AN OZONATION TREATMENT SYSTEM FOR OIL SPILL

by

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STATEMENT OF THESIS APPROVAL

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ABSTRACT

With increasing industrial activities in many parts of the world, a large amount of crude oil is being consumed daily. With the large number of offshore and onshore oil fields along with the transportation of crude oil and its products, the risk of oil spill increases accordingly. Big crude oil spill accidents have caused not only loss of the energy resource but also significant contamination to the environment and ecosystems, attracting intense attention in each occurrence. Small oil spills occur frequently, but with less notice worldwide on a daily basis on land, at sea, and throughout inland freshwater systems.

Various approaches have been proposed to decontaminate oil spill sites according to individual environmental constraints. The main methods for in situ oil spill clean-up include biodegradation, controlled burning, sorption, dispersion, along with chemical oxidation, filtration, membrane process, and adsorption for lower oil concentrations. These existing methods have their own drawbacks such as long duration and harmful intermediates; new effective methods using a combination of the existing methods are necessary.

In this study, a process train utilizing flotation, stage-1 sand filtration, heightened ozonation (HOT), and stage-2 sand filtration was used to deal with oil-contaminated water (2.5% oil) that would simulate oil spills under different water conditions, including tap water, Utah Lake water, and Great Salt Lake water representing fresh water, groundwater, and sea water contamination. Treatment was carried under different conditions and the optimum conditions were identified. Excellent operation flowrates

were found to be 5.2, 8, and 2 cm/min for the flotation column, the first-stage sand filtration, and the second-stage sand filtration, respectively. The results showed that HOT treatment of 8 cycles at 100 psi was most effective and economical in terms of dosage for achieving desirable effluent quality (84.76% O&G removal) and sand filter's life capacity (150 times the sands volume before sands were exhausted). The new treatment train achieved 99.9 % oil and grease removal and > 99.8 % COD removal, with increased sCOD and BOD/COD ratio, which indicated the potential of further polishing biological treatment if needed.

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CHAPTER 1

INTRODUCTION

Importance of Crude Oil

Crude oil (petroleum) is a naturally occurring, flammable liquid consisting of various hydrocarbons and other liquid organic compounds, which are found in geologic formations beneath the earth's surface, derived from ancient fossilized organic materials including zooplankton and algae as a fossil fuel (Kvenvolden, 2006). The molecular composition of crude oil contains a wide range of boiling points and hydrocarbon compounds with various carbon numbers, including alkanes, cycloalkanes, and aromatic hydrocarbons, and also with other compounds containing nitrogen, oxygen, sulfur, as well as metallic constituents (Speight, 2011). They vary significantly in appearance, volatility, specific gravity, and viscosity according to their compositions.

Crude oil provides high value liquid fuels, solvents, lubricants, pharmaceuticals, fertilizers, pesticides, plastics, and many other products after refinery (Purdy, 1957). The fuels derived from crude oil provide approximately one third to one half of the world's total energy supply, and become important "primary energy" source with fuel oil and petrol (Speight, 2011). Petroleum products appear in a wide variety of forms that vary from gaseous and liquid fuels to near-solid machinery lubricants, and they are used not only for transportation fuels, but also for heating buildings; in addition, asphalt (the residue of refinery process) is a premium-value product for highway surfaces, roofing

materials and miscellaneous waterproofing uses (Speight, 2011). Therefore, crude oil has become the most important energy resource for human beings and with the development of industry worldwide, approximately 10 million tons of petroleum products and derivatives are being consumed daily (Fingas, 2000). In the United States, approximately three million tons of oil and petroleum products are used daily; this constitutes 40% of total energy consumption (Fingas, 2011).

Hazard of Oil Spill

With increasing numbers of crude oil fields and transportation and storage of crude oil and its products, the risk of oil spills is also increasing, both in marine area and fresh water (Fingas, 2000; Vandermeulen and Ross, 1995). Between 1974 and 1994, there were 175 major oil spills worldwide, and it might cost as high as $20 - $200 per liter to clean up the contaminated sites, depending on the location and type of oil spill (Fingas, 2000; Abdullah et al., 2010). Big crude oil spill accidents, such as the Exxon Valdez oil spill (1989), the Prestige oil spill (2002), and most recently the Gulf of Mexico oil spill (2010), caused not only loss of the energy resource, but also significant contamination to the environment and ecolosystem, and also received extensive attention (Seymour and Geyer, 1992; González et al., 2006; Schnoor, 2010; Allan et al., 2012; Lin and Mendelssohn, 2012; Firby and Law, 2008). However, there might be thousands of oil spills much smaller in scope occurring worldwide every day – on land, at sea and in land freshwater systems, from transport by tank ships, pipeline, rail and truck, or from the production activities, which also need to be noticed. During 1998 – 2007, there were 11,000 tons of pipeline spills annually, 1,700 tons refinery spills, 1,300 tons tanker truck spills and 500 tons tank ships spills every year in United States (Fingas, 2011).

Oil spills contain various hazardous compounds, which are toxic to aquatic organisms and human beings. For example, polycyclic aromatic hydrocarbons (PAHs) are considered to be one principal contaminant during the spills, and the oil spilled during the Deepwater Horizon oil spill contained about 3.9% PAHs by weight, approximating 2.1×10^{10} g released during the spill (Reddy et al., 2011). The toxic contaminants are mainly removed by evaporation, dilution, transportation and precipitation, and impacted significantly by weather. The contaminants might require decades to be removed (Seymour and Geyer, 1992; Allan et al., 2012). They also lead to concerns of the toxicity of metabolic byproducts because of potential adverse effects associated with biodegradation processes (Zhu et al., 2004).

Oil spills adversely impact the offshore ecosystem. Coral colonies near the Macondo well after the Deepwater Horizon oil spill in the Gulf of Mexico presented widespread signs of stress, including varying degrees of tissue loss, sclerite enlargement, excessmucous production, bleached commensal ophiuroids, and covering by brown flocculent material (White et al., 2012). Threatened are vulnerable marine plants and animals in the Gulf of Mexico, including 14 marine species protected by the US Endangered Species Act (ESA), the Marine Mammal Protection Act, and the Migratory Bird Treaty Act (Campagna et al., 2011).

For coastal wetland plants, oil spills can have a widespread impacts, such as reduced plant photosynthesis, transpiration, shoot height, stem density, and biomass, and also impaired growth and re-growth, according to oil type, spill volume, mode of contact with the vegetation, and oil penetration into soil. Recovery of coastal wetlands from oil spills may require years or decades (Lin and Mendelssohn, 1998; Culbertson et al., 2008).

Participation in clean-up of oil spills also leads to health concerns. People engaged in the cleanup operation showed symptoms of back pain, skin lesions, headaches, as well as eye, neurovestibular and respiratory problems; and risk analyses showed that more frequent and greater exposure was more strongly related to higher occurrence of health problems (Sim et al., 2010). A long-term study showed that among the fishermen who participated in clean-up activities after the Prestige oil spill, exposure to oil products over days to a few months might have contributed to respiratory symptoms, which were still measurable after two years, and there were also discussions about long-term lung disease related to exposure to oil spills (Rodriguez-Trigo et al., 2010).

Oil Spill Treatment Methods

There has been a large variety of methods for in situ treatment of the spilled oil to reduce environmental damage. Generally, methods for oil spill clean-up widely used and studied include biodegradation (Saeki et al., 2009), controlled burning (Fingas, 1998; Rasmussen and Brandvik, 2011), skimming, solidifying, sorbents and dispersants (Tamis et al., 2011). The suitable situations and characters of the main methods for in situ oil spill treatment are shown in Table 1.

