

UTAH DIVISION OF WATER QUALITY

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Willard Bay Project Proposal Form

NOTE: Proposal must be no longer than 6 pages. Supplemental documents such as letters of support, information to demonstrate previous project implementation and other relative supportive documents may be submitted in addition to this form.

Applicant Name: Andy Hong

Co-Applicant Name(s) (if applicable): Otakuye Conroy-Ben

Project Title: Mobile Treatment System of Hydrocarbon Impacted Water for Immediate Release

Agency or Business Name (if applicable): Dept Civil & Environ. Eng., University of Utah

Mailing Address: 2000 MCE City: SLC State: UT Zip: 84112

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Individual Non-Profit Govt. Agency Academic Commercial Other

1. Estimated Project Costs:

Labor	\$ <u>129,579</u>
Materials	\$ <u>18,000</u>
Equipment	\$ <u>75,800</u>
Administration	\$ <u>75,254</u>
Miscellaneous	\$ <u>6,000</u>
TOTAL	\$ <u>304,633</u>

Other sources of project funding:

<u> </u>	\$ <u> </u>	<u> </u>	\$ <u> </u>
Source	Amount	Source	Amount
<u> </u>	\$ <u> </u>	<u> </u>	\$ <u> </u>
Source	Amount	Source	Amount
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Source	Amount	Source	Amount
<u> </u>	\$ <u> </u>	<u> </u>	\$ <u> </u>
Source	Amount	Source	Amount

Total project cost including other sources of funding: \$ 304,633
(please include bids for labor, equipment, rentals, etc.)

- Describe the purpose and need of the project: below
- Estimated time frame of the project with significant milestones (Note: Project must be completed with final reports filed by January 1, 2018): below

4. Describe the location of the project with attached location map, including details on the total area that will be directly enhanced by the project: _____
5. Describe how the project will specifically enhance and protect waterways affected by the Willard Bay diesel release and improve the conditions of one or more of the following: wildlife, habitat, natural vegetation, water quality or emergency response:
6. Describe project's connectivity to other natural areas or projects that further enhance wildlife, habitat, natural vegetation, water quality or emergency response:
7. Describe any additional social benefits of implementing this project:
8. Project plans and details, including rights to work on specified piece of land:
9. Describe your experience in implementing projects of similar scope and magnitude:
10. Describe how ongoing maintenance of the project will be funded and carried out:
11. List consultants or agency partners that have participated in project development (below):

Name/Company

Address

Phone

Name/Company

Address

Phone

Name/Company

Address

Phone

Signature _____

A. Han

Applicant

Date _____

5/5/14

Signature _____

Clayton

Co-Applicant (if applicable)

Date _____

5/5/14

2. Purpose and Need of this Project

Increasing volumes of petroleum crude and products being produced and transported throughout the world in recent decades have resulted in increased risks of spill and high-profile spill incidents of significant environmental and ecological impacts over extended periods of time. Monthly, thousands of oil spills in smaller scales occurred on land freshwater systems throughout the world from production activities and transports by pipeline, rail, and truck, accounting for 11,000 t of pipeline spills annually, 1,700 t of refinery spills, 1,300 t of tanker truck spills, and 500 t of tanker ship spills yearly in the US (Fingas, 2011). Oil spills release hazardous chemicals such as polycyclic aromatic hydrocarbons that are toxic to aquatic life and human and may require decades to remove (Seymour and Geyer, 1992; Allan et al., 2012).

While immediate *in situ* and *ex situ* responses have been implemented, none are available for onsite treatment of contaminated water for immediate release of the treated water. We propose here to develop and implement a treatment scheme involving ozonation and sand filtration intended for immediate treatment and discharge of the impacted water. The technology will respond to a spill event, in which recovered impacted water or wash water can be treated onsite and immediately released. It has the potential to eliminate the need to transport a large amount of impacted water from the spill location and to recycle and reuse water onsite for cleanup activities.

Technology description

Neither conventional ozonation nor sand filtration (SF) alone had been shown to treat produced water effectively. We recently demonstrated, however, a pressure-assisted ozonation technique coupled with sand filtration for removal of oil and prevention of oil sheen. Unlike ordinary ozonation practice, heightened ozonation treatment (HOT) incorporates rapid, successive cycles of compression and decompression during ozonation (Cha et al., 2010; Hong & Ting, 2013). Small O₃-containing bubbles are created that provide reactive zone of gas-liquid interface, resulting in heightened chemical conversions (see Fig. 1).

In a recent project (Hong & Ting, 2013), we spiked waters of tap, Utah Lake, and Great Salt Lake sources with crude oil of the Great Natural Butte of Utah at 2.5% and 0.025% oil (v/v) and tested for treatment. The results showed near complete removal (100%) of both Chemical Oxygen Demand (COD) and Oil & Grease (O&G) from initially 20000 and 11000 mg L⁻¹, respectively, via flotation pretreatment, ozonation in pressure cycles, and sand filtration. At lower oil level of 0.025%, complete removal of COD and O&G from waters were achieved without floatation pretreatment. The treated waters showed reduction of turbidity to < 1 from 4000 NTU and high Biochemical Oxygen Demand/COD ratio of 0.3-0.5 that reflected highly biodegradable residual organics. The results showed synergistic oil removal when two well-practiced methods, namely ozonation and sand filtration that either alone seems ineffective, are combined sequentially. It indicates a potential onsite treatment response for oil spill incidents where the collection and transport of a large amount of contaminated water may be avoided.

Research Plan

Three major tasks are to be accomplished in three years:

Task 1: Development and test of a new heightened ozonation treatment Engine (HOT Engine) for continuous treatment of impacted water

HOT Engine (Heightened Ozonation Treatment Engine) for continuous treatment operation

Previously, HOT was implemented using pressure cycles in batch mode. This project will extend HOT to a continuous mode of operation. The HOT Engine is a treatment vessel akin to the cylinder of an internal combustion engine. As illustrated in Fig. 2, the operation of a two-stroke engine cylinder consists of the compression/intake stroke and the exhaust stroke.

When the intake fuel mixture is replaced by a contaminated water and ozone gas and the crankshaft is driven by another motor, the engine cylinder becomes a treatment vessel that carries out compression and decompression. The water being treated is subjected to a designated number of pressure cycles (i.e. number of compression and decompression strokes), as controlled by how frequently the intake/exhaust valves are opened relative to crankshaft rotation (rpm).

