W, ultrasonic treatment duration of 10 min, sludge/water ratio of 1:4, without the addition of rhamnolipids).

3.3. PHC fraction analysis for recovered oil

Fig. 3.15 presents the GC profiles of samples from the combined ultrasonic and freeze/thaw treatment, and it can be found that there was no significant difference between PHC fraction distribution in the original sludge sample and the recovered oil sample, indicating that the effect of ultrasonic destruction of petroleum hydrocarbons was not significant (i.e. no significant shift of peaks towards the left of GC profile), and the main mechanism of enhanced oil recovery through the combined process was ultrasonic enhance desorption.



Figure 3.15 GC profiles of samples from oil recovery treatment (A represents oil sample after US + F/T treatment and B represents original oily sludge sample).

Samples	PHCs fraction distribution (%)		
	F2	F3	F4
Original sludge	23.0%	63.9%	13.1%
Oil recovered at 66 W for 10 minutes with no salinity and surfactant	21.8%	64.0%	13.2%
Oil recovered at 66 W for 1 minute with no salinity and surfactant	21.8%	64.9%	13.3%
Oil recovered at 66 W for 10 minutes with 3% NaCl	21.9%	64.7%	13.4%
Oil recovered at 66 W for 10 minutes with 40 mg/L biosurfactant	21.6%	64.9%	13.5%

Table 3.4 PHCs fraction distribution for samples before and after US+F/T treatment

Table 3.4 lists the PHC fraction distributions in the original oily sludge sample and several recovered oil samples under different treatment conditions. It can be found that the difference among the proportions of PHC fractions in the recovered oil under different ultrasonic treatment conditions was very small, and the average F2, F3, and F4 fractions in the recovered oil were 21.77%, 64.64%, and 13.37%, respectively. The F2 fraction in the recovered oil was slightly lower (i.e. about 1.2%) than that in the original sludge, while the F3 and F4 fractions in the recovered oil were slightly greater (i.e. about 0.8% and 0.2%) than

that in the original sludge. This may indicate that the application of ultrasound could destruct some light oil compounds such as F2, leading to slight increase of the proportion of F3 and F4 fractions in the recovered oil. However, the effect of ultrasonic destruction was not very significant. It has been reported that the destruction of organic compounds such as long-chain hydrocarbons was resulted from the production of hydroxyl radicals (Feng and Aldrich, 2000). This usually occurs when the ultrasound is in the mid frequency from 200 to 400 kHz (Breitbach et al, 2003; Petrier and Francony, 1997). In this study, the condition for the production of hydroxyl radicals was not reached at low frequency of 20 kHz, thus there was no significant destruction to change the PHC proportions in the recovered oil. However, the energy released from ultrasonic cavitation under this frequency was enough to overcome the affinity of hydrocarbon molecules with solid particles and to increase oil desorption.

4. Conclusion

Oil recovery from refinery oily sludge was investigated in this study using three different approaches, including ultrasonic treatment alone, freeze/thaw alone, and combined ultrasonic and freeze/thaw treatment. By comprehensively considering oil recovery efficiency, as well as TPH concentrations in the recovered oil and in the separated wastewater, the combination of ultrasound and freeze/thaw was identified as an effective method with satisfactory performance. Under the experimental conditions, it achieved an oil recovery rate of 64.2%, and TPH concentrations of 85.1% and 200 mg/L in the recovered oil and wastewater, respectively. The experimental results revealed that ultrasound could promote the separation of oil from solids while freeze/thaw could promote the separation of water and oil in the multiphase

system. Several different factors were further examined to investigate their individual impacts on the performance of the combined treatment process, and it was observed that under the experimental conditions, the oil recovery was improved with ultrasonic power at low power level, but further increase in ultrasonic power at level above 33 W was not associated with significant enhancement of oil recovery. The oil recovery was increased to its peak within 1 min of ultrasonic treatment, and thereafter no further significant increase of oil recovery was observed. The results of examining the individual impacts of other factors on the combined treatment process indicated an effective sludge/water ratio of 1:2, a rhamnolipids concentration of 100 mg/L, and a NaCl concentration of 1%, respectively. An oil recovery rate of up to 80.0% was observed under the experimental conditions of ultrasonic power of 66 W, ultrasonic treatment duration of 10 min, sludge/water ratio of 1:2, and no addition of bio-surfactant and salt.

The analysis of PHC fraction distributions in the recovered oil samples indicated that the effect of ultrasonic destruction of organic compounds was insignificant, and the major mechanism of oil recovery enhancement was through enhanced ultrasonic desorption of PHCs from solid particles under the low frequency application of 20 kHz. In this study, the individual impacts of different factors on the combined treatment process were examined through a series of laboratory experiments. However, the interaction effects among these factors, the identification of major influencing factors, and the optimal combination of these factors were not examined. This could be investigated through factorial experimental design method in future studies. In addition, the recovered oil from the crude oil tank bottom sludge in this study was not a pure mixture of petroleum hydrocarbons, and may need further treatment. The value of the recovered oil as fuel (such as asphaltene content, ash content, salt content, and heat of

combustion) and the detailed cost/benefit of the proposed treatment process were not analyzed, and should be examined in future studies. In summary, the combined ultrasonic and freeze/thaw process could represent an environmentally friendly and economically competitive alternative for the effective treatment of oily sludge waste from the petroleum industry, and is worth of further investigations.

Chapter 4 Treatment of oily sludge through advanced oxidation processes

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Abstract

The effective disposal of oily sludge generated from petroleum industry is a worldwide concern. Due to its complex in composition, oily sludge is relatively hard to clean up using traditional approaches. In this study, three different advanced oxidation processes were investigated for their capabilities to reduce petroleum hydrocarbons (PHCs) in oily sludge, including ultrasonic treatment alone, Fenton process alone, and the combination of ultrasound and Fenton process (US/Fenton). The results revealed that the combined process could achieve the best reduction in total petroleum hydrocarbons (TPH). The impacts of four different factors on the combined process were further examined, including the initial sludge content, the molar ratio of hydrogen peroxide to Fe^{2+} , (H₂O₂/Fe²⁺) the ultrasonic power, and the ultrasonic treatment duration. The highest TPH reduction rate of 88.1% was observed by US/Fenton process with a sludge content of 20 g/L, a H₂O₂/Fe²⁺ molar ratio of 4:1, ultrasonic treatment time for 5 minutes, and ultrasonic power of 60 W.

Key words: Oily sludge, total petroleum hydrocarbons, advanced oxidation processes,

Ultrasound, Fenton,

1. Introduction

Oily sludge is one of the major wastes generated from petroleum industry. It is formed when petroleum waste settles down to the bottom of the crude oil storage tank, or when the oily material is collected from oil-water separator, or even when heavy petroleum hydrocarbons (PHCs) accumulate after petroleum crudes are distilled in the refinery system (Bhattacharyya and Shekdar 2003; Kaushik et al, 2012). The oily sludge is a complex consisting of water, inorganic solid particles, and various petroleum hydrocarbons. It typically contains about 30-50% of oil, 30-50% of water, and 10-12% of solids by mass (Reynolds et al, 1993; Ramaswamy et al, 2007). The PHCs in oily sludge include a large amount of long-chain alkanes and alkenes as well as polycyclic aromatic hydrocarbons, coke, asphaltenes, and resins (Overcash and Pal 1979; Kaushik et al, 2012). The utility of these heavy hydrocarbons is very limited and uncontrolled dispose of them without any treatment could pose danger to the environment. Therefore, many technologies have been developed to treat oily sludge before its disposal.

The advanced oxidation processes (AOP) have received considerable attention in the past decades as potential effective methods for the destruction and degradation of recalcitrant materials (Gogate and Pandit, 2004). During the AOPs treatments, a sufficient amount of hydroxyl radicals can be generated through ultrasonic irradiation, ultraviolet radiation, photocatalysis, ozone, and/or Fenton/Fenton's like reactions (Torres et al., 2007a, b). The hydroxyl radicals are strong and non-selective oxidants which can oxidize various recalcitrant compounds due to the high oxidation potential ($E^0=2.8$) of such radicals (Al-Kdasi et al, 2004). The final products of oxidation reactions include carbon dioxide, short-chain organic acids, and inorganic ions, which are usually less toxic and favourable to
biodegradation (Adewuyi, 2005). The reactions of hydroxyl radicals with pollutants are essentially determined by the generation of radicals and the transfer of radicals to target compounds during various advanced oxidation processes (Mahamuni and Adewuyi, 2010). Generally, the reactions between hydroxyl radicals and pollutants are very fast, with the value of first order kinetic constant being observed in the range of 10^8 - 10^9 M⁻¹S⁻¹ even when extremely low radical concentration exists (i.e., about 10^{-12} to 10^{-10} M) (Esplugas et al, 2002).

Ultrasonic irradiation (US) and Fenton reagents are AOPs applied in a variety of fields. Ultrasound is regarded as a "clean" technology to remove contaminants without the generation of secondary pollutants (Pang et al, 2011), and it is easy to manage the process by the use of ultrasonic generators. Ultrasonic treatment can generate \cdot OH radicals due to the acoustic cavitation, which involves the formation and subsequent expansion of microbubbles under the periodic pressure variations (Mohajerani et al, 2010). When acoustic waves are induced, the micro-bubbles are formed and remain stable oscillation until they reach to a critical size and then violently collapse. With the sudden implosion of micro-bubbles, the temperature can rise up to 5000 K (Suslick et al, 1986) inside the residual bubbles. Thus chemical bonds between hydrogen and oxygen (H-O) in water molecules are broken inside the bubbles, causing the generation of hydroxyl radical (\cdot OH), hydrogen radical ($H \cdot$), hydroperoxyl radical ($HO_2 \cdot$) and hydrogen peroxide. The serial chain reactions under ultrasonic irradiation can be listed as following (Adewuyi 2005):

$n_2 O \rightarrow n_1 + O n_2 O \rightarrow n_2 + O n_2 $	$H_2O \rightarrow H \cdot + \cdot OH$		(1)
--	---------------------------------------	--	-----

 $HO \cdot + \cdot OH \rightarrow H_2O + O \cdot$ (2)

 $HO \cdot + H_2O \rightarrow H_2O_2 + O \cdot$ (3)

 $H \cdot + \cdot OH \rightarrow H_2O$ (4)

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$$\mathbf{H}^{\cdot} + \mathbf{H}^{\cdot} \to \mathbf{H}_2 \tag{5}$$

$$\mathbf{O} \cdot + \mathbf{O} \cdot \to \mathbf{O}_2 \tag{6}$$

$$HO^{\cdot} + \cdot OH \rightarrow H_2 + O_2 \tag{7}$$

$$HO \cdot (aq) + \cdot OH(aq) \rightarrow H_2O_2(aq)$$
(8)

$$\mathbf{H} \cdot + \mathbf{O}_2 \to \mathbf{H} \mathbf{O}_2 \cdot \tag{9}$$

$$\mathrm{HO}_{2}^{\,\cdot} + \mathrm{H}^{\,\cdot} \to \mathrm{H}_{2}\mathrm{O}_{2} \tag{10}$$

$$\mathrm{HO}_{2} \cdot + \mathrm{HO}_{2} \cdot \to \mathrm{H}_{2}\mathrm{O}_{2} + \mathrm{O}_{2} \tag{11}$$

$$O_2 \rightarrow 2 \cdot O$$
 (12)

$$\mathbf{O}_2 + \mathbf{O} \to \mathbf{O}_3 \tag{13}$$

The hot spot theory is usually used to explain the destruction and degradation of organic compounds in liquid. Two major reactions can take place due to acoustic cavitation, including: (a) pyrolytic or combustive reaction resulting from high temperature in the hot spot area, and (b) free radical attack between cavitation bubble and bulk liquid phase (Mohajerani et al, 2010). Many studies have reported the effect of ultrasonic irradiation on the removal of organic compounds. For example, Torres et al. (2007a) reported that the bisphenol-A concentration was under detection limit after treatment with ultrasonic cavitation (300 kHz and 80 W) for 90 minutes, and the oxidation intermediates were formed during ultrasonic treatment. Liang et al. (2007b) investigated the favourable ultrasonic frequency at the input power of 50 W and they found that the degradation of 4-chlorophenol was faster at higher frequency (i.e. 200 kHz) than at lower frequency (e.g., 28 kHz, 50 kHz). However, when used alone for the oxidation of chemicals, the sono-oxidation rates are relatively low (Liang et al, 2007a; Virkutyte et al, 2010).