Skimmers are mechanical devices designed to remove oil from water surface and vary in size, capacity and efficiency. The skimmers could be effective after the oil collected by booms, and affected by thickness of the oil, the weather, and the presence of debris. A skimmer's overall performance is determined by recovery rate ($0.2 - 100$ m^3/h) and percentage of oil recovered (10% - 95%) (Schulze, 1998).

Table 1 Characters of main methods for in situ oil spill treatment (Yang et al., 2009; Sueiro et al., 2011; Tamis et al., 2011; Vandermeulen and Ross, 1995; Zhu et al., 2011; Fingas, 2011; Zhu et al., 2004)

	Optimum conditions	Advantages	Disadvantages
Skimmers	When the oil slick is relatively thick, usually combined with booming	There are several types of skimmers for light or heavy oil spills	The effectiveness is limited and affected badly by weather conditions
Sorbents	To clean up the final traces of oil spills or for very small spills cleanup	Oleophilic and hydrophobic agents are chosen for better performance, and sometimes the material could be reused	The excessive use and sinking might cause cleanup problems; oil could be released from the sorbent over time and might harm the environment
Dispersants	Only acceptable on locations with high dilution rates; not suitable for heavy oil	Reduce the possibility of shoreline impact; reduce the contact of oil with sea birds and mammals; and promote biodegradation	Toxicity and long-term concerns are being considered; and the effectiveness is being doubted
In-situ burning	The vaporization of the oil must be sufficient to yield a steady state burning, and oil should achieve a certain thickness	It is easy to apply; rapid removal of large amount of oil; reduces the volume of disposal; high efficiency and less labor required	Smoke plumes and burn residues are considered, which might be harmful for the ecosystem and environment
Biodegradation	Primarily used on shorelines or land	Accelerates oil degradation is economical, and is a natural way to reduce the oil	It takes weeks or even years to remove the degradable fraction, and might not as effective at different locations; safety becomes a concern, too

Sorbents are natural or synthetic materials that recover oil through adsorption or absorption, and they have been increasingly used recently. The water pickup of sorbents is smaller than skimmers (<30%) and oil recovery varies by materials (Fingas, 2011).

Dispersants contain surfactants with water-soluble and oil soluble components to accelerate the process of oil dispersion into water, which reduces the visibility of the oil and the potential impact on the sea animals. However, because of toxicity concerns, the use of dispersants is still being debated (Tamis et al., 2011).

In situ burning is the oldest technique applied to oil spills and is still one of the main techniques being applied recently. Most oil pools burn at about $1 - 4$ mm/min rate, and the oil burn rate is about $2000 - 5000$ L/m^2·day (Fingas, 2011).

Bioremediation is the act of adding materials to a contaminated environment to accelerate the natural biodegradation processes. Although extensive research has been conducted on oil bioremediation for decades, the effectiveness of this technology has rarely been proved, and demonstrations of commercial bioremediation products are still lacking for the treatment of spilled oil in an open environment (Zhu et al., 2004).

Due to the drawbacks of existing methods, new economical and less time-consuming methods still need to be developed for various types of oil and weather conditions.

Advanced Treatment Methods for Further Oil Removal

After the bulk of oil is removed from the collected spill water, the water may still contain small oil droplets and oil sheen, requiring further treatment. Many treatment technologies for produced water and oil field wastewater are also suitable for further

treatment during an oil spill. Some widely used in-situ treatment methods are listed in Table 2.

The term biological aerated filter (BAF) refers to a class of technologies, including fixed film and attached growth processes, roughing filters, intermittent filters, packed bed media filters, and conventional trickling filters. A BAF can remove oil, suspended solids, ammonia, nitrogen, COD, BOD, iron, manganese, heavy metals, soluble organics, trace organics, and hydrogen sulfide. BAF is a well-established technology and has been used for many years in oil field produced water treatment (Colorado School of Mines, 2009).

Filtration has been used extensively for produced water treatment. It can be applied by using a variety of different types of media: walnut shell, sand, anthracite, and others, especially walnut shell filters for the removal of oil and grease (Colorado School of Mines, 2009).

Adsorption can be accomplished using a variety of materials, including zeolites, organoclays, activated alumina, and activated carbon, which are capable of removing iron, manganese, total organic carbon, BTEX compounds, heavy metals, and oil from produced water (Colorado School of Mines, 2009; Ranck et al., 2005).

Chemical oxidation treatment can be used to remove iron, manganese, sulfur, color, tastes, odor, and synthetic organic chemicals, and oxidants commonly used in water treatment applications, including chlorine, chlorine dioxide, permanganate, oxygen, and ozone. The appropriate oxidant for produced water depends on several factors including raw water quality, specific contaminants present in the water, and local chemical and power costs (AWWA, 2005).

Table 2 Characters of methods for produced water treatment (Zhao et al., 2006; Colorado School of Mines, 2009; Bureau of Reclamation, 2003)

	Optimum conditions	Advantages	Disadvantages
Biological aerated filter	Chloride level below 6000 mg/L, COD < 400 mg/L	No chemicals are required during normal operation, no cleaning is required. It can maintain high hydraulic loading rates and retain a high biomass concentration.	High concentrations of salts can decrease the effectiveness due to salt toxicity effects. It also has a large footprint and is not very mobile.
Filtration	It can be applied under various conditions.	It is not affected by salt concentration, and effective to remove oil and grease.	Backwash and frequent change of media increase the cost.
Adsorption	It is better used as secondary step because of the loading of oil.	The process can be gravity fed and does not require an energy supply, except during backwash.	Media may require frequent replacement or regeneration depending on media type and feed water quality, and waste disposal might become a problem.
Oxidation	Chemical dose needs to be chosen for different conditions.	No pretreatment is required for produced water, and equipment can have a life expectancy of 10 years.	Chemical costs might be high.

Gas Flotation

Flotation is a unit operation for separating particles from a liquid phase by injecting fine gas (mostly air) bubbles into the liquid. The bubbles attach to the particulate matter, and the buoyant force of the combined particle and gas bubbles is great enough to cause the particle to rise to the surface. It is widely used for oil recovery (Metcalf & Eddy, 2004). With the density difference between the oil and water becoming smaller nowadays (heavier oils are being produced), there is less buoyancy between the two phases, which

makes traditional treatment ineffective, such as gravity settler and cyclone approach. Gas flotation shows its advantages especially for heavy oil in combination with properties of high viscosities and foaming characteristics (Moosai and Dawe, 2003). Also, flotation works well at various temperatures and could be used for waters with both high and low TOC concentrations (Colorado School of Mines, 2009). Recently, gas flotation technology has been subdivided into dissolved gas flotation (DGF) and induced gas flotation (IGF), which are used to treat smaller oil droplets as small as 25 μm (Colorado School of Mines, 2009).

<div align="center">Pressure Assisted Ozonation for Oil Removal</div>

In situ chemical oxidation, which destroys contaminants by converting them into more biodegradable compounds and increases the effectiveness and economic feasibility, is a promising technology of degrading various hazardous wastes for oil spill sites. It does not generate large volume of wastes and is relatively more rapidly, which overcomes several deficiencies of conventional treatment technologies (Technical/regulatory Guidelines, 2001).

Ozone is one of the strongest oxidants for removing COD and mainly toxic compounds in oil spills such as PAHs, PCBs, BTEX, naphthenic acids and volatile organic compounds (VOCs), and it can oxidize phenol to less toxic products. Ozone treatment eliminates the storage and handling problems associated with other oxidants because it can be generated on site (Technical/regulatory Guidelines, 2001; Scott et al., 2008; Cañizares et al., 2007; Hong et al., 2008). It also accelerates biodegradation processes by breaking complex toxic compounds into simpler compounds that are easier to degrade (Martin et al., 2010; Goi et al., 2006). For these reasons, ozonation, used alone

or combined with other treatment processes, becomes a promising treatment technology and has been studied extensively recently.