Development of the HOT Engine treatment will start with a plunger pump as a prototype incorporating an intake system that introduces a mixture of water and ozone gas and an outlet that controls contact time and extent of treatment for the water. Treatment parameters to be studied include: ozone concentration (i.e. ozone/air mixture), gas/water volume ratio, contact time as determined by treatment throughput (L/min), compression ratio as determined by cylinder characteristics as well as the gas volume, hydrocarbon concentration, and engine speed (rpm). Effluent characteristics will be evaluated.

Task 2 in year 2: Test of integrated system (HOT engine & sand filtration) for treatment of contaminated water and wash water.

The hydrocarbon impacted water will be treated in sequence by the HOT Engine treatment vessel and a sand filter at rapid filtration velocity (e.g. 6 cm/min) and hydrocarbon removal will be determined. Optimization will be performed to identify practicable operation ranges including ozonation extent and filtration velocity. Effluents will be characterized by standard tests including COD, BOD, turbidity, and hydrocarbon contents. Biodegradability and potential toxicity of any residual compounds will be determined.

Task 3 in year 3: Design, construction, and test of mobile unit

Once treatment effectiveness and operation requirements are optimally defined in the previous tasks, a mobile trailer unit housing various process equipment will be built and tested. Various equipment units include the treatment cylinder, gas/liquid mixture pump, ozone generator, sand filtration cartridge, water tanks, electrical generator, and the necessary plumbing infrastructure. The constructed unit will be tested at an oil production site where produced water will be tested for hydrocarbon removal.

The Process – Expanding Microbubbles

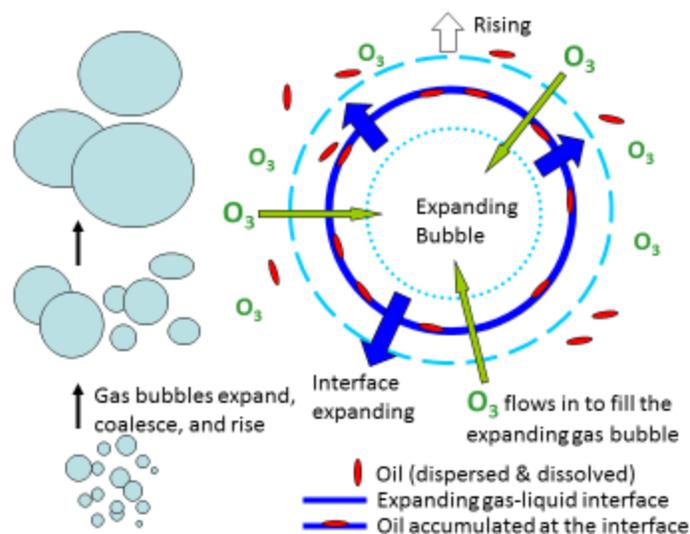


Figure 1. Expanding microbubbles provide ample reactive interfacial zone for ozone and hydrocarbon contaminants to react.

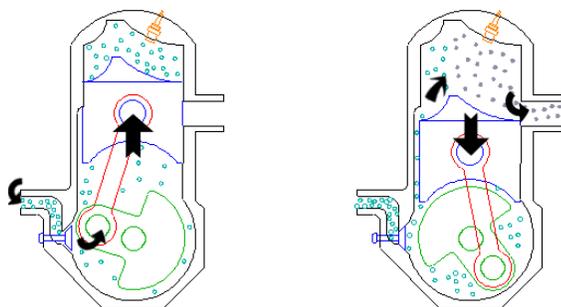


Figure 2. Two-stroke Engine as treatment vessel (illustration from <http://www.animatedengines.com/twostroke.html>)

References:

- Fingas, M., 2011. *Oil Spill Science and Technology: Prevention, Response, and Clean Up*. Elsevier. Burlington, MA.
- Seymour, R.J., Geyer, R.A., 1992. Fates and effects of oil spills. *Annu. Rev. Energ. Env.* 17, 261-283.
- Allan, S.E., Smith, B.W., Anderson, K.A., 2012. Impact of the deepwater horizon oil spill on bioavailable polycyclic aromatic hydrocarbons in Gulf of Mexico coastal waters. *Environ. Sci. Technol.* 46, 2033-2039.
- P.K.A. Hong and T. Xiao, "Treatment of oil spill water by ozonation and sand filtration," *Chemosphere*, vol. 91, pp. 641-647, 2013.
- Z.Chu, C.-F. Lin, C.-J. Cheng and P.K.A. Hong, "Removal of oil and oil sheen from produced water by pressure-assisted ozonation and sand filtration," *Chemosphere*, vol. 78, pp. 583-590, 2010.

3. Estimated time frame of the project with significant milestones

Year 1 (June 1, 2014 – May 31, 2015): Development and test of the HOT Engine

Year 2 (June 1, 2015 – May 31, 2016): Treatment test of the integrated treatment system (HOT/SF)

Year 3 (June 1, 2016 – May 31, 2017): Construction and test of mobile treatment system

July 1, 2017: Final report to be turned in

4. Location of the project

Research will be conducted in laboratories of the University of Utah. Natural water will be obtained from Willard Bay within the location of the East and West booms. The water will be spiked with diesel fuel and crude oil for hydrocarbon removal experimentation.

5. Waterways that will be enhanced

This project to develop onsite treatment system for emergency response will benefit future releases at Willard Bay and other locations of incidents throughout the country.

6. Project's impact on other natural areas and emergency response

The system being developed will treat all impacted waters including wash water collected by booms during response to release sources of land and waterways. The ability to contain spread by booms will be greatly enhanced if technologies for onsite treatment and immediate release are also available.

7. Social benefits

The ability to respond effectively to spill incident and provide treatment for wash water will minimize environmental impacts of the incident and reduce impacts to wildlife of affected areas.

8. Project plans to work on land

The project involves sampling natural water from Willard Bay for experimentation. The technology deployment is intended for future incident at Willard Bay or other locations. At the third year, the team will perform field test of the mobile treatment unit at an oil production site where produced water with hydrocarbon contaminants is generated. The team and University has a significant list of interested parties in the oil and gas industry with produced water concerns.