Another advanced oxidation method is the use of Fenton 's reagents for degradation of compounds. As compared to other oxidants, Fenton's reagents (hydrogen peroxide and iron) are inexpensive and environmentally friendly (Pignatello et al, 2006). Because of its simplicity and strong oxidation power, the Fenton's process has been frequently used as an advanced process for the oxidation of various organic contaminants. During the chain reactions associated with Fenton's reagents (Eq. 14-18) (Pignatello et al, 2006), hydrogen peroxide serves as an oxidizing agent. A metal salt, usually ferrous (Fe²⁺) salt or metal oxide, generally works as a catalyst for the chain reactions. The ferric ion (Fe³⁺) can also be used as a catalyst for the generation of hydroxyl radicals, and the related reactions are usually called "Fenton-like" reactions. The generation of hydroxyl radicals during Fenton reactions can be described below:

$$Fe^{2^+} + H_2O_2 \longrightarrow Fe^{3^+} + \cdot OH + OH^-$$
(14)

$$Fe^{3+} + H_2O_2 \longrightarrow Fe-OOH^{2+} + H^+$$
 (15)

$$Fe-OOH^{2+} \longrightarrow Fe^{2+} + HO_2.$$
 (16)

$$HO_2 + HO_2 \rightarrow H_2O_2 \tag{17}$$

$$Fe^{3+} + HO_2 \cdot \longrightarrow Fe^{2+} + O_2 + OH^-$$
 (18)

During Fenton's reactions, a large amount of hydroxyl radicals are generated simultaneously if the hydrogen peroxide approaches to Fe^{2+} ion (Eq. 14). The same amount of Fe^{3+} is also produced along with the formation of free radicals, which later precipitates in the form of amorphous ferric oxyhydroxides (Fe-OOH), causing the increase of pH from strongly acidic to neutral, and generating an undesirable sludge. It has been reported that the favorable pH range to maximize oxidation in water is approximately 3.0-4.0 (Lu et al. 2010a).

For example, Pham et al (2011) reported a DEHP decrease of 31% in the slurry by Fenton pre-treatment with a pH of 4.3. The application of Fenton process has been widely reported in many studies which focused on the treatment of pollutants either in water or in soil. For instance, Sedlak and Andren (1991) investigated the ability of Fenton's reagent to degrade the chlorinated aromatic hydrocarbons. Masomboon et al (2010) examined the degradation of 2.6-dimethylaniline using Fenton process, and almost completely removal of 2,6-dimethylaniline could be obtained in 4 hours of electro-Fenton treatment with a pH value of 2, ferrous ion 1 mM, and hydrogen peroxide concentration of 20 mM. They also proposed a general pathway for the degradation of 2,6-dimenylaniline initiated by ·OH (Masomboon et al., 2010). Villa et al (2008) evaluated the effect of Fenton process on the degradation of DDT and diesel in soil, and they observed that 80% of diesel and 75% of DDT present in contaminated soil were removed after 64 hours of reaction. Along with the degradation of pollutants, 80% of organic matter naturally present in soil was also degraded during the Fenton process (Villa et al., 2008).

The oxidation efficiency of AOPs in treating chemical waste can be affected by two aspects, including the production rate of free radicals and the extent of the produced radicals contacting with contaminant molecules (Gogate and Pandit 2004). The application of individual AOPs might not be able to achieve high degradation efficiency and good economics. However, there is a similarity between the pollutant oxidation mechanisms among various AOPs, and the individual AOPs might be complementary to one other. As a result, it is expected that the combination of AOPs can achieve better results as compared to single AOP. In fact, the combination of ultrasonic irradiation and the use of oxidants (hydrogen peroxide, ozone, and Fenton/Fenton-like agents), has become popular recently since the hybrid method has been revealed more effective in degrading some recalcitrant compounds. For example, Neppolian et al (2004) reported that the degradation rate of para-chlorobenzoic acid (p-CBA) was 7.3 $\times 10^{-3}$ min⁻¹ under the combination process of ultrasound and Fenton-like reactions as compared to the value of 4.5×10^{-3} min⁻¹ under the process of only using 20 kHz ultrasound. Sun et al (2007) observed that the optimum concentration of Fe²⁺ for the decolorization of acid black 1 (AB1) solution was 0.025 mM under the combination of ultrasound and Fenton process when the concentration of H₂O₂ was 8.0 mM and the pH value was around 3.0. Virkutyte et al (2010) investigated the effect of sono-Fenton-like process on the degradation of naphthalene when the mineral iron in soil was used as the catalysts, and they observed that the optimum degradation efficiency of naphthalene reached 97% when 600 mg/L of H₂O₂ was added into the soil with initial naphthalene concentration of 200 mg/kg while the ultrasonic power was at 200 W and 400 W. The chain reactions in such Sono-Fenton system can be described by Eqs. 19-26 (Gogate and Pandit, 2004; Mohajerani et al, 2010). In those combined processes, hydroxyl radicals are generated by the decomposition of hydrogen peroxide, during which Fe²⁺ ions are converted to F^{3+} . Meanwhile, the application of ultrasonic energy could isolate Fe^{2+} from Fe-OOH²⁺ by the reaction of Eq. 26 (in which US stand for the application of ultrasonic irradiation), and the isolated Fe²⁺ in its turn could react with hydrogen peroxide to generate hydroxyl radicals (Eq.19). As a result, the iron catalysts could be regenerated during the process combining ultrasonic irradiation with Fenton reagents.

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + \cdot OH + OH^-$$
(19)

$$Fe^{3+} + H_2O_2 \longrightarrow Fe-OOH^{2+} + H^+$$
 (20)

 $HO \cdot + H_2O_2 \longrightarrow H_2O + HO_2 \cdot$ (21)

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$$Fe^{3+} + HO_2 \rightarrow Fe^{2+} + O_2 + H^+$$
 (22)

$$Fe^{2+} + OH \longrightarrow Fe^{3+} + OH^{-}$$
 (23)

$$\mathbf{F}^{2+} + \mathbf{HO}_2 \cdot + \mathbf{H}^+ \longrightarrow \mathbf{Fe}^{3+} + \mathbf{H}_2\mathbf{O}_2$$
 (24)

$$Fe^{3+} + HO_2 \cdot \longrightarrow Fe^{2+} + O_2 + OH^-$$
(25)

$$Fe-OOH^{2+} \longrightarrow Fe^{2+} + HO^2$$
 (26)

US

Given the advantages for the degradation of organic contaminants, AOPs have been widely studied to treat various wastes, especially when the pollutants are not amenable for biodegradation. Oily sludge is complex mixture of various petroleum hydrocarbons, many of which are hard to be destructed by the means of conventional remediation technologies. Therefore, it is reasonable to introduce AOPs into oily sludge treatment. However, the previous studies have mainly focused on the degradation of individual target contaminants, and only a few studies have extended the application of AOPs to treat contaminated systems containing a mixture of hazardous organic compounds.

The objective of this study is then to evaluate the degradation efficiency of the advanced oxidation processes for oily sludge treatment, and the ultrasonic irradiation (US), the Fenton reagents, and the combined US and Fenton process (US/Fenton) were examined. A variety of factors, including the initial sludge content, the molar ratio of hydrogen peroxide to Fe^{2+} , ultrasonic power, and ultrasonic treatment duration, were investigated for their effects on oxidation of petroleum hydrocarbons (PHCs) through the combined method (US/Fenton). The results would provide a sound basis for developing efficient and economically competitive methods for oily sludge treatment.

2. Materials and methods

2.1. Oily sludge and chemicals

The oily sludge was obtained from the bottom of a crude oil tank in an oil refinery plant in western Canada (Prince George). The sludge was kept at 4°C in a capped stainless-steel bucket. The sludge was very sticky and its viscosity was not available to measure. The summary of its characteristics is listed in Table 3.1. The concentration of petroleum hydrocarbon (PHCs) in sludge was analyzed based on the sample extraction process which will be described in Section 2.5 for solid sample extraction. The content of metal elements was measured with Inductively Coupled Plasma (ICP) in accordance with the method given in ASTM D5185 (2009), the water content was measured using the method ASTM D1744 (1992), and the solid content was calculated with the content of water and PHCs in sludge.

Hexadecane (nC16; >99% pure), nonadecane (nC19; >99% pure), tetratracon (nC34; >99% pure), and pentacontane (nC50) were purchased from Sigma and they were mixed in toluene as standard compounds for PHCs analysis and fractional analysis. The dichloromethane (DCM) (>99%, HPLC) was used for sample extraction. Cyclohexane (>99%, HPLC) was used with DCM to rinse columns packing with silica gel. Toluene (>99%, HPLC) was used as solvent of samples with PHCs for GC analysis. Silica gel (purchased from Sigma) was activated at 105 °C for 12 h and then used to clean up extraction solution, and anhydrous sodium sulfate dried at 400 °C for 12 was used to dewater extraction samples. FeSO₄· 7H₂O (purchased from Sigma) and H₂O₂ (30% w/w) solution were used as Fenton's reagents deployed either with ultrasound or without ultrasound.

2.2. Ultrasonic apparatus

The ultrasonic apparatus used in this experiment was a Misonix Sonicator 3000 generator with a titanium sonic probe and the diameter of the tip horn was 0.5 inch (Fig. 4.1). The frequency of ultrasound originated from this generator was constant at 20 kHz, but the power could be adjusted from 0 up to about 75 W. When ultrasonic irradiation was applied, the sonic probe was inserted into the sample and the tip horn was always kept under liquid during the treatment process.



Figure 4.1 Oxidation of oily sludge using ultrasound

2.3. Experiment on oxidation of PHCs in oily sludge by three different processes

Laboratory experiments were carried out to examine the effect of three different

advanced oxidation processes on oily sludge treatment, including ultrasonic irradiation alone, the Fenton's reaction alone, and the combination of ultrasound and Fenton's reaction.

In terms of the ultrasonic (US) process alone, 1 g of oily sludge was put into a 100 ml beaker with 25 ml deionized water. The ultrasonic probe was then placed into the sludge/water system for ultrasonic oxidation (Fig 4.1). The ultrasonic power was fixed at 60 W and the treatment duration time was set up as 1, 3, 5, and 8 minutes, respectively. After ultrasonic irradiation, the mixture in the beaker was transferred into a 50 ml tube for centrifugation to separate the solid from the liquid for further analysis of petroleum hydrocarbons within liquid and solid phases.