Pressure assisted ozonation with sand filtration has been proven to remove PAHs and PCBs effectively from contaminated sediments (Hong et al., 2008). It has successfully removed oil and oil sheen from water containing oil content of COD at about 300 mg/L. It is more effective than traditional ozonation (Cha et al., 2010) using small O_3-containing bubbles, which provide reactive zones at the gas-liquid interface to accelerate the chemical conversions. The presence of an expanding gas bubble interface created by pressure cycles appeared to be more effective than bubbling ozone alone to react with hydrophobic compounds, resulting in ketons, aldehydes and acids (Beltran, 2004; Cha et al., 2010). When the small droplets of oil contact with ozone at the reactive interface, the nonpolar aliphatic compounds are functionalized with keto and carboxylic groups; their surface properties changes resulting in larger droplets through interactions of bonding and bridging, which become easier to be captured by sand filter (Cha et al., 2010). The mechanism is shown in Figure 1. More cycles can be used for higher contaminant level. Hence, HOT has application potential for oil spill cleanup.

Objectives

An important goal is to develop a potentially viable on-site treatment technique in the event of an oil spill, reducing the need to remove and transport a large amount of contaminated water from site. In this study, a laboratory-scale HOT-SF system was tested for removal of oil from contaminated water simulating oil spills in freshwater, groundwater, and sea water. Two treatment stages were used in which flotation and sand filtration were used in the first stage to remove the bulk of the oil and pressure-assisted

ozonation and sand filtration were used in the second stage to remove and polish the
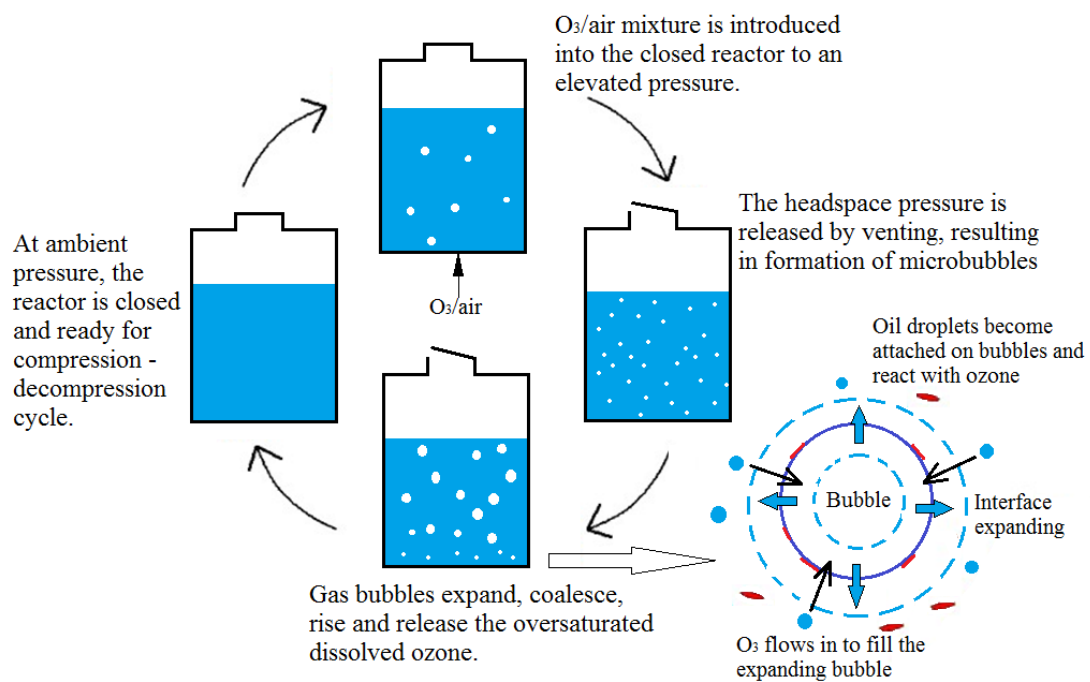
water to acceptable discharge level.

O₃/air mixture is introduced into the closed reactor to an elevated pressure.

At ambient pressure, the reactor is closed and ready for compression - decompression cycle.

O₃/air

The headspace pressure is released by venting, resulting in formation of microbubbles

Oil droplets become attached on bubbles and react with ozone

Bubble

Interface expanding

Gas bubbles expand, coalesce, rise and release the oversaturated dissolved ozone.

O₃ flows in to fill the expanding bubble

Figure 1 Mechanism of heighted ozone treatment for hydrophobic compounds (Hong et al., 2008; Cha et al., 2010)

CHAPTER II

MATERIAL AND METHODS

<u>Synthetic Oil Spill – Preparation and Characteristics</u>

The synthetic oil spill sample was prepared by mechanically stirring a mixture of 2.5% (volume) of Great Natural Butte crude oil (UT, USA) and water until homogeneous at room temperature (~20 °C). Tap water, Utah Lake water and Great Salt Lake water were chosen to represent oil-contaminated fresh water, ground water and sea water. The characteristics of the waters are shown in Table 3. COD (HACH 800, high range and low range), dissolved COD (filtered by 0.45 μm filter paper), BOD (5 day test), pH, turbidity (HACH 2100N turbidimeter), oil and grease (EPA method 1664), and oil sheen (Lehr et al., 1994) are triplicate tested before and after the treatment.

Table 3 Typical quality characters of the waters

	pH	Turbidity, NTU	Total hardness, $CaCO_3$ mg/L	Ca hardness, $CaCO_3$ mg/L	Alkalinity, $CaCO_3$ mg/L	TS, mg/L	VTS, mg/L
Tap water	7.70	0.445	129	98	135.9	294	N/A
Utah Lake water	8.48	0.228	180	80	1087.1	762	N/A
Great Salt Lake warer	8.18	2.73	--	--	462.2	101×10^3	19.7×10^3

The water sample to be analyzed was extracted by DCM (200 mL of water sample by 50 mL of DCM), and the extract was concentrated to 1 mL by a gentle N_2 stream and analyzed by GC-MS. The GC–MS system with a GC 6890 N (Agilent Technologies) installed with a capillary column (HP-5 ms, nonpolar column, 30 m × 0.25 mm × 0.25 μm, Agilent Technologies) coupled with a MSD 5973 (Agilent Technologies) and controlled by the MSD Productivity ChemStation software (Agilent Technologies). One μL of sample was injected into a splitless inlet at 250 ˚C. The sample was carried by helium gas at 35 cm/s and the mass range from 50 to 550 m/z was scanned. The oven temperature was programmed from 50 ˚C (initially held for 1 min) to 100 ˚C at 25 ˚C/ min, followed by 100 to 350 ˚C at 5 ˚C/ min and at the end the temperature was maintained for 5 min. The NIST Mass Spectral Library – G1033 was used for species identification.

The Flotation – SF – HOT – SF System

The synthetic spill sample was treated by sequential processes of flotation, stage-1 sand filtration (SF1), heighted ozone treatment (HOT) and stage-2 sand filtration (SF2). A schematic diagram of the system is shown in Figure 2 and Figure 3.