9. PI experience in implementing projects

The PI Andy Hong, P.E., professor of civil and environmental engineering, has over 25 years of experience in research and technology development and secured 6 patents in various water treatment and remediation technologies (see enclosed relevant article on hydrocarbon removal). He published over 60 journal articles and 100 conference presentations. Dr. Conroy, Co-PI, has expertise in microbiology and will evaluate the biodegradability aspect of the treated effluent.

10. Ongoing maintenance of the project

The project will result in a demonstration mobile unit that can be deployed in future release incidents at Willard Bay or nearby locations. It will establish the design and operation of the mobile treatment system that can be replicated and be ready at various locations.



Removal of oil and oil sheen from produced water by pressure-assisted ozonation and sand filtration

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ARTICLE INFO

Article history:

Received 26 August 2009

Received in revised form 20 October 2009

Accepted 20 October 2009

Keywords:

Interface
Produced water
Treatment
Ozonation
Pressure
Sheen
Oil

ABSTRACT

Ever increasing energy demand worldwide necessitates energy supply, inevitably leading to an increasing volume of process waters containing hydrocarbon contaminants. Among them, dispersed and dissolved oils in produced water need to be removed adequately in order to reuse or avoid surface sheen from coastal discharge. We have recently developed a new ozonation technique coupled with sand filtration to quickly remove oil from process water and prevent oil sheen. The technique incorporates rapid, successive cycles of compression and decompression during ozonation. Gas bubbles expanding from small to large sizes occur that provide ample reactive zones at the gas–liquid interface, resulting in heightened chemical conversions—notably the conversion of hydrophobic hydrocarbon molecules into hydrophilic ones. This study examined the removal of hydrocarbons and sheen according to treatment parameters and configurations, as assessed by changes in turbidity, COD, BOD, and sheen presence following treatment. When a synthetic produced water containing 120 ppm of oil (about 100 ppm of dispersed and 20 ppm of soluble oil at a total COD of 320 mg L⁻¹) was subjected to 10 pressure cycles (reaching 1.0 MPa; 20 s each) of ozonation and sand filtration at 6 cm min⁻¹ and then repeated by 20 cycles of ozonation and sand filtration, it resulted in removal of oil to 20 ppm as water-soluble organic acids, decrease of turbidity from 200 to 2 NTU, and complete sequestration of surface sheen. The new technique offers a treatment alternative for produced water and likely other tailings waters, promoting safe discharge to the environment and beneficial uses of the water.

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1. Introduction

Produced water containing hydrocarbons is produced concomitantly when oil or gas is produced (Veil et al., 2004), reaching 3×10^3 Mt annually in the US alone (Sullivan et al., 2004; Veil et al., 2004). It is increasingly produced as an oil well approaches its end. Development of unconventional sources such as extraction of bitumen from oil sands and in situ extraction of kerogen from oil shale result in large quantities of water with hydrocarbons. Dispersed and dissolved oils in these waters pose treatment and disposal challenges, often preventing beneficial uses (ERIN and OCL, 2003; Veil et al., 2004; Yang and Nel, 2006). In many regions, sustainable energy supply and new development will critically depend on availability and sound management of water.

When discharged near shoreline, produced water with trace oil results in oil sheen at the water surface, which is a concern out of potential impact on plankton and birds and of aesthetics (ERIN and

OCL, 2003). Hydrocarbon concentrations at 20–40 ppm or even lower have been found to cause sheen, while at times higher hydrocarbon concentrations (>50 ppm) do not result in surface sheen (McCay, 2002). International regulatory guidelines vary. Discharge of produced water into the North Sea is subject to Oslo-Paris Commission, which limits dispersed oil at 30 ppm but does not regulate dissolved oil. In the US, state and federal programs prohibit oil sheen and staining of shorelines (Doyle and Brown, 1997). The US EPA set offshore sub-category limits for oil and grease in produced water at a monthly average of 29 mg L⁻¹ and a daily maximum of 42 mg L⁻¹ (US EPA, 2007).

Removal of dispersed and dissolved hydrocarbons from water is challenging. Produced water treatment technologies were recently reviewed (Hayes and Arthur, 2004). While API separator, hydrocyclone, flotation, filtration, and membrane processes had been shown to remove constituent oil with various degrees of success, none were without drawbacks such as the ability to handle soluble oil or high oil contents or susceptibility to fouling (Simms et al., 1992; Tibbetts et al., 1992; Lohne et al., 1996; ERIN and OCL, 2003). For other produced water constituents such as salts and soluble organics, biological processes, freeze-thaw evaporation, electrodialysis, activated carbon, reverse

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osmosis, and membrane electro dialysis were used (Arthur, 2004; Sirivedhin et al., 2004; Zwijnenberg et al., 2005). While ozonation had been well established for waste treatment, few applications were reported for produced water. Ozonation even with H₂O₂ addition was found ineffective for surrogate produced water over a wide pH range (Klasson et al., 2002). Recently, significant reduction of oil and grease and other contaminants in petroleum refinery waters was reported using a heterogeneous system of O₃/TiO₂/UV followed by contact with macroalgae (Corrêa et al., in press). Dissolved BTEX, which are constituents of produced water, were effectively removed from salty water when small bubbles of O₃ gas were generated by electrostatic spraying or a small-pore bubble diffuser, albeit with the former device inhibited by high ionic contents (Walker et al., 2001). In no cases was successful removal of free and soluble oils by ozonation reported.

Neither conventional ozonation nor sand filtration (SF) alone had been shown to treat produced water effectively. We demonstrate, however, a pressure-assisted ozonation technique coupled with SF for removal of oil and prevention of oil sheen. Unlike ordinary ozonation practice, the recently developed technique incorporates rapid, successive cycles of compression and decompression during ozonation (Hong et al., 2008). Small O₃-containing bubbles are created that provide reactive zones at the gas–liquid interface, resulting in heightened chemical conversions. This study examined the removal of dispersed and dissolved hydrocarbons with a focus on sheen prevention according to treatment configurations and varied parameters. An important goal is to promote safe discharge and beneficial use of process waters.