Figure 4.2 Fenton's reaction process for degradation of oily sludge

In terms of the Fenton's reaction (Fenton) alone, 1 g of sludge was put into a 100 ml beaker, and then 0.63 g of FeSO₄·7H₂O was added into the system (Fig 4.2). The volume of 68

hydrogen peroxide added to the beaker was set at 5, 10, 15, and 20 ml, respectively. The total aqueous volume in the beaker was consistent with that for ultrasonic treatment, and therefore the volume of DI water added varied according to the dosage of hydrogen peroxide solution consumed in samples during the Fenton process, and they were 20, 15, 10, and 5 ml, receptively. Due to the violent reaction, hydrogen peroxide was gradually added into the system until the appropriate volume by the use of 1 ml pipette. The mixture in the beaker was manually stirred during the Fenton process.



Figure 4.3 Samples after US/Fenton treatment

In terms of the combination of ultrasound and Fenton process (US/Fenton), the reaction was also conducted in a 100 ml beaker. 1 g of oil sludge was added into the beaker with 10 ml of deionized water and 0.63 g of $FeSO_4 \cdot 7H_2O$. The ultrasonic probe was then placed

under the liquid for ultrasonic treatment with the power of 60 W. 15 ml H_2O_2 solution was added into the system at the rate about 3 ml per minute during the US/Fenton treatment for 5 minute.

As shown in Fig 4.3, the "iron sludge" can be formed due to the reaction of Fenton's reagents, either through the Fenton process alone or through the combined process of ultrasound and Fenton reaction. Thus, the petroleum hydrocarbons (PHCs) remained after treatment would be distributed among both the aqueous phase and solid phases (e.g., "iron sludge" and solid particles in oily sludge). Two distinctive extraction procedures were conducted to extract PHCs from both the liquid and solid phases. Since the mass of "iron sludge" varies from sample to sample, it is difficult to determine the concentration of PHCs in the solid phase. Accordingly, the reduction in the total mass of PHCs in a sample after treatment was used to analyze the efficiency of the treatment processes based on Eqs. (1) and (2).

Mass of PHCs in one sample (mg) =

 $Reduction Rate = \frac{Mass of PHCs before treamtent (mg) - Mass of PHCs after treatment(mg)}{Mass of PHCs before treatment(mg)} \times 100\%$ (2)

2.4. Experiment on factors affecting the combined process (US/Fenton)

The impacts of different factors on the combined process of ultrasound and Fenton's reaction were also investigated. These factors include the initial oily sludge content (sludge content), the molar ratio of H_2O_2 to Fe^{2+} (H_2O_2/Fe^{2+}), the ultrasonic power, and the ultrasonic 70

treatment duration. Each factor was examined at 3 levels. The details of experimental factors and their levels were listed on Table 4.1. The Taguchi orthogonal experimental design method was used to arrange the experiments, and the L27 array was arranged using the software Minitab 16 as shown in Table 4.2. This experimental design method can allow for the examination of the main effect of each factor and the interaction effect between the sludge content and the molar ratio of H_2O_2/Fe^{2+} , between the sludge content and US time, and between the molar ratio of H_2O_2/Fe^{2+} and US time.

Factors	Levels						
-	1	2	3				
(A) Initial oil sludge content (sludge content) (g/L)	20	40	60				
(B) Molar ratio of H_2O_2 to Fe^{2+} (H_2O_2 /Fe ²⁺)	4:1	10:1	50:1				
(C) Ultrasonic power (US power) (W)	20	40	60				
(D) Ultrasonic treatment time (US time) (min)	1	3	5				

 Table 4.1 Experiment factors and their three levels

There were 27 experimental runs according to the design, and each run was replicated for two times. The volume of H_2O_2 used in the experiment was set as a constant (i.e. 15 ml) for all of the 27 experimental treatments. The experimental operating procedure for each run was similar to that as described in section 2.3, including (a) adding different amount of oily sludge (e.g. 0.5 g, 1.0 g, 1.5 g) into a 100 ml beaker with 10 ml of de-ionized water, and producing a total liquid volume of 25 ml after adding 15 ml of H_2O_2 solution (the initial sludge content listed in Table 4.1 was determined by dividing the mass of oily sludge by the volume of 25 ml), (b) different amount of FeSO₄·7H₂O was used to adjust the molar ratio of H_2O_2/Fe^{2+} to 4:1, 10:1, and 50:1, respectively, and (c) after starting the ultrasonic treatment, hydrogen peroxide was added into the beaker at the rate of 15 ml, 5 ml, and 3 ml per minute for the 1-minute, 3-minute, and 5-minute treatment, respectively.

Europin antal tast #	Sludge content	H_2O_2 / Fe^{2+}	US time	US power
Experimental test #	(g/L)	(mole/mole)	(minute)	(W)
L 1	20	4:1	1	20
L 2	20	4:1	3	40
L 3	20	4:1	5	60
L 4	20	10:1	1	40
L 5	20	10:1	3	60
L 6	20	10:1	5	20
L 7	20	50:1	1	60
L 8	20	50:1	3	20
L 9	20	50:1	5	40
L 10	40	4:1	1	40
L 11	40	4:1	3	60
L 12	40	4:1	5	20
L 13	40	10:1	1	60
L 14	40	10:1	3	20
L 15	40	10:1	5	40
L 16	40	50:1	1	20
L 17	40	50:1	3	40
L 18	40	50:1	5	60
L 19	60	4:1	1	60
L 20	60	4:1	3	20
L 21	60	4:1	5	40
L 22	60	10:1	1	20
L 23	60	10:1	3	40
L 24	60	10:1	5	60
L 25	60	50:1	1	40
L 26	60	50:1	3	60
L 27	60	50:1	5	20

 Table 4.2
 L27 array orthogonal experimental design

2.5. Sample extraction after advanced oxidation processes

The sample in the beaker after oxidation treatment was transferred into a 50 ml tube for centrifugation for 30 min at 5000 rpm. After centrifugation, the supernatant (about 25 ml)

was transferred into a separating funnel for liquid extraction, and the solids residue left at the bottom of the centrifugation tube was used to extract PHCs in the solids.

In terms of the liquid-liquid extraction, 15 ml of DCM was added into the separating funnel containing about 25 ml of supernatant (Fig 4.4), and the funnel was manually shaken for several minutes (SW-846 EPA, 1993). After equilibrium for 30 minutes, the upper layer in the funnel was collected into a glass tube. Another 15 ml of DCM was then added to the separating funnel for another liquid-liquid extraction, and such extraction was conducted for three times. All of the extraction solution was collected into the glass tube for further cleanup.



Figure 4.4 Liquid-liquid extraction

In terms of the solids extraction, 10 ml of DCM was added into the 50 ml centrifugation tube containing solids at the bottom. The tube was placed on a mechanical shaker for 30 minutes of shaking at 120 rpm (Fig. 4.5), and was then sent for centrifugation at 5000 rpm for 15 minutes. After centrifugation, the liquid was transferred into a glass tube. Another 10 ml of DCM was added into the centrifugation tube for a second extraction, and such extraction was conducted for three times. All of the extraction solution was collected into the glass tube for further cleanup.

To analyze the initial PHCs concentration in the oily sludge before any treatment, 25ml DI water was added into a tube with 1g oily sludge and the tube was centrifuged for 30minutes at 5000rpm. And then similar liquid extraction and solids extraction procedures were implemented.



Figure 4.5 Mechanical shaking for the extraction of PHCs from solids

The extraction solution was sent to a silica gel column (Fig. 4.6) for cleanup to remove moisture, particulate, and unwanted polar organic compounds (CCME, 2000). The column was packed with silica gel and anhydrous sodium sulfate and rinsed with 20 ml of solvent (1:1 cyclohexane/DCM) before use. After the extraction solution passed through, another 20-30 ml of solvent (1:1 cyclohexane/DCM) was poured to elute the column. A round flask was used to collect extraction at the rear of the column. The cleaned extraction was then reduced to about 1 ml by using a rotary evaporator, and toluene was used as solvent to transfer the concentrated extraction into a 15-ml vial bringing to a final volume of 12 ml. 2 ml of this extraction solution was then transferred into a 2-ml vial for GC analysis.



Figure 4.6 Extraction solution cleanup using silica gel column

2.6. PHCs analysis

2 ml of the final extraction solution was used for PHCs analysis and TPH fraction analysis using a Varian CP-3800 Gas Chromatograph with flame ionization (GC-FID) (Fig 3.9 in Chapter 3). The external standard method was used for the analysis. Decane (C10), hexadecane (C16), tetratriacontane (C34), and pentacontane (C50) were used as external standards to determine the concentration of PHCs and PHC fractions (CCME, 2001), where Fraction 1 (F1), Fraction 2 (F2), Fraction 3 (F3) and Fraction 4 (F4) is defined as the group of petroleum hydrocarbons from C6 to C10, C10 to C16, C16 to C34, and C34 to C50, respectively. The GC analysis conditions were set up as: ZB-capillary column (Phenomenex Torrance, CA) with 30 m × 0.25 mm ID (inner diameter) and 0.25-µm film thickness; inject volume of 1 µL; injector and detector (F1D) temperatures at 320 °C; carrier gas (helium) at a constant flow rate of 1.5 mL/min during analysis. The split-less injection mode was performed on the 1079 PTV injector and after 0.7 min the split mode was activated at split ratio of 10:1. The capillary column temperature program was initially held at 50°C for 1 min, then ramped at 15.0 °C/min to 110 °C and further increased at 10.0 °C/min to 300 °C and then was held for 11 min. The total running time for a sample was 45 minutes.

3. Results and discussions

3.1. Comparison of methods

3.1.1. TPH reduction using ultrasonic irradiation alone

Table 4.3 and Fig. 4.7 present the results of TPH reduction in oily sludge using ultrasonic irradiation alone. The initial TPH mass in the system with 1 g of oily sludge was 431.5 ± 11.4 mg (i.e. the total mass of PHCs measured from both liquid and solid phases). After ultrasonic treatment alone, the TPH mass remained in the system ranged from 334.0 ± 8.6 mg to

363.8±22.6 mg, with the highest TPH reduction rate being 22.6% after US treatment for 5 minutes (Table 4.3). The TPH reduction rate was slightly increased to 22.6% from less than 20% when the ultrasonic treatment time was prolonged from 1 minute to 5 minutes. However, longer treatment than 5 minutes in this study did not improve the ultrasonic treatment performance, and the TPH reduction rate was slightly decreased to 16.3% after US treatment for 8 minutes.

Ultrasonic treatment duration (min)1358TPH reduction rate18.0%15.7%22.6%16.3%

 Table 4.3 TPH reduction in oily sludge through US treatment alone



Figure 4.7 Remaining TPH mass in samples after different ultrasonic treatment durations (error bar stands for standard deviation; the value at the time of 0 stands for the initial TPH mass)

The performance of ultrasonic irradiation on degradation of organic hydrocarbons in liquid systems can be affected by the cavitation phenomena (Liang et al, 2007 a). The thermal cracking due to the collapse of cavitation bubbles and the free radicle reactions initiated by hydroxyl radicals at the interfacial region and in bulk liquid are the two major mechanisms for the degradation of organic compounds via ultrasonic irradiation. The thermal cracking of petroleum hydrocarbons under ultrasonic irradiation has been reported by many researchers based on their studies in upgrading heavy gas oil and vacuum residue (Gopinath et al, 2006; Kaushik et al, 2012). The cavitation bubbles filled with vapor and/or gas formed via ultrasound can violently collapse to form "hot spots" in the corresponding region, where the temperature and pressure can reach up to 5000 K and several hundred atmospheres (Suslick et al, 1986). The cumulative energy generated by these bubbles is extremely high, and thus the thermal scission of carbon-carbon (C-C) bonds could occur in heavy petroleum hydrocarbon molecules. And also some organic compounds with higher vapor pressure could directly decompose inside the cavitation bubbles due to thermal pyrolysis (Liang et al, 2007 a; Pang et al, 2011).