The flotation column was with 7 cm diameter and 60 cm depth of water. A bubbling diffuser for gas was installed at the bottom that was connected to a small compressor capable of delivering 4.5 L/min of air (Petco). The bubble sizes were 1~2 mm. A 1 cm thick straw disk was constructed by adhering a bundle of straws of 1 cm in length with silicon gel; the straw disk was installed inside the column at 40 cm from the bottom to direct bubble flow to prevent sinking of the oil droplets. Continuous, downward flow was operated at 5.2 cm/min.
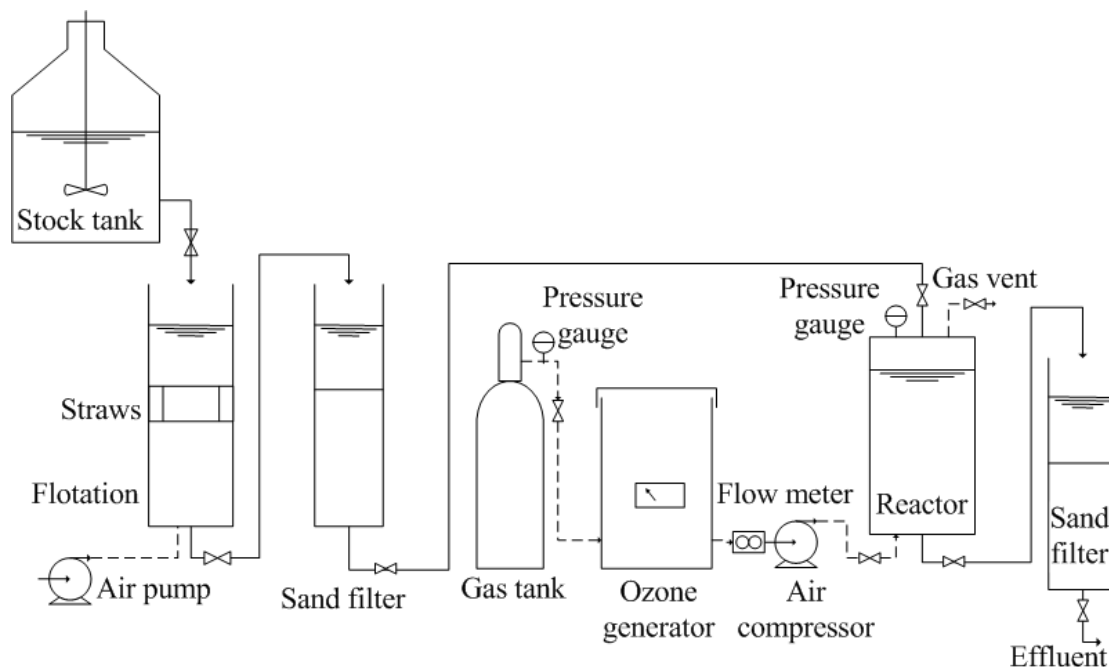
Figure 2 Treatment train of the system

After about 5 L of spill water were collected, the floating oil at the water surface was removed. The oil recovery rate via the flotation column was 58% ~74%, which was not influenced by the water type. The content of the recovered oil was analyzed and found similar to the crude oil spike, which is shown in Figure 4 of GC/MS results.

The stage-1 sand filter was 5.5 cm in diameter and filled with 20 cm in depth of 0.25~0.42 mm sands. Continuous filtration rate of 8 cm/min was used. At the exhaustion when the effluent COD reached 200 mg/L, the sands were regenerated by transferring to a beaker and heating in 500 mL boiling water (sand water ratio was about 1:1). The water containing the recovered oil was returned to the flotation column of the process train, and regenerated sands were returned to the sand filter for continued use.
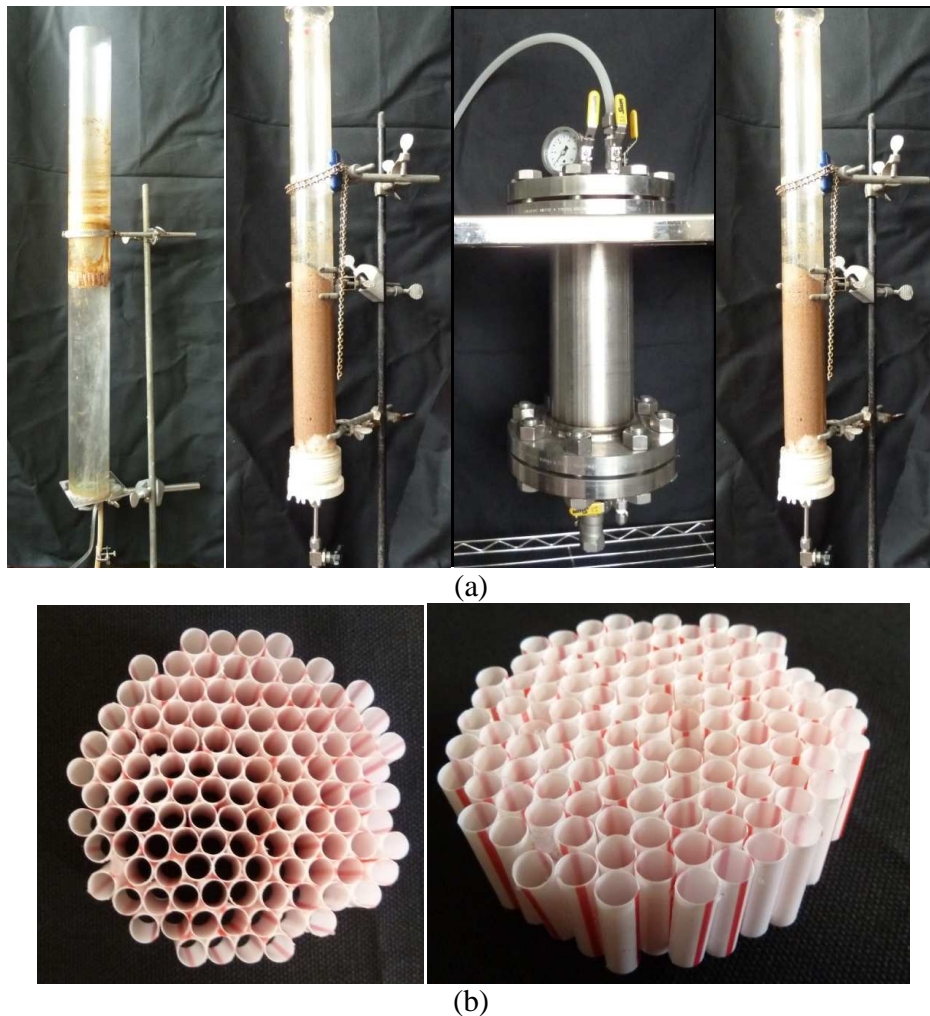
(a)

(b)

Figure 3 Photographs of the system: (a) photographs of the flotation column, stage-1 sand filter, HOT reactor, and stage-2 sand filter; (b) straws bundle installed in the flotation column.

Ozone (~1.5% by volume) was generated at 2 L/min by an ozone generator (Model T-816, Polymetrics Corp.) from dry, filtered oxygen at 100 V. HOT effectiveness and SF capacities were performed with bubbling ozonation which was carried out in a 2-L beaker containing 1.8 L of water at room temperature (~20 ˚C). In the HOT effectiveness experiment the duration was 20 min and in the SF capacity experiment the duration was 5 min.

Pressure assisted ozonation was performed in a 2.2 L closed stainless steel reactor containing 2 L water sample. The pressure reactor design featured a gas vent, pressure gauge and water inlet at the top; gas inlet and water outlet were in the bottom. The reactor was filled with water sample, and the treatment began with a compression stage when the gas inlet valve was opened to allow ozone/air mixture to enter that was driven by a gas compressor (GAST). Once the designated pressure was reached (100 psi for 10 s, 80 psi for 8 s, 50 psi for 5 s, with 0.2 L head space; 100 psi for 18 s, 80 psi for 15 s, 50 psi for 10 s, with 0.7 L head space), the gas inlet valve was turned off, and the gas vent valve was turned on and adjusted to the speed of the gas to proceed with the decompression for 1 min, thus completing the pressure cycle. The compression-decompression pressure cycle was repeated as specified, each cycle requiring about 70 s to be completed. The operation time of each cycle depended on the headspace volume (or water sample volume) and the pressure operated.