2. Experimental

2.1. Synthetic produced water – preparation and characteristics

The test synthetic produced water (SPW) was prepared by mechanically stirring a mixture of 1.5 mL of Rangely crude oil (CO, USA) and 2000 mL of deionised water at 500 rpm for 30 min at room temperature (25 ± 2 °C). The Rangely crude oil is a medium-gravity, low-asphaltenic crude oil produced from the Rangely field of Northwestern Colorado (Oh and Deo, 2007). Dispersed oil droplets in SPW rose slowly and spread to form a thin layer of oil sheen on the water surface. Vacuum filtration of oil samples through a 0.45-µm glass filter paper was used to distinguish the dispersed and the dissolved portions of oil. Dispersed oil was estimated by the total suspended solids (TSS), i.e., the retained “solids” on the filter. The total and dissolved hydrocarbon concentrations were determined from COD measurements before and after vacuum filtration and from a measured COD to hydrocarbon concentration ratio. Oil droplet sizes were estimated by COD measurements at different times at a fixed sampling depth, as decreases of COD with time were determined by rise velocities of droplets based on Stokes equation. Accordingly, mean oil droplet sizes were estimated to be <80, 20, and 10 µm after 5, 60, and 300 min of agitation, respectively. The thickness of oil sheen was estimated by sheen color (Netherlands Ministry of Transport Public Works, 1985; Lehr et al., 1994). The SPW was visually inspected for presence or absence of surface sheen after treatment. In this study, iridescent oil sheen was observed for COD between 50 ± 10 and 100 ± 10 mg L⁻¹ (i.e., hydrocarbon concentration of 20–40 mg L⁻¹). A brown oil sheen was observed for COD >120 ± 15 mg L⁻¹. Following treatment, SS were found on the water surface and were collected and included in mass balance calculations. In this study, the ratio of COD to the total hydrocarbon concentration was determined by mass balance calculation to be 2.8, i.e.,

$$\text{COD} = \frac{\text{Total hydrocarbon concentration}}{\text{Weight of solids retained on the filter paper}} = \frac{(\text{COD}_{\text{Before filtration}} - \text{COD}_{\text{After filtration}})(\text{Liquid volume})}{\text{Weight of solids retained on the filter paper}}$$

The filtrate was extracted by hexane (200 mL of filtrate by 50 mL of hexane twice). The hexane extract was concentrated to 1 mL by a gentle N₂ stream and analyzed by GC–MS. Hydrophilic compounds in the treated sample were extracted by solid phase extraction (SPE) method. For samples with low COD, the filtrate samples were adjusted to pH > 12 and concentrated 10 times by heating before passing the concentrate through the SPE column (IST ISOLUTE C18 (EC), Biotag). The SPE column was eluted with 20–30 mL of methanol, and this solution was reduced to 0.5 mL by a N₂ stream before GC–MS analysis.

Analyses were by a GC–MS system with a GC 6890 N (Agilent Technologies) installed with a capillary column (HP-5 ms, non-polar 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 microliters of sample was injected into a splitless inlet at 250 °C. The sample was carried by helium gas at 35 cm s⁻¹ 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⁻¹, followed by 100 to 350 °C at 5 °C min⁻¹ and at the end the temperature was maintained for 5 min. The NIST Mass Spectral Library – G1033 was used for species identification.

2.2. Two-stage treatment by ozonation in pressure cycles and SF

The SPW was treated by ozonation involving pressure cycles as well as by conventional bubbling ozonation for comparison. Ozone was generated from dry, filtered air at 100 V. Different ozone flowrates at 5, 10, and 20 L min⁻¹ were used, corresponding to gas phase ozone concentrations of 0.52, 0.29, and 0.16% (v/v), respectively, as determined by the Indigo colorimetric method (Bader and Hoigné, 1982). Bubbling ozonation was carried out in a 2-L beaker containing 1.8 L of water. Solution pH at 11 was maintained by manually adding 4-M NaOH solution. Pressure-assisted ozonation (i.e., ozonation in pressure cycles) was performed at room temperature (25 ± 2 °C) in a closed reactor of stainless steel containing 1 L of SPW as previously described (Hong et al., 2008). The pressure reactor featured a gas vent and a pressure gauge at the top, inlet and outlet at the bottom, and a magnetically coupled stirrer. To start, the reactor was loaded with SPW, and a pressure cycle began with the compression stage when the inlet valve was opened to allow entrance of an O₃/air mixture driven by a compressor (GAST) at the desired flowrate. The gas passed through a diffuser plate at the reactor bottom and through the liquid to pressurize the closed headspace to reach the designated pressure (e.g., 1.0 MPa); once the designated pressure was reached, the pressure was rapidly released by opening the outlet solenoid valve at the reactor top. The time for compression to reach the designated pressure depended on the headspace volume and gas flowrate (e.g., reaching 1.0 MPa in 28, 15, and 7 s at 5, 10, and 20 L min⁻¹, respectively); the time for decompression varied with venting speed but typically in 2–3 s. The pressure cycles could be repeated as many times as prescribed. During ozonation, the magnetic stir operated at 60 rpm. At the conclusion of pressure cycles, the water was allowed to sit for 3 min following pressure release. Additionally, a two-stage treatment for SPW was tested that consisted of a first stage involving ozonation in pressure cycles followed by SF and a second stage repeating the tandem processes once. The sands were of 0.25–0.42 mm, and about 1 kg were used in the circular bed of 10 cm in depth and 9 cm in diameter. The bed was operated at 6 cm min⁻¹ via vacuum, it had large filtration

capacity relative to the amount of suspended organics (mostly $<100 \text{ mg L}^{-1}$) contained in each treated batch. Typically after filtration of several batches of treated produced water, a thin layer of suspended matters was observed on the surface of the top sand layer. At this time the uppermost centimetres of sands were stirred to break up the film and allowed to settle again, which facilitated constant filtration velocity without noticeable head loss throughout the experiments.

2.3. Biodegradability test

Four 10-L glass rectangular aquariums, each with a side-hanging filter housing unit (Aqua Clear 20, Hagen), were used for biodegradability tests. Each housing unit contained a biofilter bag (Whisper, by Tetra) of $11 \times 16\text{-cm}^2$ polyethylene pocket for attachment by microbes. Aquarium water (8 L) was continuously circulated through the biofilter bag by means of a power head (Aqua Clear 20, Hagen) at $1.1 \pm 0.1 \text{ L min}^{-1}$. The biofilter bag was loaded with acclimated microbes. Microbial acclimation was performed by adding glucose at 0.1 g d^{-1} to a 1-L beaker holding 700 mL of water with continuous shaking. Over a 14-d period, ozonated SPW (COD = 1000 mg L^{-1}) was increasingly mixed into a 100-mL glucose solution to be added daily into the beaker while the glucose concentration was gradually reduced, and at the last day 100 mL of ozonated SPW only was added. Supplemented within each addition were buffering agents and nutrients (KH_2PO_4 , 85 mg L^{-1} ; K_2HPO_4 , 220 mg L^{-1} ; Na_2HPO_4 , 330 mg L^{-1} ; NH_4Cl , 17 mg L^{-1} ; $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 230 mg L^{-1} ; CaCl_2 , 280 mg L^{-1} ; $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 3 mg L^{-1}). At each addition, the same volume of supernatant was withdrawn from the beaker to keep the culture volume constant. The culture was acclimated for five more days with ozonated SPW prior to transfer into the 10-L aquariums (200 mL of culture each) for attachment. An additional week of water circulation with intermittent ozonated SPW additions was allowed for the suspended culture to attach to the filter bag.