Meanwhile, the hydroxyl radicals (OH·) are formed inside the cavitation bubbles by water pyrolysis when these bubbles collapse intensely. These radicals can then be transferred to the bubble interface and bulk liquid and react with hydrophobic organic compounds present in bulk liquid (Liang et al 2007a). Therefore, the free-radical reactions caused by the generation of hydroxyl radicals also contribute to the reduction of petroleum hydrocarbons under ultrasound treatment alone. The petroleum hydrocarbons in oily sludge usually contain a large number of carbon atoms, and they have low vapor pressure and low solubility in water. Most of such heavy petroleum hydrocarbons are hardly able to permeate into the cavitation bubbles. Thus, the free radical reactions can occur near the interface of cavitation bubbles and more often in the bulk liquid where the heavy hydrocarbon compounds are largely present. Moreover, it has been reported that the presence of solid particles in liquid can affect the collapse of cavitation bubbles and generate high-speed microjets of liquid through the cavity (Suslik 1990). In this study, solid particles present in oily sludge produced a heterogeneous system for ultrasound treatment. The liquid microjects resulting from ultrasonic irradiation in such system could enhance the transport of hydroxyl radicals into the interface region and the bulk liquid (Liang et al, 2007 b). This would facilitate the contact of hydroxyl radicals with the petroleum hydrocarbons. In addition, the ultrasonic irradiation could promote the desorption of petroleum hydrocarbons from the solid phase and their subsequent dispersion into the liquid phase (Gaikwad et al, 2008). The dispersion of petroleum hydrocarbons molecules with the free hydroxyl radicals, and thus facilitate the oxidation reactions.

3.1.2 TPH reduction through Fenton's reaction process

Table 4.4 and Fig. 4.8 present the TPH reduction results under the Fenton process alone. After Fenton's oxidation process alone, the remaining TPH mass in the sample systems (i.e. the total PHCs mass measured from both liquid phase and solid phase) ranged from 372.7 ± 11.9 mg to 379.6 ± 36.4 mg, as compared to the initial TPH mass of 431.5 ± 11.4 mg. It can be found that the relatively higher TPH reduction (i.e. 13.8%) was achieved with the H₂O₂ dosage of 15 ml and 20 ml, equivalent to 600 ml/L and 800 ml/L of 30% (w/w) hydrogen peroxide solution in the system. The amount of H₂O₂ added into the system was much more excessive than the amount needed for the degradation of all petroleum hydrocarbons. For example, if 5 ml of H₂O₂ was added, the number of moles of hydrogen peroxide was about 50 mmol. The initial TPH mass in 1 g of oily sludge was about 0.43g ($\pm 0.01g$), and thus the moles of carbon atoms in hydrocarbons were about 29 mmol (i.e. assuming that this oily sludge is made of saturated hydrocarbons and that the mass of carbon element counts for about 80% of the total mass of PHCs), which was less than the moles of H_2O_2 present in system. However, further increase in the H_2O_2 dosage to 10 ml, 15 ml, and even 20 ml, did not result in any further improvement in oxidation of petroleum hydrocarbons (Fig.4.8).

H₂O₂ dosage (ml) 5 10 15 20 TPH reduction rate 12.0% 13.8% 13.2% 13.8% 400 Mass of PHCs mg) 300 200 100 0 0 5 10 15 20 dosage of hydrogen peroxide (ml)

Table 4.4 TPH reduction in samples under Fenton process alone

Figure 4.8 Remaining TPH mass in samples after Fenton process alone (error bar stands for standard deviation; the value at the dosage of 0 stands for the initial TPH mass)

Fenton's reactions have been reported for the oxidization of organic contaminants in water and soil, and the oxidation mechanism was demonstrated in the sequence of reactions (Eqs. 14 to 18). The free hydroxyl radicals (•OH) have been proved to be essential for the degradation of organic pollutants in the course of Fenton's process. These free radicals are

strong electrophilic and nonselective oxidizing species, with an oxidation potential (E^0) of 2.8. The pathways of petroleum hydrocarbon destruction can be described below (Buxton et al., 1988; Von Sonntag and Schuchmann, 1997):

$$\cdot OH + R - H \longrightarrow R \cdot + H_2 O \tag{27}$$

$$\cdot OH + C = C \longrightarrow HO - C - C \cdot$$
 (28)

$$\cdot OH + \bigcirc \longrightarrow \bigotimes_{OH} \longrightarrow_{H} \longrightarrow Further reactions$$
(29)

where R represents carbon chain, and R stands for the intermediate product of carbon-centered radicals. The •OH radicals react with organic compounds by abstracting H from the C-H, N-H, or O-H bonds (Eq.27), adding to C=C bonds (Eq.28), or adding to the aromatic rings (Eq.29). In this study, the oily sludge contains a large amount of petroleum hydrocarbons, including straight-chain alkanes, branched alkanes, alkenes, and aromatic compounds. These hydrocarbons can react with •OH radicals in accordance with reactions (Eqs. 27- 29) during the Fenton's process.

$$\mathbf{R} \cdot + \mathbf{O}_2 \to \mathbf{R} - \mathbf{H}^+ + \mathbf{HO} \cdot \tag{30}$$

$$\mathbf{R} \cdot + \mathbf{O}_2 \to \mathbf{R} - \mathbf{OO} \cdot \to \to \mathbf{R} - \mathbf{O} \cdot \tag{31}$$

$$\mathbf{R}^{\cdot} + \cdot \mathbf{OH} \rightarrow \mathbf{ROH}$$
 (32)

$$2H_2O_2 \rightarrow O_2 + 2H_2O \tag{33}$$

Sequentially, the intermediate products ($R \cdot$) can either react with O_2 to generate peroxyl radicals (R-OO \cdot) when air is present in the liquid or react with \cdot OH to form alcohols (ROH) as the oxidation products (Adewuyi, 2005). The reactions of carbon-centered radicals are

described in Eqs.30-32. In addition, the net reaction of Fenton's process is the conversion of H_2O_2 into O_2 and water with iron as catalyst (Eq.33) (Pignatello et al, 2006). The decomposition of H_2O_2 could also provide extra O_2 for the oxidation of hydrocarbons.

In the termination step, the intermediate radicals of R·, R–OO·, and R–O· could couple or disproportion with each other, leading to the decomposition of hydrocarbons and the generation of various by-products (Von Sonntag and Schuchmann, 1997; Stark, et al 2011). Meanwhile, alcohols formed in reaction (Eq. 32) could further react with ·OH to form ketones, esters, and finally lead to carboxylic acids (Benner, et al, 2000). Many studies in the remediation of petroleum contamination confirmed the occurrence of various oxidation products after Fenton or Fenton-like treatment. For instance, Lu et al (2010b) investigated the use of Fenton-like oxidation to treat soil contaminated with petroleum hydrocarbons. They reported that the concentration of hydrocarbons was decreased in soil. However, residues in soil after Fenton treatment contained higher proportion of more condensed compounds $C_nH_{2n+z}O_2$ with the z value of much less than 0, indicating the presence of fused-ring structure, as compared with compounds initially present in contaminated soil (Lu et al., 2010b).

As discussed above, although there are advantages of the free-radical oxidation of petroleum hydrocarbons in the course of Fenton process alone, the TPH reduction in oily sludge through Fenton's oxidation alone in this study was relatively low. This may be explained by the inadequate contact of hydroxyl radicals with petroleum hydrocarbons. A large amount of hydroxyl radicals were formed in the aqueous phase under Fenton's reaction process, while the majority of petroleum hydrocarbons in oily sludge were present in non-aqueous form or attached into solid particles. In such case, it was difficult for these

radicals to contact substantial petroleum hydrocarbon molecules for achieving high degree of PHC oxidation. Alternative methods such as ultrasonic irradiation may be required to improve the desportion and dispersion of oil into the aqueous phase. Moreover, not all the hydroxyl radicals take part in in the oxidation of PHCs, and some amount of them could be consumed by reacting with H_2O_2 molecules and Fe²⁺ ions, in which case H_2O_2 and Fe²⁺ serve as radical scavengers (Eqs. 34 and 35).

$$HO \cdot + H_2O_2 \rightarrow HO_2 \cdot + H_2O \tag{33}$$

$$HO \cdot + Fe^{2+} \rightarrow Fe^{3+} + OH^{-}$$
(34)

In summary, the results of TPH oxidation by Fenton's reaction process indicated that the petroleum hydrocarbons in oily sludge could be oxidized by the free radicals to some extent, and the Fenton oxidation was considered as a relatively low effective approach for oily sludge treatment with regard to its TPH reduction rate. However, the Fenton' reaction process is still a very attractive option to treat many organic compounds, especially for the resistant compounds with complex structures. When comparing with other oxidation processes, substantial hydroxyl radical are generated through Fenton's reaction process, serving as strong and nonselective oxidants. The Fenton's reagents (e.g., hydrogen peroxide and iron) are relatively inexpensive; the process is easily operated and does not require any energy supply. Therefore, it is reasonable to combine conventional Fenton's reaction process with other technologies to improve the radical-leading oxidation and/or enhance the cycle of Fe²⁺ for further generation of free radicals in the process.

3.1.3 TPH reduction through the combination of ultrasound and Fenton's reaction process (US/Fenton)

Laboratory experiments were carried out to investigate the effect of the combination of ultrasonic irradiation and Fenton's reaction (US/Fenton) on the TPH reduction in oily sludge. 5 minutes of ultrasonic treatment time and the hydrogen peroxide dosage of 15 ml were selected for the US/Fenton process based on the TPH reduction results of each method (i. e. US alone and Fenton alone). In Fig 4.9 is presented the remaining TPH mass in oily sludge samples treated by three oxidation processes (i. e. US alone, Fenton alone, and US/Fenton), and TPH reduction rate for samples is listed in Fig. 4.10. TPH mass (measured from both the liquid and the solid phases) in the sample after US/Fenton treatment was 245.4±23.8 mg, with 43.1% TPH reduction (Fig 4.10). This reduction of 43.1% in TPH by US/Fenton is greater than the sum of reduction rate by US alone for 5 minutes and Fenton's reaction alone with H_2O_2 dosage of 15 ml. This indicates the emergence of some synergistic effect when combining US with Fenton for the degradation of petroleum hydrocarbons in oily sludge.

Moreover, the reduction in different PHC fractions was shown in Fig. 4.10. The reduction in Fraction 2 was less than 30% by US alone and by Fenton alone (i. e. 23.7% and 29.6%, respectively); the reduction of 20.6% in Fraction 3 (F3) was observed for ultrasonic treatment alone and only 8.9% for Fenton's reaction treatment alone; Fraction 4 (F4) was reduced by 36.9% for ultrasonic treatment alone and 12.7% for Fenton's reaction treatment alone. However, during US/Fenton process the highest reduction of 56.7% was observed for Fraction 2, followed by 46.5% for F4 and 39.1% for F3.