The stage-2 sand filter was 7 cm in diameter and filled with 25 cm in depth of 0.25~0.42 mm and 0.12~0.25 mm sands with 1:1 volume ratio. The filtration rate was 2 cm/min. When the flowrate dropped to 1 cm/min, the bed was backwashed with tap water at equal volume to the sands and the backwashing water was sent to SF-I. However, after repeated back washings, oil sheen in the effluent water began to develop. At this point, the sands were removed and regenerated in an oven at 550 ˚C for 30 min. In preparation for fresh use, the sands were sieved and washed with 10 M HCl and 10 M NaOH solutions sequentially, and then washed with tap water and DI until stable in pH. The sands were dried and heated by 550 ˚C for 30 min.
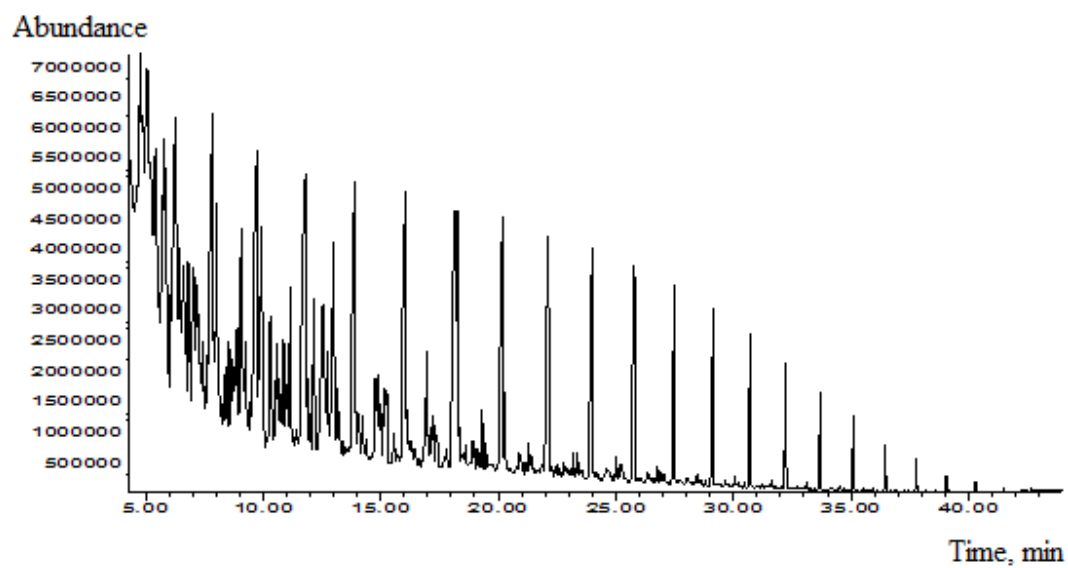
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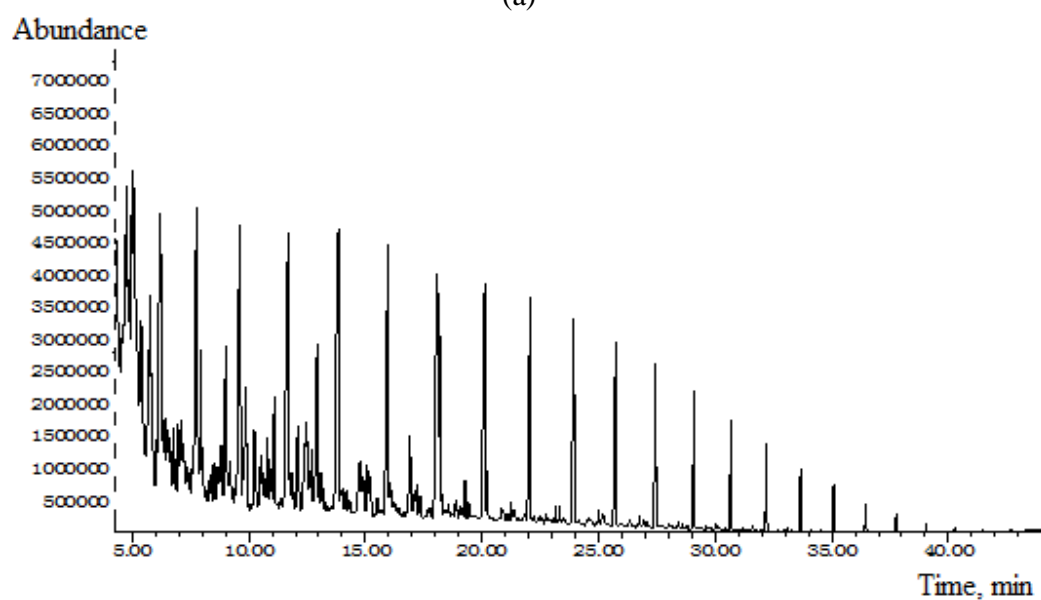
(b)

Figure 4 GC/MS result of crude oil and regenerated oil: (a) crude oil; (b) oil regenerated

HOT Effectiveness and SF Capacity

HOT was operated with varied pressure and pressure cycles with tap water samples spiked with 0.025% (v) crude oil, representing the average oil content after SF-I. Removal of O&G and COD were measured in triplicate.

Because of its high capacity, sand filtration capacity was tested in small 10-mL syringes packed with sands. The syringes were filled with 7 mL 1:1 0.25~0.42 and 0.12~0.25 mm sands. The flowrate was 2 cm/min and the ratio of diameter and depth of this small syringe was the same as the full size column. Filtration capacities were measured for water samples treated under different HOT conditions with tap water samples spiked with 0.075% (v) crude oil, representing the maximum oil content after SF-1. Filtration capacities were measured in triplicate as defined by the effluent quality in terms of the presence of oil sheen, COD, BOD, pH, turbidity, and O&G. The results were used to determine optimal operation conditions of HOT.

CHAPTER III

RESULTS AND DISCUSSION

Treatment Condition Optimization

The effects of pressure and operation cycles on HOT on treatment outcomes are shown in Figure 5.

COD and O&G have been tested because COD represents the status of carbon (organic or inorganic), and O&G represents the structure of organic carbon (solubility). From the results, it was quite obvious that pressure-assisted ozonation broke down crude oil (removal rate up to 87%). The hydrocarbon molecules were likely transformed into organic acids and became more soluble; thus the COD removal rate was low compared to O&G (27%~35% on average). Scott et al. showed 50% COD removal but no TOC removal and naphthenic acid removal to < 2 mg/L from 60 mg/L after 130 min ozonation, suggesting ozone was capable of breaking the hydrocarbon structures to simpler organic forms. Compared to ozonation alone, pressurization and depressurization enhanced the treatment. Removal of O&G under ozonation alone for 20 min was 55.38%; however, it was 81.97% when 100 psi of pressure cycles were applied while the reaction time decreased to about 6 min. The latter was more rapid and effective. With increased pressure and pressure cycles, removal rate increased to a certain degree; however, the removal rate of O&G did not increase significantly with the pressure beyond 80 psi. With

compression pressure of 100 psi, O&G removal did not increase with pressure cycles beyond 5.