Treated SPW samples (8 L) were introduced into the aquarium for contact with microbes on the biofilter. COD was measured after 12 and 24 h of biological contact. BOD of SPW after ozonation was determined and comparison with COD made to assess biodegradability of residual organics.

3. Results and discussion

3.1. Physicochemical treatment of synthetic produced water – ozonation and SF

Table 1 shows the SPW before and after different treatments. Both soluble COD (i.e., COD of filtrate) and total COD were measured. While soluble COD was mostly indicative of dissolved oil, the total COD represented both dispersed and dissolved oils. Before treatment, SPW was highly turbid (200 NTU) with total and soluble CODs at 320 and 48 mg L^{-1} , respectively, and sheen appearance was obvious at the water surface. Subjecting the SPW to ozonation in pressure cycles resulted in reduced total COD but increased soluble COD (No. 5–13, Table 1). Contrarily, subjecting SPW to aeration in pressure cycles reduced mostly dispersed oil but with little effect on dissolved oil or sheen appearance, as evidenced by reduction in total COD but little in soluble COD (No. 2–4).

Subjecting the SPW to ozonation with different pressure cycles and flowrates (requiring different compression times to reach 1.0 MPa) resulted in varied degrees of changes in pH, turbidity, CODs, and presence or absence of sheen (No. 5–13, Table 1). The most desirable outcome (No. 10, Table 1) resulted when longer compression time (28 s; i.e., via slower flowrate) and more pressure cycles (30) were used, eliminating sheen appearance at 1 h

and 1 d following treatment. BOD that could indicate biodegradability was measured following treatment and compared to total COD; the highest BOD/COD ratio of 0.61 was achieved under favourable treatment conditions (No. 10).

Effluent quality improved when ozonation in pressure cycles was followed by SF. For example, results of No. 14 with SF showed improvements over those of No. 5 without SF in terms of turbidity (21 vs. 100 NTU), total COD ($73 \text{ vs. } 150 \text{ mg L}^{-1}$), BOD/COD (0.58 vs. 0.48), and sheen formation (negative vs. positive after 1 h). The effectiveness of oil removal was further examined by a two-stage ozonation–SF process in which the tandem treatment of ozonation by pressure cycles and SF was repeated once (No. 16–19, Table 1). The two-stage ozonation–filtration process showed significant improvements in turbidity, total COD, BOD/COD, and sheen formation (e.g., No. 18 demonstrated effluent turbidity of 2.1 NTU, total COD and soluble COD of 59 and 55, respectively, BOD/COD of 0.58, and absence of sheen even after 24 h). Fig. 1 shows pictures of SPW before and after the two-stage treatment process. It should be noted that ozonation treatment increased soluble COD, which indicated increased dissolved organics that were likely organic acid, aldehyde, and ketone products from ozonation of dissolved oil. The changes in total and soluble CODs showed a change in water compositions, i.e., a decrease in dispersed oil but increase in water-soluble organics. Apparently, these soluble products along with reduced dispersed oil placed a smaller strain on the biodegradability of the treated SPW, as indicated by a higher BOD/COD ratio of 0.58.

To delineate the viability of pressure cycles and SF for oil removal (without O_3), the SPW was likewise subjected to aeration in pressure cycles plus filtration treatment and repeated to simulate a two-stage treatment process (No. 20). The results showed a significant amount of remaining oil and sheen occurrence. Thus, while aeration in pressure cycles and SF removed a portion of dispersed oil leaving the dissolved oil unchanged, this two-stage process in the absence of O_3 did not achieve sufficient removal of dispersed oil to eliminate sheen formation.

To test further removal of hydrocarbons and their daughter products remaining after ozonation treatment (with and without SF), various effluents were added to aquarium holding tanks and circulated with a side-hanging biofilter unit with attached microbes that were acclimated as already described. The results show removal of total COD to $\leq 20 \text{ mg L}^{-1}$, corresponding to $\leq 7 \text{ mg L}^{-1}$ of soluble organics remaining in the water; remaining organics were as low as several mg L^{-1} (or 10 mg L^{-1} in COD) for effluents treated by the two-stage ozonation–filtration process. It should be noted here we have assumed a COD/products (e.g., acids, aldehydes, and ketones) ratio of 2.8 that was measured for COD/hydrocarbon mixture as described in Experimental; the assumption was based on roughly similar ratios for the products after the olefins were converted (e.g., theoretical COD/nonanal ($\text{C}_9\text{H}_{18}\text{O}$) ratio = 2.9). At these levels, none of the samples were observed to form sheen at the water surface. It should be noted that although significant amounts of residual organics (mostly soluble) were removed from water during 24 to 48 h of biological contact, the removal had not been sufficiently studied to affirm that though likely these compounds were biodegraded by microbes of the filter bag, to the exclusion of removal by other adsorption or filtration processes or by all of which. Additional study would be required to establish removal mechanism and biofilter bag capacity.

3.2. Chemical conversion by ozonation in pressure cycles

Fig. 2 shows chromatograms of major compounds in the SPW before and after treatments. These compounds were extracted by non-polar solvent hexane and tentatively identified by GC–MS as long-chain aliphatic compounds with C–C double bonds, but were

Table 1
SPW characteristics after SF following pressure-assisted (PA) ozonation under different conditions^a (triplicate or quadruplicate results with std. dev. shown).