Figure 4.9 TPH mass remained in samples after three different methods (US alone for 5 minutes; Fenton alone with 15 ml H₂O₂; US/Fenton with 5 minutes of ultrasound and 15 ml of H₂O₂) (Error bar stands for standard deviation)



Figure 4.10 TPH and fraction reduction via three different processes (US alone for 5 minutes; Fenton alone with 15 ml H₂O₂; US/Fenton with 5 minutes of ultrasound and 15 ml of H₂O₂) (error bars stand for standard deviation)

As mentioned above, the use of Fenton' reagents alone cannot achieve high degree of petroleum hydrocarbon oxidation due to the inefficient contact of hydroxyl radicals in the 85

aqueous phase with hydrocarbon molecules in the oily sludge. However, the ultrasonic irradiation would significantly improve the desorption and dispersion of hydrocarbons into the aqueous phase. As a result, combining US and Fenton's reaction process would provide with a large amount of hydroxyl radicals in situ and at the same time enhance the contact of substantial radicals with hydrocarbons in the oily sludge, thereby increasing the oxidation efficiency. Another apparent benefit of the combined process was to improve the recycling of iron catalyst. As discussed before, ultrasonic irradiation could isolate Fe²⁺ from the complex Fe-OOH formed through serial reactions catalyzed by Fe²⁺, and the isolated Fe²⁺ can in turn react with hydrogen peroxide to generate more free radicals for oxidization of petroleum hydrocarbons. At the same time, the application of ultrasound during Fenton's reaction process might help reduce the formation of "iron sludge".

In addition, the heterogeneous system might affect the TPH reduction under the combined process. The system under the US/Fenton process was heterogeneous due to the presence of solid particles in oily sludge. The liquid-solid interface would provide extra active area for the reaction of hydroxyl radicals with the absorbed organic compounds. A large amount of hydrocarbons were attached on the solid surface and the radicals were largely generated in the bulk liquid. However, the microjets resulting from ultrasonic irradiation in such heterogeneous system could deliver the radicals from bulk liquid to the interface region where considerable hydrocarbons are present, thus enhancing the mass transfer in the system and improving the contact of radicals with the target hydrocarbons. Moreover, as shown in Table 3.1, the oily sludge contains some metals such as Fe and Cu. These metals might be present at their oxidant state in solid particles. The solid particles containing metals could be regarded as extra catalyst for the generation of hydroxyl radicals

if the hydrogen peroxide reached onto the solid surface.

Furthermore, the cavitation of ultrasound might increases the local temperature and pressure and make it more convenient for the oxidation of hydrocarbons under the combined process. When the ultrasonic irradiation was applied in the system containing petroleum hydrocarbons, the energy released due to collapse of cavitation bubbles can cause the cleavage of carbon-carbon bonds in hydrocarbon molecules, producing alkyl radicals. Meanwhile, reactions related to Fenton's process can provide with a large amount of hydroxyl radicals, which attack the hydrogen in hydrocarbon molecules to form alkyl radicals. Therefore, during the combined process, the generation of alkyl radicals would be improved by the thermal cleavage due to ultrasound and by the attacking of hydrogen radicals associated with Fenton's reactions. Consequently, more alkyl radicals are formed under combined process than that under either individual process, and these unstable intermediate radicals would either react with each other or with hydroxyl radicals to form more stable oxidation products. Thus the oxidation of hydrocarbons would benefit from the combination of ultrasound and Fenton process.

In terms of the degradation of petroleum hydrocarbon fractions, the decomposition of long-chain hydrocarbons (i.e. Fraction 4) were more significant than the other two groups under US treatment alone (Fig 4.10). This indicates that the release of ultrasonic energy can provide more convenient conditions for the cleavage of heavy hydrocarbons. Meanwhile, as for the Fenton process alone (Fig 4.10), the effect of Fenton's reactions on the degradation of Fraction 2 (F2) was relatively more significant compared with degradation of F3 and F4, indicating that the lighter hydrocarbons are more easily decomposed under the attack of free radicals. Combining US and Fenton process, therefore, appears to improve the TPH

reduction in samples by enhancing the degradation of petroleum hydrocarbon in all fractions (i.e. F2, F3, and F4). However, as for each of the three treatments, the reduction rate for Fraction 3 is less than that for Fraction 4. This might be attributed to the accumulation into Fraction 3 of intermediate products resulting from the decomposition of heavy PHCs in Fraction 4. Some by-products from the degradation of heavy hydrocarbons might not be easily for further decomposition or even complete mineralization.

In summary, with the combination of ultrasonic irradiation with Fenton's reaction, the degradation of hydrocarbons in oily sludge was improved in comparison to US alone and Fenton process alone and thus the combined US/Fenton process was proved to be a reliable and more effective method to treat oily sludge.

3.1.4 Petroleum hydrocarbons distribution in samples and fractional analysis after oxidation processes

The distribution of petroleum hydrocarbons in the liquid and the solid phases after treatments was also investigated and Table 4.5 lists the results. Due to the high viscosity of oily sludge, most of the petroleum hydrocarbons are present in the form of non-aqueous phase or adsorbed onto the solid particles. As a result, the TPH mass in aqueous phase was very low before any treatment (i.e. 31.4 mg out of 431.5 mg TPH in the initial samples with 1g oily sludge and 25 ml water). However, the TPH mass in the aqueous phase was increased (i.e. 65.3 mg) after US treatment alone for 5 minutes, which indicated the emulsification effect of ultrasonic irradiation for the dispersion of hydrophilic compounds. Furthermore, pH was decreased to 1.9 after US/Fenton process and some iron sludge was formed (Fig 4.3). The petroleum hydrocarbons remained in the aqueous phase might need further treatment

such as bioremediation. The oxidation products, such as carboxyl compounds and other oxidants, might be more amenable for biodegradation by microorganisms. However, the value of pH for samples in this study was too low (about 2 for US/Fenton). The strong acidic condition is not in favor of microbial activity for biodegradation. Therefore, pH should be adjusted if bioremediation technologies would be subsequently applied for further contamination elimination.

Table 4.5 TPH content in aqueous and solid phases of samples* before and after advanced oxidation processes

		Oxidation proces	SS	
	Fenton alone	US alone (5 minutes of	US/Fenton (15 ml H ₂ O ₂ + 5minutes	Initial
	$(15 \text{ ml of } H_2O_2)$	ultrasound)	of ultrasound)	
TPH in aqueous phase (mg)	49.7	65.3	48.3	31.4
TPH in solid phase (mg)	322.0	268.7	197.2	400.1
TPH (aqueous + solid)	371.7	334.0	245.5	431.5
рН	2.3	5.0	1.9	

*1g oily sludge in each sample was treated with different processes and the volume of liquid was assumed 25 ml for all samples.



Figure 4.11 Fractional distribution of petroleum hydrocarbons in samples before and after three different processes (US alone for 5 minutes; Fenton alone with 15 ml H₂O₂; US/Fenton with 5 minutes of ultrasound and 15 ml of H₂O₂)

Fig 4.11 presents the distribution of petroleum hydrocarbons in different fractions in samples before and after three oxidation processes: US, Fenton, and US/Fenton. The samples with the highest TPH reduction rate after each process were chosen for comparison. It can be found that there was difference in the distribution of petroleum hydrocarbons in three fractions after oxidation treatments. For example, after the US/Fenton treatment, the percentage of Fraction 2 was decreased to 17.0% from 21.7% and to 8.3% from 8.8% for Fraction 4, while the percentage of Fraction 3 increased to 74.7% from 69.5%. Similar patterns were observed in the samples after Fenton's treatment. Meanwhile, for samples treated with US alone, the percentage of F2 was 22.0% compared with the value 21.7% in the original oil sludge samples, the percentage of F3 increased to 71.4% from 69.5%, while the percentage of F4 decreased to 6.6%. The observation of increase in the percentage of F3 in all the samples implied the accumulation of by-products due to the oxidation/decomposition of F4 hydrocarbons. However, the structures of petroleum hydrocarbons after oxidation treatments would be different from those in the oily sludge. The carboxyl acid might be formed as the main by-products. The alkanes and branched alkanes would also be oxidized into ketones and alcohols with less carbon numbers. Further study should be conducted to investigate the composition of oxidation products in detail.

3.2. Degradation of petroleum hydrocarbons after different treatments through US/Fenton process

The TPH degradation results of individual oxidation processes (i. e. US alone, Fenton alone, and US/Fenton) indicated the synergistic effect on the oxidation of oily sludge by combining ultrasonic irradiation with Fenton's reaction. It is thus of importance to investigate the effect of different factors on the combined process (US/Fenton). The orthogonal experiments were further carried out in this study to examine the impact of four factors on the degradation of petroleum hydrocarbons through the combined US/Fenton treatment.

Table 4.6 lists the mass of TPH and the mass of petroleum hydrocarbons (PHCs) in different fractions (F2, F3, and F4) in samples before and after US/Fenton treatment for each orthogonal experimental run, and Table 4.7 lists the degradation rate of TPH and PHCs in different fractions for each run. The S/N ratio was also listed in Table 4.7. It can be found from Table 4.6 that the TPH mass in the samples (measured from both liquid phase and solid phase) was decreased to the range of 22.6 ± 3.5 mg/L to 91.6 ± 3.8 mg from the initial TPH mass of 170.2±17.2 mg (with 0.5 g of oily sludge initially added in the sample and sludge content 20g/L) for treatments L1 to L9. The TPH degradation rate was in the range of 51.9% to 88.1% (Table 4.7). When 1 g of oily sludge was added to the system (sludge content 40 g/L) for treatments L10 to L18, the initial TPH mass was increased to 444.6 \pm 20.7 mg. The TPH mass remained in the samples dropped to the range of 71.7 ± 13.9 mg to 256.6 ± 32.2 mg, and the TPH degradation rate ranged from 42.3% to 83.9%. The largest initial TPH mass (i.e. 638.5±22.6 mg) occurred for treatments L19 to L27 when 1.5 g of oily sludge was added in samples (sludge content 60 g/L). The remaining TPH mass in samples of these experimental runs ranged from 119.5 ± 2.5 mg to 408.5 ± 24.4 mg/L, and the corresponding TPH degradation rate ranged from 36.0% to 81.3%. Among all 27 runs, the best TPH reduction rate 88.1% was observed for treatment L3 when sludge content was set at 20 g/L, the ratio of H_2O_2 to Fe^{2+} at 4:1, US time for 5 minutes and US power set at 60W.