After various HOT treatments, the waters were filtered by sands. Table 4 shows filtration capacities for various effluents. For untreated water or water inadequately treated by HOT, the volume that could be effectively treated by sand filtration is very limited, and backwashing would not eliminate oil sheen in the effluent. Small oil droplets were likely trapped in the sands by adsorption and adhesion, and once the space was saturated, oil sheen occurred in the effluent. Pressure-assisted ozonnation may have caused the small oil droplets to agglomerate more easily to become larger, more readily intercepted on the sands surface via filtration. With ozonation, the oil's characteristics were changed, which might interact more strongly with the sands to be retained. With increased pressure and number of pressure cycles treatment followed by sand filtration, the BOD/COD ratio increases to some degree, which indicated their being more amenable to biological treatment if needed. However, backwash is not always effective for regenerating the filtration effectiveness. After some operation time, oil sheen in the effluent began to appear. At this point, the sands needed to be regenerated by heating at 550 °C for 30 min to get rid of adhered organic matters on the sands' surface and crevices. Because heating sands would be a relatively more expensive process, an extended operation time prior to heat regeneration would be important for practical applications. The filtration capacity of sands reached 151 times of its own bed volume when 8 cycles of ozonation at 100 psi were applied, and increasing the cycle number did not enhance the capacity significantly. Thus HOT of 8 cycles at 100 psi were seen as optimal.

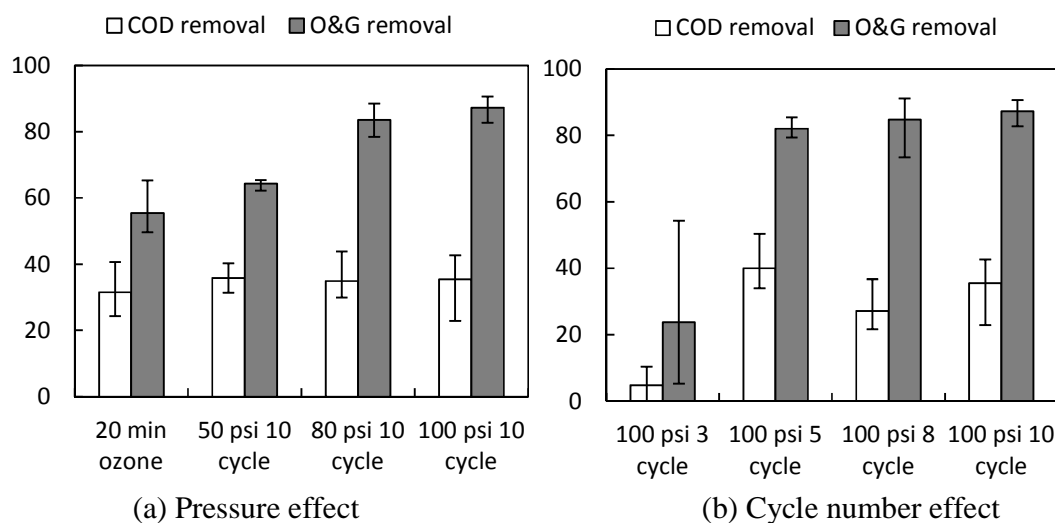(a) Pressure effect   (b) Cycle number effect

Figure 5 Effects of pressure and pressure cycle of HOT on removal of COD and O&G
(Initial COD: 100 mg/L, Initial O&G: 70 mg/L)

Table 4 Sand filtration capacity under different HOT conditions (Initial COD: 300 mg/L)

Effluent quality	COD, mg/L	BOD/ COD, %	pH	Turbidity, NTU	O&G, mg/L	Treated volume / sand bed volume before oil sheen	Back wash # before oil sheen
80 psi 10 cyc	34.0±1.2	34.50±1.27	7.37–8.77	2.32±0.66	NA	37.6±4.7	1
100 psi 5 cyc	36.8±9.2	31.6±9.3	8.30–8.46	1.06±0.66	NA	57.6±3.8	2
100 psi 8 cyc	41.5±3.3	30.9±4.0	7.80–8.30	0.58±0.37	NA	151.4±2.8	3
100 psi 10 cyc	43.3±4.3	31.5±4.4	8.10–8.32	1.40±0.41	NA	135.7±2.8	3
Ozonation 5 min	38.6±0.6	21.5±4.0	8.24–8.28	1.02±0.49	NA	31.0±1.0	1
100 psi 8 cycle without ozone	14.8±2.0	26.0±17.0	8.13–8.27	1.18±0.20	NA	30.0±2.9	1
No treatment	11.3±4.3	--	8.25–8.33	0.69±0.33	NA	10.0±2.0	0

Oil Spill Removal

Table 5 shows the effectiveness of oil removal from different types of water using the entire process train.The overall removal rate of COD and O&G reached 99.8 % for all three types of contaminated water, showing no apparent influence on effectiveness by the presence of salts (hardness and alkalinity). Turbidity was from thousands to around 0.6, which was similar to the tap water turbidity. O&G was removed to below the detection limit and no oil sheen was seen after 24 h. Effluent COD was 20 – 36 mg/L, which was deemed biodegradable because of BOD/COD > 30%, suggesting possible further biological degradation if needed. In the effluent, most organic matters were soluble (sCOD/COD > 85%); this was consistent with GC/MS results of Figure 6, which indicated very limited compounds (small molecules) in the final effluent from SF2.

Ozonation produced some organic acids, while sands might have allowed ions to dissolve into the water, thus influencing the pH. With more salts present in the water, the contaminated water was more stable in pH, because of the buffering salts.

Extensive research was on salinity (salt concentration) effect on treatment by flotation and ozonation (Honn and Chavin, 1976; Strickland, 1980; Oliveira et al., 1999; Moosaiet et al., 2003).

Studies (Marrucci and Nieoclemo, 1967; Strickland, 1980) showed that bubble size decreased from 1 mm in distilled water to 400 μm in diameter at 3% NaCl but no further decrease at higher salinity up to 20% NaCl. Furthermore, with decreasing bubbles size, oil recovery increased significantly with salt concentration from 0 to about 3% but no further recovery increased beyond that concentration.