No. and treatment	Flowrate (L min ⁻¹)	Comp. time (s)	pH range	Turbidity (NTU)	Tot. COD (mg L ⁻¹)	Sol. COD (mg L ⁻¹)	BOD/COD ratio	Sheen at		COD (mg L ⁻¹) after additional biofiltration	
								1 h	1 d	24 h	48 h
<i>Characteristics after PA treatment</i>											
1. No treatment	–	–	6.8–7.0	196 ± 13	325 ± 34	48 ± 4	0.45	Y	Y		
2. PA/air/10 cy	10	15	6.8–7.0	98 ± 11	142 ± 23	42 ± 7	0.45	Y	Y		
3. PA/air/20 cy	10	15	6.7–6.9	72 ± 7	99 ± 6	45 ± 4	0.45	Y	Y		
4. PA/air/30 cy	10	15	6.8–7.0	34 ± 5	84 ± 7	39 ± 4	0.46	Y	Y		
5. PA/O ₃ /10 cy	10	15	6.0–6.4	101 ± 10	152 ± 17	50 ± 7	0.48	Y	Y		
6. PA/O ₃ /20 cy	10	15	5.9–6.3	86 ± 3	124 ± 18	54 ± 5	0.54	Y	Y		
7. PA/O ₃ /30 cy	10	15	4.8–5.4	89 ± 7	123 ± 12	69 ± 7	0.57	N	Y (50%)		
8. PA/O ₃ /10 cy	5	28	5.6–6.0	55 ± 8	120 ± 9	52 ± 4	0.48	Y	Y	17 ± 4	12 ± 3
9. PA/O ₃ /20 cy	5	28	5.3–5.7	80 ± 5	122 ± 6	64 ± 4	0.54	Y	Y	20 ± 3	17 ± 4
10. PA/O ₃ /30 cy	5	28	4.0–4.6	86 ± 7	115 ± 17	72 ± 7	0.61	N	N	22 ± 3	15 ± 3
11. PA/O ₃ /10 cy	20	6	6.3–6.5	124 ± 10	179 ± 15	46 ± 6	0.50	Y	Y	18 ± 4	14 ± 2
12. PA/O ₃ /20 cy	20	6	6.0–6.4	103 ± 12	161 ± 8	50 ± 3	0.52	Y	Y		
13. PA/O ₃ /30 cy	20	6	5.5–5.9	96 ± 6	147 ± 21	55 ± 4	0.51	Y (25%)	Y (50%)		
14. PA/O ₃ /10 cy/SF	10	15	7.4–7.8	21 ± 4	73 ± 14	48 ± 3	0.58	N	Y (50%)		
15. PA/O ₃ /10 cy/SF	20	7	7.6	78 ± 5	102 ± 7	41 ± 6	0.49	Y	Y	14 ± 3	8 ± 4
16. PA/O ₃ /10 cy/SF and PA/O ₃ /10 cy/SF	10	15	7.4–7.8	3.8 ± 1.1	58 ± 11	51 ± 7	0.55	N	Y (25%)	13 ± 4	13 ± 4
17. PA/O ₃ /10 cy/SF and PA/O ₃ /20 cy/SF	20	7	7.5	28 ± 5	73 ± 11	45 ± 4	0.58	N	N	11 ± 3	7 ± 3
18. PA/O ₃ /10 cy/SF and PA/O ₃ /20 cy/SF	10	15	7.5	2.1 ± 0.3	59 ± 8	55 ± 6	0.58	N	N	12 ± 3	12 ± 3
19. PA/O ₃ /10 cy/SF and PA/O ₃ /20 cy/SF	5	28	7.2	1.7 ± 0.4	65 ± 7	57 ± 3	0.61	N	N	12 ± 2	4 ± 4
20. PA/air/10 cy/SF and PA/air/20 cy/SF	10	15	7.6	79 ± 8	112 ± 11	38 ± 5	0.51	Y (50%)	Y	21 ± 4	17 ± 4

^a The notation of "PA/O₃/10 cy/SF and PA/O₃/20 cy/SF" indicates pressure-assisted ozonation with 10 pressure cycles and then SF, which is immediately followed by a two-stage ozonation with 20 pressure cycles and then SF.



Fig. 1. SPW before (left) and after treatment (right) by PA/O₃/10 cy/SF and PA/O₃/20 cy/SF (flowrate = 5 L min⁻¹).

not authenticated. After 10 min of bubbling ozonation at ambient pressure, there were little changes in the SPW's contents (Fig. 2b). After 50 min of like treatment, significant conversions

of the aliphatic compounds to aldehydes as oxidation products occurred while the bulk of hydrocarbons and their long chains remained (Fig. 2c). However, when the SPW was ozonated in 30 pressure cycles completed within 20 min, all of the long-chain hydrocarbons disappeared (Fig. 2d), suggesting that the non-polar crude oil compounds might have been degraded or converted into polar compounds that were not extractable by hexane. Thus, the treated SPW was also extracted by SPE method and analyzed. Fig. 3 shows compounds as extracted by SPE before and after ozonation in pressure cycles. Before ozonation, relatively small amounts of hydrocarbons were collected by SPE (lowest chromatogram), and increasing polar compounds were collected with 20 and 40 cycles of ozonation (middle and upper chromatograms). These products were hydrophilic compounds that were absent in the hexane extract but collected by SPE. Among the compounds tentatively identified by GC–MS were various substituted forms of ethanone, benzoic acid, propenoic acid, carboxylic acids, and other compounds, notably with keto and carboxylic groups as shown in Fig. 3 and caption.

The reaction of hydrocarbons with ozone appeared to have followed the well established Criegee mechanism, in which a five-