	Initial mass of TPH and PHCs in different fractions (mg)									Aass of PH	ICs in dif	ferent frac treatmen	tions after nts (mg)	different US	/Fenton	
	ТРН	SD for TPH	F2	SD for F2	F3	SD for F3	F4	SD for F4	TPH	SD for TPH	F2	SD for F2	F3	SD for F3	F4	SD for F4
LI	170.2	17.2	38.4	4.2	128.4	16.3	3.4	0.6	90.4	9.3	16.5	2.2	70.4	7.5	3.5	0.4
L2									23.2	1.1	2.6	0.2	20.0	1.2	0.6	0.2
L3									22.6	3.5	2.4	0.1	19.8	3.5	0.4	0.1
L4									47.9	6.7	7.6	0.9	38.1	5.7	2.2	0.1
L5									37.8	5.3	4.9	1.1	30.3	4.7	2.6	0.5
L6									52.4	5.1	8.4	2.0	42.5	3.5	1.5	0.1
L7									91.6	3.8	13.2	0.5	75.6	2.7	2.8	0.6
L8									65.9	12.67	11.1	3.4	53.0	9.4	1.8	0.2
L9									68.1	0.4	10.8	0.2	55.6	0.3	1.7	0.1
L10	444.6	20.7	100.1	4.2	337.9	16.3	6.59	2.3	192.5	3.6	44.1	1.7	144.7	2.7	3.7	0.8
LH									71.7	13.9	12.2	2.9	57.7	10.8	1.8	0.4
L12									238.9	35.8	39.4	7.9	195.6	27.2	3.9	0.7
L13									215.0	10.1	35.5	1.8	176.8	90.9	2.7	0.3
L14									248.4	15.2	44.6	0.2	200.5	91.3	3.3	0.1
L15									139.3	24.9	21.9	5.5	114.3	18.5	3.1	0.9
L16									256.6	32.2	48.2	1.0	204.3	33.3	4.1	0.1
L17									200.7	30.2	36.3	3.2	160.8	33.0	3.6	0.4
L18									161.1	8.3	29.5	4.7	128.3	12.9	3.3	0.0
L19	638.5	22.6	161.2	7.2	463.1	27.9	14.2	1.8	382.9	20.7	93.9	5.2	281.7	15.4	7.3	0.1
L20									224.3	31.3	41.1	4.9	179.0	26.5	4.2	0.2
L21									119.5	2.5	23.6	1.2	91.3	0.2	4.6	1.1
L22									398.0	16.9	91.3	5.2	298.2	12.6	8.5	0.9
L23									339.6	20.6	56.8	0.5	272.6	18.6	10.2	2.4
L24									212.4	5.7	40.8	1.7	165.8	3.8	5.8	0.2
L25									348.4	6.2	80.4	3.1	260.1	2.3	7.9	0.9
L26									348.2	9.9	78.1	1.2	261.6	8.9	8.5	0.1
L27									408.5	24.4	89.9	3.7	308.7	18.8	9.9	1.8

Table 4.6 Remaining TPH mass in samples after different US/Fenton treatments

]	Degradati	on rate (%	ó)		S/N ratio					
	Sludge content (g/L)	Ratio of H_2O_2 to Fe^{2+}	US time(min)	US power (W)	ТРН	F2	F3	F4	ТРН	F2	F3	F4
Ll	20	4	1	20	52.6	52.9	53.6	11.8	21.44	34.47	34.58	21.44
L2	20	4	3	40	87.8	92.5	86.6	84.5	38.54	39.32	38.75	38.54
L3	20	4	5	60 40	88.1	93.1	86.9	90.1	39.09	39.38	38.78	39.09
L4	20	10	1	40	/4.8	/8.1	74.9	45.8	33.22	37.85	37.49	33.22
L5	20	10	3	60	80.2	86.0	80.0	36.2	31.17	38.69	38.06	31.17
1.0	20	10	5	20	12.5	/5.8	/1.8	70.9	37.01	37.39	37.12	37.01
L7	20	50	l	60	51.9	62.2	50.1	30.7	29.74	35.88	34.00	29.74
L8	20	50	3	20	65.5	68.1	65.0	56.1	34.98	36.66	36.26	34.98
L9	20	50	5	40	64.2	69.2	63.3	58.0	35.27	36.80	36.03	35.27
L10	40	4	1	40	56.7	56.0	57.2	43.5	32.77	34.96	35.15	32.77
LII	40	4	3	60	83.9	89.1	84.6	71.4	37.07	39.00	38.55	37.07
L12	40	4	5	20	46.4	61.0	42.1	40.9	32.23	35.71	32.49	32.23
L13	40	10	1	60	51.6	64.6	47.7	58.3	35.31	36.20	33.57	35.31
L14	40	10	3	20	44.1	55.5	40.7	50.3	34.03	34.89	32.19	34.03
L15	40	10	5	40	68.7	78.1	66.2	53.6	34.58	37.85	36.42	34.58
L16	40	50	1	20	42.3	51.8	39.5	38.1	31.62	34.29	31.93	31.62
L17	40	50	3	40	54.9	63.8	52.4	45.5	33.16	36.10	34.39	33.16
L18	40	50	5	60	63.8	70.6	62.0	50.4	34.05	36.98	35.85	34.05
L19	60	4	1	60	40.9	44.6	40.2	22.3	26.97	32.99	32.08	26.97
L20	60	4	3	20	64.9	74.5	61.3	70.7	36.99	37.44	35.75	36.99
L21	60	4	5	40	81.3	85.4	80.3	67.4	36.57	38.63	38.09	36.57
L22	60	10	1	20	37.7	43.3	35.6	39.9	32.02	32.73	31.03	32.02
L23	60	10	3	40	46.8	64.7	41.1	28.0	28.94	36.22	32.28	28.94
L24	60	10	5	60	66.7	74.7	64.2	59.8	35.53	37.47	36.15	35.53
L25	60	50	1	40	45.4	50.2	43.8	43.9	32.85	34.01	32.83	32.85
L26	60	50	3	60	45.5	51.6	43.5	39.6	31.95	34.25	32.77	31.95
L27	60	50	5	20	36.0	44.2	33.3	30.5	29.69	32.91	30.45	29.69

Table 4.7 Degradation of petroleum hydrocarbons in samples after different US/Fenton treatments and the S/N ratio results

3.3. Impact of factors on TPH degradation through the combined (US/Fenton) process

The main effect of individual factors on TPH degradation was presented in Fig 4.12. The main effect plot (i.e. mean S/N ratios) in Fig 4.12 shows the contribution to the change of response (i.e. S/N ratio) due to the change in one of the influence factors from one level to another. It can be found that the S/N ratio decreased with the increase in sludge content and with the increase in the ratio of H_2O_2 to Fe²⁺, while S/N ratio was increased when ultrasonic irradiation time was extended. However, the pattern of S/N ratio change with ultrasonic power is different from that with the other three factors. The S/N ratio increased along with ultrasonic power increasing from level 1 to level 2 (i.e. from 20 W to 40 W), but it then slightly decreased when the power was increased to 60 W (i.e. level 3) from 40 W (i.e. level 2). The greater change in S/N ratio occurred when sludge content and US time increasing from level 1 to level 3, indicating that the sludge content and US time were the significant factors on petroleum hydrocarbon degradation using the US/Fenton process. And it is shown in Fig4.12 that the optimal condition for TPH reduction would be: sludge content at 20 g/L, the ratio of H₂O₂ to Fe²⁺ at 4:1, the ultrasonic irradiation time for 5 minutes, and the ultrasonic power at 40 W, respectively.

An interaction plot represents the interaction between two different factors with multiple levels. In an interaction plot, the levels of one parameter are set on the x-axis and a separate line stands for the mean S/N ratio of each level for the other parameter. It can be very clear to illustrate the interaction of two factors in the interaction plot: the further apart the separate lines, the stronger interaction between the two factors. However, if the separate lines are parallel to each other, no matter how far they are apart from each other, there is no interaction between the two factors. In this study, three individual interaction plots were obtained and presented in Fig 4.13a, b, and c. Since there are three levels for each factor, three curves were displayed in each plot, and each of which represents the mean S/N ratio at one level for a factor. The degree of interaction between the factors depends on the departure of a curve from the trend of the previous curve in the order of successive increasing or decreasing of the category factor (Torres et al, 2009; Wang et al., 2009). It was observed in Fig 4.13 that the higher degree of interaction appeared between the ratio of H₂O₂ to Fe²⁺ and the US time. The minimum interaction occurred between the sludge content and the US time. Furthermore, the interaction plot of the ratio of H₂O₂ to Fe²⁺ and the US time showed that the greater TPH degradation was obtained when the ratio was at 4:1 and the US treatment time for 3 minutes.



Figure 4.12 Main effect plot of factors on the TPH degradation through US/Fenton process


Figure 4.13 Interaction of factors on TPH degradation through US/Fenton process: (a) interaction of sludge content and ratio of H_2O_2 to Fe^{2+} ;(b) interaction of sludge content and US time; (c) interaction of ratio of H_2O_2 to Fe^{2+} and US time

Statistical analysis of the experimental data is necessary to further understand the oxidation treatment process in addition to the S/N ratio analysis. In this study, the analysis of variance of means (ANOVA) was carried out to verify the impact of the design factors and the interactions of factors on the TPH degradation in oily sludge. The ANOVA was implemented by using MINITAB 16, and the results were shown in Table 4.8. There are several parameters generated during the ANOVA process, including the degree of freedom (DF), the sequential sums of squares (Seq SS), the adjusted sum of squares (Adj SS), and the adjusted means squares (Adj MS). F-test was performed with 95% confidence interval. It was verified that sludge content and US time had significant impact on TPH degradation in oily sludge as shown in Table 4.8 (i.e. with P value less than 0.05). The other two factors didn't show significant impact on the US/Fenton treatment performance. The ANOVA results also illustrated that there was no significant interaction between factors to affect the TPH degradation, with the P values of the interaction effects all greater than 0.1.

	-					
Sources	DF	Seq SS	Adj SS	Adj MS	F	Р
Sludge content	2	39.646	39.646	19.823	8.34	0.019
Ratio of H_2O_2 to Fe^{2+}	2	18.395	18.395	9.1975	3.87	0.083
US time	2	24.982	24.982	12.491	5.25	0.048
US power	2	22.422	22.422	11.211	4.72	0.059
Sludge content*Ratio of H_2O_2 to Fe^{2+} (a)	4	5.597	5.597	1.3994	0.59	0.684
Sludge content*US time ^(a)	4	2.595	2.595	0.6488	0.27	0.885
Ratio of H_2O_2 to Fe^{2+} *US time ^(a)	4	13.544	13.544	3.3861	1.42	0.332
Residual Error	6	14.262	14.262	2.377		
Total	26	141.444				

 Table 4.8 Analysis of Variance for TPH degradation after different treatments through US/Fenton process

(a) * denotes the interaction between two factors.

3.2.1. The effect of sludge content

As illustrated in Fig 4.12 and further verified by ANOVA, the initial content of sludge in

samples played a very significant role on the performance of US/Fenton for the TPH degradation. As discussed before, the reaction of radicals with target organic compounds is determined largely by two aspects: the generation of radicals and the extent of radicals contacting with target compounds. The effect of sludge content could be investigated in terms of these two aspects.

Given the same excessive amount of hydrogen peroxide added, a large amount of radicals were generated in situ, while the amount of target petroleum hydrocarbons (PHCs) can be increased significantly as more oily sludge was added initially, and more hydrocarbons would be in the form of non-aqueous phase or attached to the solid particles. This would decrease the possibility of radicals getting contact with PHCs, and thus the degradation of hydrocarbons would decline accordingly. For example, when the initial sludge content was increased from the lower level to the higher level (i. e. from 20 g/L to 40g/L and 60g/L), the TPH degradation rate ranged from 51.9% to 88.1% at level 1, from 42.3% to 83.9% at level 2, and from 36.0% to 81.3% at level 3 respectively. This trend was consistent with other previous studies. For example, Virkutyte et al (2010) reported the sono-oxidation of naphthalene-contaminated soil combining with Fenton-like process, and they found that higher degradation efficiency (94-97%) was achieved with lower initial naphthalene concentration (200 mg/kg), and the efficiency dropped to 58-76% when the initial concentration of naphthalene was doubled (i.e. 400 mg/kg). Moreover, when the initial sludge content was high in the sample, the viscosity of the bulk liquid was increased by the presence of large hydrocarbon molecules and the increased viscosity could impede the formation and collapse of cavitation bubbles (Gaikwad et al, 2008). And then the desorption of petroleum hydrocarbons due to ultrasonic irradiation was retarded. In addition, more

hydrocarbons present in system could inhibit the thorough dispersion of hydrocarbons into the aqueous medium, and the larger-size hydrocarbon drops could not be easily broken down into smaller ones. Therefore, higher sludge content could decrease the contact of hydrocarbons with radicals in the bulk liquid.