Table 5 Oil removal from different spiked waters

|		COD, mg/L (Removal, %)	sCOD /COD, %	BOD/ COD, %	pH	Turbidity, NTU	VDS, mg/L (Removal, %)	O&G, mg/L (Removal, %)
Tap water	Influent	17700±4200	--	--	8.14–8.24	2764±82	466±22	6703±1134
	Flotation	6293± 1153 (64.4)	1.4	0.70	8.41–8.47	370±40	92±5 (80.3)	863±243 (87.1)
	SF1	170±40 (99.0)	27.1	26.7	8.39–8.49	8.4±2.4	98±18 (79.0)	110±17 (98.4)
	HOT	91±26 (99.5)	50.5	33.1	8.03–8.23	7.9±1.8	97±21 (79.2)	5.2±1.0 (99.9)
	SF2	29±7 (99.8)	94.3	32.7	8.33–10.39	0.57±0.34	N/A	N/A
		COD, mg/L (Removal, %)	sCOD /COD, %	BOD/ COD, %	pH	Turbidity, NTU	VDS, mg/L (Removal, %)	O&G, mg/L (Removal, %)
Utah lake water	Influent	19530±2400	--	--	8.24–8.34	3875±28	712±94	9152±1315
	Flotation	2050± 250 (89.5)	4.0	3.3	8.34–8.50	121±25	104±2 (85.4)	159±26 (98.3)
	SF1	80.4±6.4 (99.6)	62.7	42.3	8.40–8.48	4.6±0.2	118±14 (83.4)	42.1±8.7 (99.5)
	HOT	59.6±0.4 (99.7)	65.2	49.7	8.28–8.32	9.1±0.8	N/A	7.6±2.4 (99.9)
	SF2	22±2.8 (99.9)	86.9	48.0	8.39–8.49	0.61±0.04	N/A	N/A
		COD, mg/L (Removal, %)	sCOD /COD, %	BOD, mg/L	pH	Turbidity, NTU	VDS, mg/L (Removal, %)	O&G, mg/L (Removal, %)
Great salt lake water	Influent	--	--	--	8.18–8.30	3938±12	--	11371±904
	Flotation	--	--	54.7±0.5	8.17–8.23	291±6	--	1361±611 (88.0)
	SF1	--	--	19.8±0.5	8.13–8.19	6.8±0.1	--	51.0±9.6 (99.5)
	HOT	--	--	12.0±2.8	8.11–8.13	14.6±4.0	--	7.5±2.1 (99.9)
	SF2	--	--	N/A	7.92–8.06	0.66±0.02	--	N/A
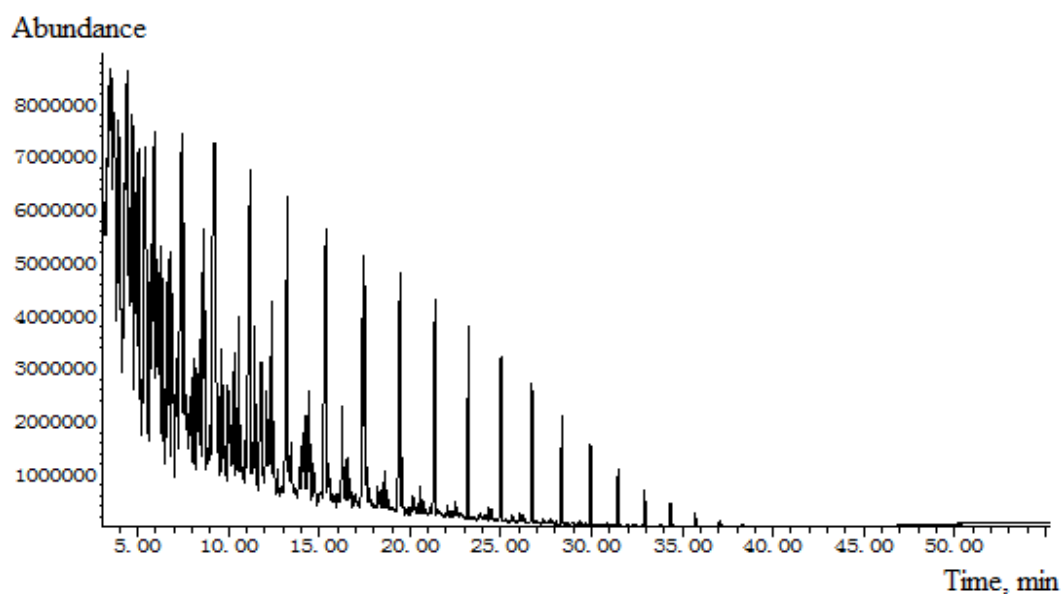
(a) Influent
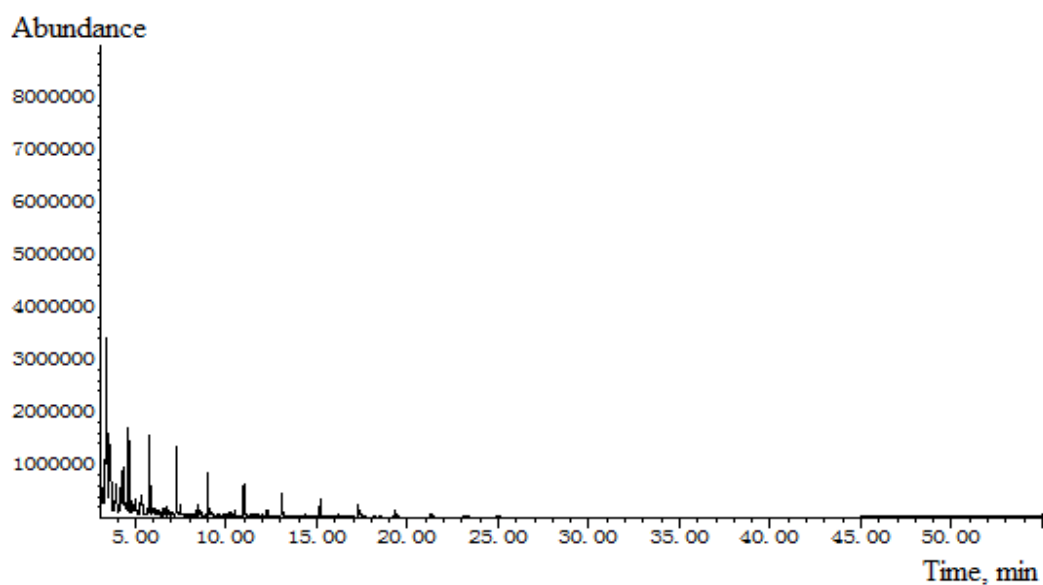
(b) Flotation