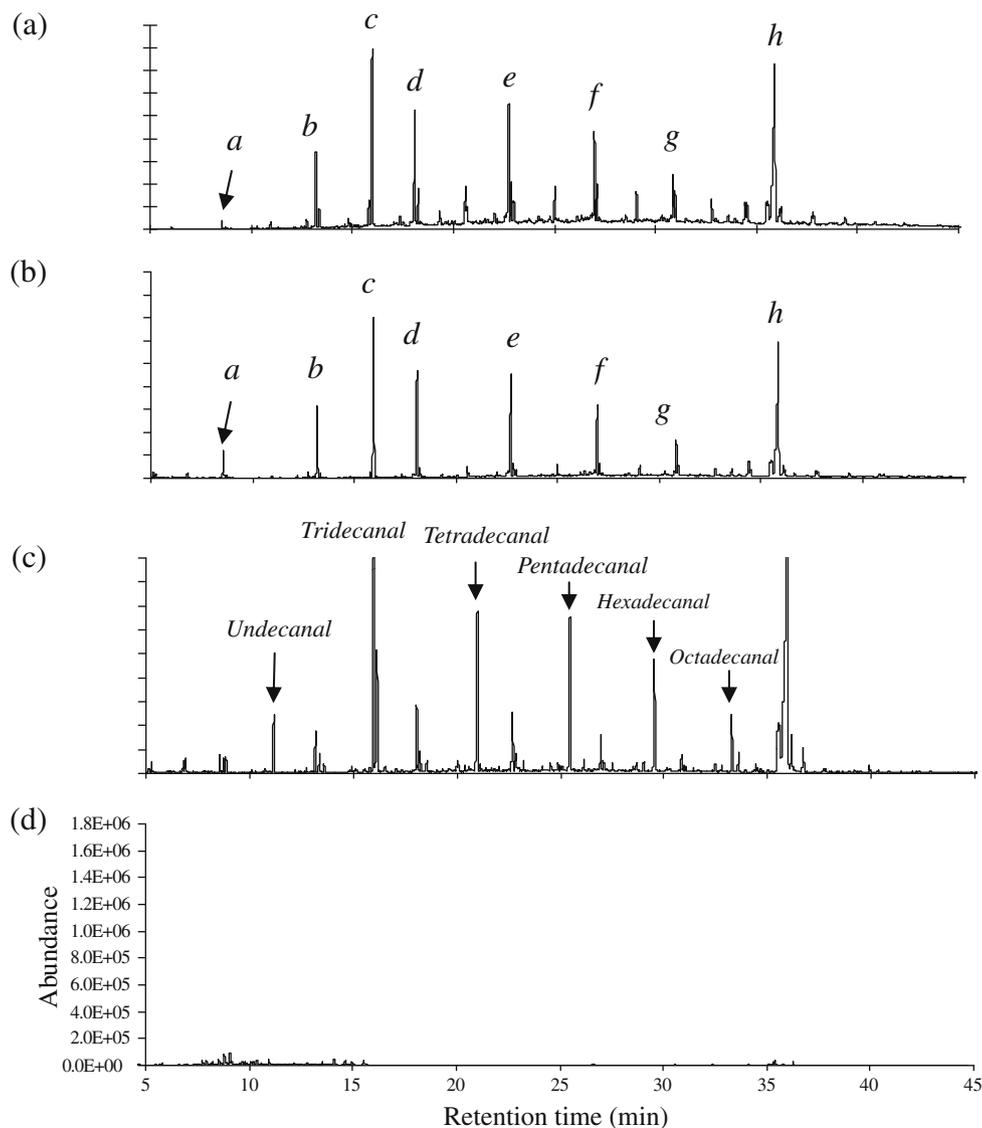


Fig. 2. GC–MS chromatograms of hexane extractable organics in filtered SPW samples after various ozonation at 5 L min⁻¹ flow rate: (A) no treatment, (B) bubbling ozonation (10 min), (C) bubbling ozonation (50 min), and (D) PC ozonation (30 cycles, ~19 min). Identified compounds: a, 1-dodecene; b, 1-tetradecene; c, 2,4-bis[1,1-dimethylethyl]phenol; d, 1-hexadecene; e, 1-octadecene; f, 1-nonadecene; g, 1-docosene; h, diethylene glycol dibenzoate.

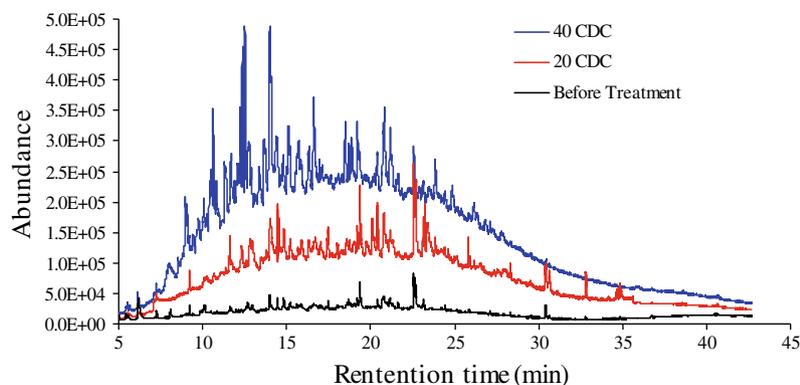


Fig. 3. GC-MS chromatograms showing increasing abundance of hydrophilic organics as extracted by SPE method in SPW before treatment (lowest chromatogram), after PA/O₃/20 cy (middle), and PA/O₃/40 cy (upmost). Tentatively identified with database with match quality >90% but not authenticated were: (2,2-Dimethyl-1,3-dioxolan-4-yl)methanol (4.89 min), 5-methyl-2-benzofuran-1,3-dione (11.31 min), 2-acetylbenzoic acid (12.08 min), methyl 3-(4-hydroxyphenyl)acrylate (12.52 min), (1,1'-biphenyl)-2,2'-dicarboxaldehyde (18.71 min), methyl (9Z,12Z)-octadeca-9,12-dienoate (22.57 min), methyl hexadecanoate (19.37 min), methyl (Z)-octadec-9-enoate (22.68 min), and 2-(2-ethylhexoxycarbonyl)benzoic acid (30.43 min).

member ring of ozonide was formed between the olefin molecule and ozone and followed by breaking up of the ring to form aldehydes (Fig. 4, Path a). This accounted for a significant amount of aldehydes formed during bubbling ozonation at ambient pressure. These aldehyde products with their long-alkyl chains intact remained largely extractable by hexane. While the formation of aldehydes signified an apparent maximum extent of conversion by bubbling ozonation (over 50 min), the presence of an expanding gas bubble interface by ozonation in pressure cycles appeared to have carried ozonolysis further within 20 min in which the oxyhydroperoxide intermediates further reacted resulting in the formation of ketones, aldehydes, and acids (Fig. 4, Path b) (Beltran, 2004). As the ozone generation rate and flowrate were kept the same in both methods of ozonation (ambient and pressure cycles), we inferred that more extensive ozonolysis, thus more polar products, resulted with ozonation in pressure cycles (formation of ketone, aldehyde, and acid products in 20 min) than with bubbling ozonation at ambient pressure (mostly long-chain aldehydes in 50 min). The kinetics and mechanisms of reactions of ozone with organics at the water–air interface could be significantly different from those in the bulk aqueous phase (Enami et al., 2008a,b).