On the other hand, the presence of solid particles in oily sludge could also be taken into account for the degradation of hydrocarbons. It has been proved that the behavior of cavitation bubbles in heterogeneous system was essentially different from that in homogeneous system (Liang et al., 2007 b). The presence of solid particles could affect the cavitation phenomena, and the microjets are formed when cavitation bubbles collapse asymmetrically near solid particles. The microjets towards the inside of the bubbles might help the diffusion of radicals either in the bulk liquid or inside the cavitation bubbles, thus enhancing the contact of hydrocarbons with radicals. More solid particles were brought into the system due to the increase in sludge content, which might cause the reduction of the cavitation threshold (Liang et al., 2007 a) and enhance the free radical transfer. Moreover, these solid particles could also provide more interfacial areas for the formation of HO radicals (Pang et al., 2011) and the occurrence of free radical reactions. It has been reported that many metal compounds could be served as catalysts to trigger the chain reactions similar to reactions associated with Fenton process. For example, copper oxide (CuO) is known as an effective oxidation catalyst to enhance the formation of reactive radicals for the oxidization of organic compounds (Pang et al., 2011). Metals elements, such as Fe, Al, Ca, Cu, Zn, were found in the oily sludge, and these metals might be served as other sources of catalysts for Fenton-like reaction to improve the degradation efficiency of PHCs.

In addition, the yield of oxidation intermediates was increased when sludge content was raised and the accumulation of the intermediates might impact the degree of PHCs degradation by the use of AOPs. Lin et al. (2008) examined the oxidation reaction rate of azo dyes at high initial concentration under ultrasonic irradiation with Fenton-like reagents, and they found that the lower degradation efficiency was due to the formation of recalcitrant by-products. Since oily sludge was a mixture of many petroleum hydrocarbons, the intermediates (e.g., carboxyl acids, alkene, ketones) could be accumulated when a large amount of petroleum hydrocarbons were oxidized. And the resistance to further decomposition might increase due to the cumulation of more oxidation intermediates when more petroleum hydrocarbons were introduced into the system under the combined process. As a result, lower PHCs degradation efficiency was observed when the initial sludge content was increased. In summary, high sludge content in the sample would significantly affect the performance of the combined AOPs process (i.e.US/Fenton). The highest degradation of PHCs was achieved at the lowest level (i.e. 20 g/L) of sludge content. However, relatively higher degradation rate of PHCs was also achieved at higher level (i.e. 60 g/L) of sludge content, such as the TPH degradation of 66.7% for experimental run of L24, and the TPH degradation of 81.3% for experimental run of L21. This might indicate the complicated impact of other factors on the US/Fenton process or other interactions of factors.

3.2.2. The effect of ultrasonic treatment time

It was observed in Fig 4.12 that the ultrasonic treatment time had a positive impact on the degradation efficiency of PHCs, which was also confirmed by ANOVA (Table 4.8). As discussed before, the benefit for the application of US during Fenton process is mainly to enhance the contact of radicals with the target organic compounds. The increase in US treatment time could help the desorption of petroleum hydrocarbons from solid particles and the dispersion of hydrophilic compounds into the bulk liquid. At the same time, the microjects generated from the heterogamous system could enhance the transfer of radicals toward solid-liquid interface where petroleum hydrocarbons are attached. As a result, higher TPH degradation rate was achieved under US/Fenton process when the longer US treatment (i.e. 5 minutes) was applied. Moreover, the abundant intermediates of Fe-OOH²⁺ which are related to the Fenton's reactions, can be decomposed into Fe^{2+} and hydroperoxyl (HO²⁺) by ultrasonic irradiation. With longer ultrasonic treatment duration, more Fe²⁺ could be recycled to engage in the reactions with H_2O_2 , causing the generation of more hydroxyl radicals. Under the US/Fenton process, another benefit for PHCs degradation from prolonged ultrasonic irradiation is that ultrasonic irradiation might have the ability to facilitate the decomposition and cleavage of petroleum hydrocarbons. When ultrasound treatment continues, more heavy hydrocarbons could be decomposed. In summary, the positive effect of ultrasonic irradiation suggests that the longer ultrasonic treatment time during the US/Fenton process might increase the degradation of PHCs. However, economical factors should also be taken into account besides high degradation efficiency, when identifying the optimal ultrasonic treatment duration.

3.2.3. The effect of the ratio of H_2O_2 to Fe^{2+}

Although the ANOVA results did not confirm the significant impact of H_2O_2/Fe^{2+} ratio on TPH degradation through the US/Fenton treatment performance, it is very interesting to investigate the effect of this ratio on the PHCs degradation. Many studies have examined the impact of molar ratio of H_2O_2 to Fe^{2+} for wastewater treatment when using Fenton's reaction process alone. The optimal ratio has been reported with a wide range by studies on decomposition of various organic pollutants. Casero et al (1997) reported the optimum molar ratio was 5 to 40 by the use of Fenton's reagents to degrade aromatic amines in wastewater, and Tekin et al (2006) found that the molar ratio was between 150 and 250 with the highest COD removal when Fenton process was applied to treat pharmaceutical wastewater. And the addition of excessive iron did not improve the degradation efficiency since the iron would behave like radical scavenger to consume hydroxyl radicals as described in Eq. 34. However, in this study, the highest TPH degradation rate was achieved when the ratio of H₂O₂ to Fe²⁺ was 4:1. Since Fe²⁺ is able to engage in the oxidation of hydrocarbons by the reactions with carboxyl radicals (Eq.35 and 36), the presence of extra Fe²⁺ could play important role in the fate of radicals and the oxidation of hydrocarbons (Mansano-Weiss et al., 2002). Furthermore, other experiments (Ronen et al, 1994; Watts and Stanton, 1999) indicated that the mineralization of organic compounds can be increased with the increase of Fe²⁺.

$$Fe^{2+} + R - OO \rightarrow Fe^{3+} OOR$$
 (35)

$$Fe^{3+}-OOR + Fe^{2+} + 3H^+ \rightarrow 2Fe^{3+} + ROH + H_2O$$
 (36)

3.4. Impact of factors on degradation of PHCs in different fractions through the combined (US/Fenton) process

In addition to the analysis of TPH degradation results, it is also interesting to investigate the performance of the combined process (i.e. US/Fenton) on the degradation of petroleum hydrocarbons (PHCs) in different fractions. The residual mass and the degradation rate results of three PHC fractions (i. e. Fraction 2, Fraction 3, and Fraction 4) were shown in Table 4.6 and Table 4.7, respectively. Tables 4.9, 4.10, and 4.11 list the ANOVA results for the degradation of Fraction 2, Fraction 3, and Fraction 4, respectively. Figs. 4.14 and 4.15 present the main effect plot and the interaction plots for the degradation of Fraction 2 (F2 degradation), respectively. As shown in Fig 4.14, the pattern of each factor for F2 degradation was similar to that for the TPH degradation (Fig. 4.12). As in Fig 4.14, F2 degradation was decreased with the increase in sludge content and the ratio of H_2O_2 to Fe^{2+} , and the better performance of F2 degradation was obtained when the sludge content was 20 g/L and the ratio of H_2O_2 to Fe^{2+} was 4:1. Meanwhile, the S/N ratio was increased with the increase of US time from 1 minute to 3 minutes, but no significant enhancement was observed when the US time was extended to 5 minutes. Similar pattern occurred for the effect of US power. The enhancement of S/N ratio was observed when the US power grew from 20 W to 40 W, but no further improvement was found when the US power was increased to 60 W. With respect to the interaction of factors for F2 degradation (Fig 4.15), it can be found that significant interaction occurred between the ratio of H_2O_2 to Fe^{2+} and the US time. The ANOVA result revealed the relative significance of such interaction, with P value of this interaction was 0.058 (Table 4.9).

Sources	DF	Seq SS	Adj SS	Adj MS	F	Р
Sludge content	2	22.255	22.255	11.1275	13.49	0.006
Ratio of H_2O_2 to Fe^{2+}	2	12.496	12.496	6.2481	7.58	0.023
US time	2	28.367	28.367	14.1834	17.20	0.003
US power	2	15.848	15.848	7.9239	9.61	0.013
Sludge content * Ratio of H_2O_2 to $Fe^{2+(a)}$	4	3.454	3.454	0.8635	1.05	0.456
Sludge content*US time ^(a)	4	2.147	2.147	0.5368	0.65	0.647
Ratio of H_2O_2 to Fe^{2+} *US time ^(a)	4	13.919	13.919	3.4798	4.22	0.058
Residual Error	6	4.948	4.948	0.8246		
Total	26	103.434				

Table 4.9 Analysis of variance for Fraction 2 (F2) degradation after different US/Fenton treatments

(a): * denotes the interaction between two factors

Sources	DF	Seq SS	Adj SS	Adj MS	F	Р
Sludge content	2	51.230	51.230	25.6148	7.88	0.021
Ratio of H_2O_2 to Fe^{2+}	2	21.616	21.616	10.8082	3.32	0.107
US time	2	23.055	23.055	11.5275	3.55	0.096
US power	2	26.365	26.365	13.1825	4.06	0.077
Sludge content*Ratio of H_2O_2 to $Fe^{2+}(a)$	4	7.094	7.094	1.7735	0.55	0.710
Sludge content*US time ^(a)	4	3.275	3.275	0.8188	0.25	0898
Ratio H_2O_2 to Fe^{2+} *US time ^(a)	4	14.888	14.888	3.7219	1.14	0.419
Residual Error	6	19.504	19.504	3.2507		
Total	26	167.02				

Table 4.10 Analysis of variance for Fraction 3 (F3) degradation after different treatments through US/Fenton treatments

(a): * denotes the interaction between two factors

Table 4.11 Analysis of variance for Fraction 4 (F4) degradation after different treatments through US/Fenton treatments

Sources	DF	Seq SS	Adj SS	Adj MS	F	Р
Sludge content	2	10.246	10.246	5.123	0.67	0.546
Ratio of H_2O_2 to Fe^{2+}	2	5.284	5.284	2.642	0.35	0.721
US time	2	91.064	91.064	45.532	5.97	0.037
US power	2	14.677	14.677	7.339	0.96	0.434
Sludge content*Ratio of H_2O_2 to Fe^{2+} (a)	4	6.388	6.388	1.597	0.21	0.924
Sludge content*US time ^(a)	4	61.059	61.059	15.265	2.00	0.214
Ratio of H_2O_2 to Fe^{2+} *US time ^(a)	4	135.118	135.118	33.779	4.43	0.053
Residual Error	6	45.777	45.777	7.629		
Total	26	368.613				

(a): * denotes the interaction between two factors



Figure 4.14 Main effect of factors for F2 degradation through US/Fenton process



Figure 4.15 Interaction of factors on F2 degradation through US/Fenton process: (a) interaction of sludge content and ratio of H_2O_2 to Fe^{2+} ; (b) interaction of sludge content and US time; (c) interaction of ratio of H_2O_2 to Fe^{2+} and US time

Figs. 4.16 and 4.17 present the main effect plot and the interaction plots for the degradation of Fraction 3 (F3 degradation). It can be found that the main effect plot (Fig 4.16) and the three interaction plots (Fig 4.17) for F3 were similar to those for the F2 (Fig. 14 and Fig. 15). They were also similar to plots for the TPH degradation (e.g., Fig.13 and Fig.14). It was observed that both the sludge content and the ratio of H_2O_2 to Fe²⁺ played negative roles on the F3 degradation. The ultrasonic treatment time and ultrasonic power could enhance the performance of the US/Fenton process to some extent, but further increase in the magnitude of these two factors did not enhance the degradation efficiency. Meanwhile, the interaction between the ratio of H_2O_2 to Fe²⁺ and US time was the most obvious among the three interactions as illustrated in Fig 4.17. However, the ANOVA result (Table 4.10) only confirmed the significant effect of sludge content on F3 degradation (with P value of 0.021), while no significant interaction among factors was confirmed.