Figure 6 GC/MS results for the treatment process: (a) Influent: 2.5% oil in tap water; (b) Flotation: HRT 11 min, flowrate 5.2 cm/min; (c) SF1: HRT 2.5 min, flowrate 8 cm/min, grain size 0.25~0.44 mm; (d) 100 psi 10 cycles, ozone flowrate 2 L/min, ozone concentration ~1.5 %, compressed ozone concentration 0.02%; (e) SF 2: HRT 12 min, flowrate 2 cm/min, grain size 0.25~0.44 mm/0.12~0.25 mm at 1:1 ratio.
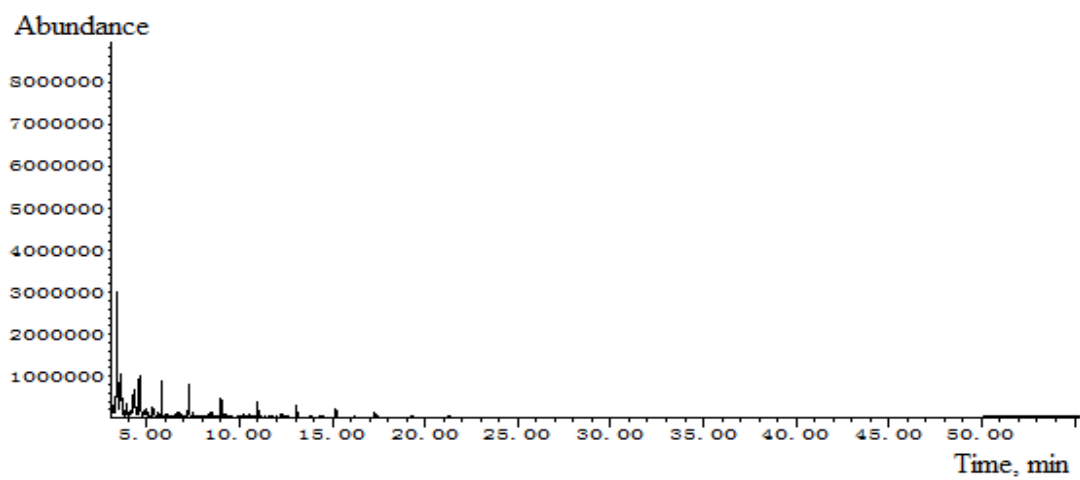
(c) SF-1
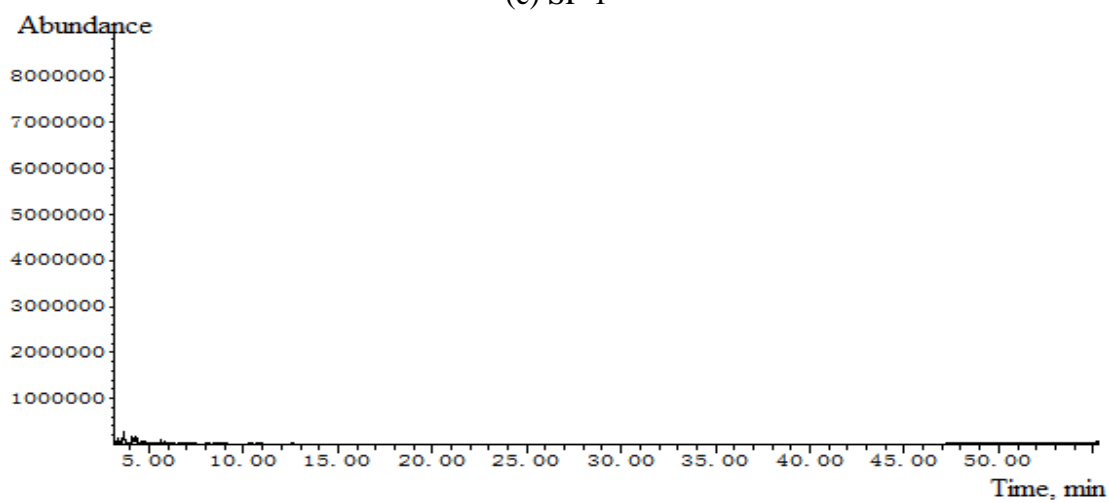
(d) HOT
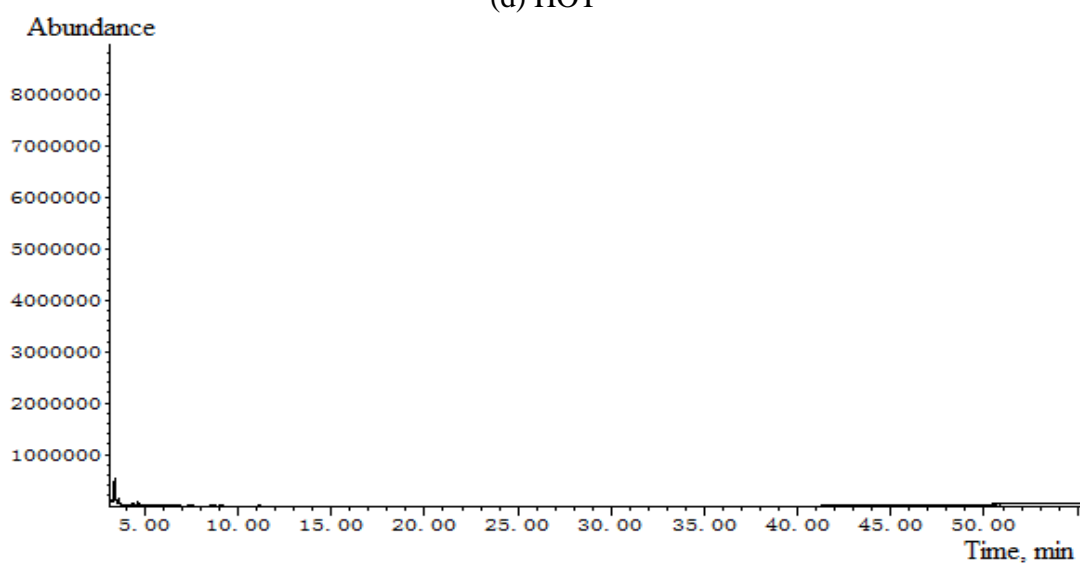
(e) Final effluent

Figure 6 Continued

Oliveira et al. (1999) also showed that salinity increased the flotation efficiency by reducing the induction time and increasing collision efficiency in the study of dissolved gas flotation. In this study, oil recovery from flotation column showed a significant increase from 87% to 98% with Utah Lake water, whose salinity was about 1‰ (Utah Lake Report, 2006), which was similar to past results; however, the recovery decreased to 88% with the water salinity at 25‰ for Great Salt Lake water, which did not show a further increase or high recovery rate.

Honn and Chavin (1976) showed that ozonation was a rapid and effective process to treat seawater; and Anderson et al. (2012) showed that salinity or other inorganic constituents did not affect the treatment process for oil sands. In this study, pressurized ozonation presented a stable operation at a wide range of salinity, agreeing with the prior results of ozonation studies.

<u>Comparison of Treatment Methods</u>

Presently, oil recovery by sorbents is most common (Lin et al., 2012). Numerous studies have focused on sorbent materials from natural to manmade fibers with reported recovery of 10 - 150 g oil/g sorbent (Choi and Cloud, 1992; Lin et al., 2012; Zhu et al., 2011). However, most of these were performed in small scale in the laboratory where sorption capacity was found at equilibrium, which was uncommon under field conditions. Furthermore, regeneration and handling of the materials were rarely discussed, nor were organic reagents used to regenerate the sorbents. Hussein et al. (2011) suggested composting of used sorbents; however, not all sorbents could satisfy the compost requirements. Cheng et al. (2011) developed a device for oil spill response with

integrated functions of oil containment booms, oil-sorption materials, oil skimmers, and water oil separation. However, the material was mainly silver and nickel, which were of high-cost, and organic solvents were needed to clean the device afterward. Furthermore, the removal rate was about 90% and the toxicity and the oil concentration were not discussed. In contrast, HOT system may have shown advantages beyond mechanical recovery of oil by sorbents. The studied HOT treatment train removed the oil from contaminated water, apparently leaving biodegradable products in the water, and regeneration of the process appeared practicable. Thus, the HOT treatment train has potential as an onsite treatment response to oil spills.

CHAPTER IV

CONCLUSIONS

In this study, a laboratory-scale treatment train involving flotation, sand filtration (SF I), heighted ozonation treatment (HOT), sand filtration (SF II) system was constructed and tested to treat oil-contaminated waters of different salinities simulating impact from an oil spill.

The flotation was operated at a downward flow velocity of 5.2 cm/min at room temperature. Oil was recovered from the column periodically at a recovery rate of 58 % – 74 %. The first-stage sand filter was operated at a filtration velocity of 8 cm/min until the effluent COD of 300 mg/L, at which time the sands were regenerated by hot water. Optimum operation conditions for HOT were 8 cycles using compression pressure of 100 psi; achieving best effluent quality (84.76% O&G removal and 27.14% COD removal) and the longest filtration life for the second-stage sand filter. Before the exhaustion of the sand filter (SF-II), backwash was adequate to maintain the filtration velocity at 2 cm/min; after the throughput of 150 times the sands volume, the sands required regeneration at 550 ˚C for 30 min.

The system removed > 99.9 % of Oil and Grease, 99.8 % of COD, and complete removal of VDS. The effluent turbidity was under 0.7 NTU, similar to tap water turbidity. The HOT – SF-II treatment increased soluble COD by > 85% and BOD/COD ratio by > 30%, which suggested the possibility of further biological degradation if desired. Although affected by sand filtration and HOT processes, the pH of the water after

treatment was relatively stable at about 8.0, which would not adversely impact receiving natural water.

Increasing salinity from fresh water to groundwater increased oil removal by flotation, albeit no further increases were seen at the level of seawater salinity. For HOT and SF processes, there were no significant differences in varied salinities. Overall, salinity had little effect on treatment outcomes.

The treatment process could treat 0.22 L/min for oil spill with 2.2 L HOT reactor. No other chemicals were used in the process other than air or oxygen used to generate ozone, and the treated water removed of oil and the potential of oil sheen formation was fit to discharge. About 60% of the oil used for spiking was recovered. These features showed a potential of the system as an onsite treatment response to the event of an oil spill.

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