Figure 4.16 Main effect of factors for F3 degradation through US/Fenton process



Figure 4.17 Interaction of factors on F3 degradation through US/Fenton process: (a) interaction of sludge content and ratio of H_2O_2 to Fe^{2+} ; (b) interaction of sludge content and US time; (c) interaction of ratio of H_2O_2 to Fe^{2+} and US time

Figs. 4.18 and 4.19 present the main effect plot and the interaction plots for the degradation of Fraction 4 (F4 degradation), respectively. The patterns of main effect plot and interaction plots for F4 degradation were greatly different from those for F2 and F3 degradation. As shown in Fig 4.18, the best F4 degradation was achieved when the sludge content was 40 g/L instead of 20 g/L, compared with F2 and F3 degradation. When the ratio of H_2O_2 to Fe²⁺ changed from 4:1 to 10:1, there was no significant improvement for the F4 degradation. However, the S/N ratio decreased as this ratio was increased to 50:1. In the meantime, the US time had positive impact on the performance of US/Fenton process for F4 degradation was obtained that the best performance of US/Fenton process on the F4 degradation was obtained when ultrasonic power at 40 W. It can also be found that the interaction between the ratio of H_2O_2 to Fe²⁺ and US time was the most significant among the three interactions as shown in Fig 4.19. The ANOVA result (Table 4.11) verified the significant effect of US time (P value of 0.037) and the interaction of the ratio of H_2O_2 to Fe²⁺ and US time (P value of 0.053).



Figure 4.18 Main effect of factors for F4 degradation through US/Fenton process



Figure 4.19 Interaction of factors on F4 degradation through US/Fenton process: (a) interaction of sludge content and ratio of H_2O_2 to Fe^{2+} ; (b) interaction of sludge content and US time; (c) interaction of ratio of H_2O_2 to Fe^{2+} and US time

The effect of factors on F4 degradation was different from that on F2 and F3 degradation due to the degradation mechanisms. As discussed before, the degradation of petroleum hydrocarbons largely depends on the free radical reactions and the thermal cracking of hydrocarbons introduced by ultrasonic irradiation. Substantial heavy hydrocarbons in F4 group can be decomposed by thermal cracking under ultrasonic irradiation through the US/Fenton process, and thus the duration of US was the most significant factor among four factors. Furthermore, the intermediate products from thermal cracking could be further attacked by hydroxyl radicals or react with other alkyl radicles related to hydroxyl radicles reactions, and so the interaction of US and the ratio of H_2O_2 to Fe^{2+} affected the performance of the combined process on F4 degradation. However, higher content of oily sludge (i.e. 60 g/L) in the treatment system would affect the performance of ultrasonic irradiation, and then the thermal cracking of heavy hydrocarbons would be impeded, resulting in the decline in degradation efficiency. For example, F4 degradation rate dropped when the original sludge content was increased from 40 g/L to 60 g/L.

As compared with the main effect on the degradation of three PHC fractions, the F2 degradation was significantly affected by all of the four study factors, while the US time was the only significant factor impacting F4 degradation and sludge content was the only significant one for F3 degradation. First of all, as it was discussed before, the light hydrocarbons are much more vulnerable for free radical attacking through advanced oxidation processes, and thus the F2 degradation could be simply improved by either adjusting the US parameters or by adding more catalysts for Fenton' reactions to enhance the generation of hydroxyl radicals and the contact of radicals with hydrocarbons. As a result, all of the four factors accounted for significant factors on the F2 degradation through the

combined process. Secondly, the oxidation intermediates formed due to decomposition of F4 and F3 might accumulate in F3, and this cumulation of recalcitrant intermediates may impede the oxidation efficiency. As a result, no significant impact factor was observed for F3 degradation except for sludge content. Meanwhile, ultrasonic irradiation alone was proved a high efficiency process in decomposing heavy hydrocarbons in F4 group (Fig 4.10) as compared with the Fenton's reaction. Thus, the US time played important role on the F4 oxidation under the combined US/Fenton process. It is also interesting to note the interaction of the H_2O_2 /Fe²⁺ ratio and US time on PHCs degradation. For F2 and F4 degradation, the interaction effect was significant, which might indicate the synergistic effect due to the combination of US and Fenton. As shown in Fig 4.15 and Fig 4.19, the best performance of US/Fenton on the degradation of hydrocarbons in F2 and F4 was obtained when the ratio was 4:1 and the US time was 3 minutes.

4. Conclusion

Three advanced oxidation methods were investigated in this study to treat the oily sludge. These include the ultrasonic irradiation alone, the Fenton's reaction process alone, and the combination of ultrasonic irradiation and Fenton's reaction. The highest reduction of petroleum hydrocarbons in oily sludge was found to be 43.1% for the combined process, indicating that the combined process could be an effective way to treat the oily sludge. By combining ultrasonic irradiation with the Fenton's reaction, free radical reactions might be improved by increasing the contact of sufficient hydroxyl radicals with petroleum hydrocarbons. The analysis results of the reduction in PHC fractions revealed that the reduction of all three fractions (e.g., F2, F3, and F4) in oily sludge was improved with the application of the combined process. The shift of petroleum hydrocarbon fraction distribution in samples was observed after AOP treatments. The percentage of F3 was increased, indicating the accumulation of oxidation intermediates due to the decomposition of F4 hydrocarbons under the treatment of advanced oxidation processes.

Taguchi experimental design was applied to investigate the impact of several factors on the performance of the combined advanced oxidation process (US/Fenton). The best TPH degradation rate of 88.1% was observed when the sludge content was set at 20 g/L, the H_2O_2/Fe^{2+} ratio was set at 4:1, the US power was set at 60 W, and the ultrasonic treatment time was set at 5 minutes. The sludge content and ultrasonic treatment time were confirmed to have significant impact on the degradation of petroleum hydrocarbons. There was no substantial interaction between factors with respect to total petroleum hydrocarbon (TPH) degradation. The TPH reduction rate was decreased with the increase in sludge content, while TPH degradation increased as ultrasound treatment time increased. There was no significant interaction between factors with respect to TPH degradation. However, significant interaction was observed between the ultrasonic treatment time and the H_2O_2/Fe^{2+} ratio when considering F2 degradation and F4 degradation. In summary, the advanced oxidation process by the combination of ultrasonic irradiation with Fenton's reagents was proved to be an effective treatment approach to reduce petroleum hydrocarbons in oily sludge, and the degradation efficiency of such method could be improved under optimal experimental conditions. Oxidation products of petroleum hydrocarbons after advanced oxidation treatment might need further investigation.

Chapter 5 General Conclusion

Oily sludge is one of the major wastes generated in the petroleum industry. Traditional methods to dispose of oily sludge are relatively time-consuming and inefficient. It is thus of importance to explore novel approaches to treat oily sludge before direct disposal of it into the environment. In this thesis research, three distinctive approaches were investigated for their capabilities to treat oily sludge.

Chapter 2 is focused on the enhanced bioremediation technology to improve the degradation of petroleum hydrocarbons when oily sludge was spiked into soil. One bacterium strain *Luteibacter sp.* was isolated from petroleum hydrocarbons contaminated soil and was then reintroduced into the soil to biodegrade the hydrocarbons, along with the addition of nutrients and bio-surfactants (rhamnolipids). The impacts of initial TPH content in soil/sludge mixture, nutrient addition, and the bio-surfactant were examined by the use of Taguchi experimental design. The results indicated that the optimal bioremediation condition for TPH reduction was: initial TPH content at 9690 mg/kg, nutrient addition at the ratio of 100:50:10 for C:N:P, and the addition of rhamnolipid at 400 mg/kg. The degradation results of the heavy petroleum hydrocarbons suggested that the isolated bacterium was effective for degrading long-chain PHCs.

Chapter 3 investigates the oil recovery approach to treat oily sludge. Three methods, including ultrasonic irradiation alone, freeze/thaw treatment alone, and the treatment of combining ultrasound with freeze/thaw, were applied to recover oil from the oily sludge. The results indicated that the combined method was considered as an effective approach to recover oil from sludge with regard to oil recovery efficiency and TPH concentrations in the recovered oil and in the separated wastewater. Under the experimental conditions, oil recovery rate of 64.2% was achieved by using the combined treatment process, with TPH

concentrations of 85.1% and 200 mg/L in the recovered oil and wastewater, respectively. When considering the impact of different factors, the increase in oil recovery was observed as the ultrasonic power was set at a lower level of 33 W, a sludge/water ratio of 1:2, a rhamnolipids concentration of 100 mg/L, and a NaCl concentration of 1%, respectively. The main mechanism of oil recovery enhancement was found to be the improved desorption of PHCs from solid particles under ultrasonic irradiation.

The study in Chapter 4 explores the ability of advanced oxidation processes to degrade petroleum hydrocarbons in oily sludge. Three advanced oxidation methods were examined, including ultrasonic irradiation alone, Fenton's reaction process alone, and the combination of ultrasonic irradiation and Fenton's reaction. The highest reduction of petroleum hydrocarbons was 43.1% under the combined process, indicating that the combination of ultrasound with Fenton's reaction could be considered as an effective approach to remove petroleum hydrocarbons in oily sludge. The fractional analysis of petroleum hydrocarbons indicated that the removal of hydrocarbons in all three fractions was improved by using the combined process. When evaluating the impact of individual factors on the combined US/Fenton process, the best TPH degradation rate of 88.1% was obtained when sludge content was set at 20 g/L, the H_2O_2/Fe^{2+} ratio was set at 4:1 with US power at 60 W and US time for 5 minutes. The sludge content and ultrasonic treatment time were confirmed to have significant impact on the degradation of petroleum hydrocarbons.

Limitations and future research

In the study of oil recovery technique, the individual impacts of different factors on the combined treatment process were examined through a series of laboratory experiments.

However, the interaction effects among these factors, the identification of major influencing factors, and the optimal combination of these factors were not examined. This could be investigated through factorial experimental design method in future studies. In addition, the recovered oil from the crude oil tank bottom sludge in this study was not a pure mixture of petroleum hydrocarbons, and may need further treatment. The value of the recovered oil as fuel (such as asphaltene content, ash content, salt content, and heat of combustion) and the detailed cost/benefit of the proposed treatment process were not analyzed, and should be examined in future studies. In summary, the combined ultrasonic and freeze/thaw process could represent an environmentally friendly and economically competitive alternative for the effective treatment of oily sludge waste from the petroleum industry, and is worth of further investigations.

For the advanced oxidation techniques, the performance of AOPs was examined by the reduction or degradation rate of hydrocarbons and the results indicated that a large amount of hydrocarbons were oxidized. However, the presence of oxidation products and intermediates was not provided in this study. More evidence of oxidation products might be necessary for the investigation of combining AOP on the oxidation of various hydrocarbons at the same time. Furthermore, the combined ultrasound and Fenton process was proved to be an effective way to reduce contaminant concentration in oily sludge, but there is still some amount of hydrocarbons remained in samples after treatment. Further treatment of such residue might be necessary to eliminate petroleum hydrocarbon pollution, such as the bioremediation technologies.

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