Whereas ozonation in pressure cycles converts non-polar crude oil compounds into a complex mixture of highly water-soluble or-

ganic acids, bubbling ozonation at ambient pressure leads only to aldehyde compounds with long carbon chains remaining. The different product outcomes have different implications for subsequent removal and sheen prevention. Water-soluble organic acids exist as diffuse solute state and will not coalesce into a thin oil film at the water surface, thus they are not prone to formation of sheen at the surface. The bulk of sheen-causing dispersed oil in the SPW awaiting discharge was in the form of tiny droplets of oil, estimated by measurements of rise velocities in water to be 5–50 μm under preparation conditions of this study. When the small droplets were brought to intense contact with ozone enabled by pressure cycles, non-polar aliphatic compounds at the oil surface were functionalized with keto and carboxylic groups, thus altering the surface properties of the oil droplets thereby increasing their ability to interact and agglomerate with other small droplets such as via hydrogen bonding and bridging. Thus, the converted oil droplets increased in size (much of them now clearly visible as oil patches) and became more susceptible to SF. The functionalized surface of oil droplets, e.g., with carboxylic groups, is expected to have more electrostatic interactions with hydroxyl groups of silicates abundant at the sand surface. Thus, we see ozonation in pressure cycles not as a tool to completely degrade dispersed oil, but to convert the oil droplets that enables its eventual capture by the

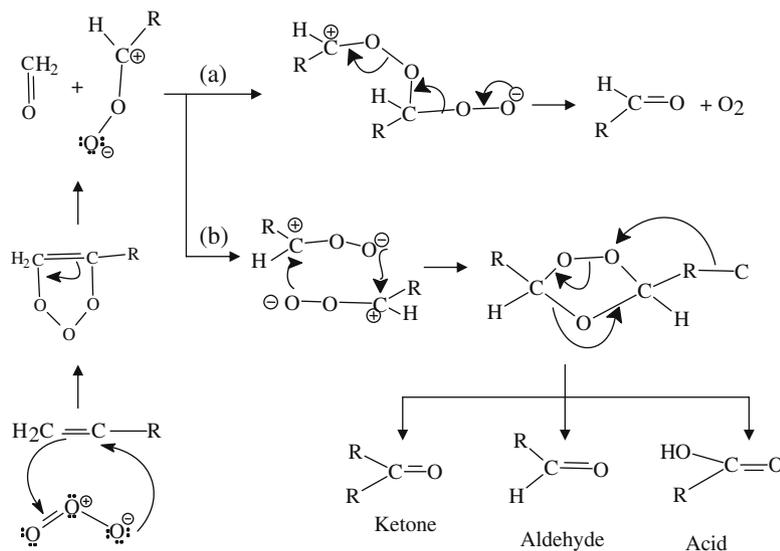


Fig. 4. Reactions of ozone with hydrocarbons and their products.

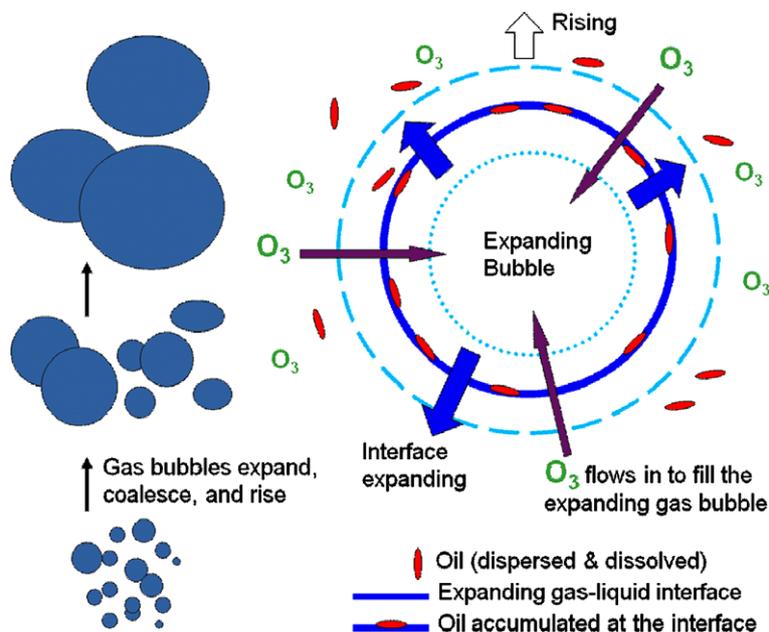


Fig. 5. Expanding gas–liquid interface providing ample active zone for accumulation of hydrophobic droplets and heightened interaction with ozone.

sand bed. It is anticipated that accumulated oil in the sand bed can be thermally regenerated (e.g., 550 °C) and be available for redeployment.

3.3. Mechanism of heightened removal

Ozonation in pressure cycles appears to be more effective than conventional bubbling ozonation in converting non-polar hydrocarbons to hydrophilic compounds that are more amenable to removal by SF. We attribute the heightened interaction of ozone with hydrocarbons to the appearance of expanding microbubbles during pressure cycles, with enabling actions as depicted in Fig. 5:

1. “Sweeping” of contaminants: During compression the bulk of ozonation gas dissolves into water, saturating it under pressure (e.g., 1.0 MPa); during decompression the now oversaturated gas exits the liquid phase by formation and growth of microbubbles throughout the liquid volume. The expanding gas–liquid interface of microbubbles acts to “sweep” the water body thoroughly and accumulate contaminants at the interface. By calculation, a reactor with a 20% headspace volume subjected to 10 pressure cycles up to 1.0 MPa would facilitate sweeping of the water body 10 times, each time with O_3 -carrying gas at 2.5 times the water volume.
2. Confluence of contaminants and O_3 at the interface: To fill the expanding gas volume of microbubbles during decompression, O_3 molecules are drawn across the interface where hydrophobic and amphiphilic contaminants (including dispersed and dissolved hydrocarbons) are accumulated. This results in heightened contact and reaction of O_3 with contaminants that otherwise exist at diffuse state throughout, thus leading to heightened ozonation treatment.
3. Non-polar droplets of suspended oil are converted at the surface into organic acid groups (e.g., carboxylic groups that interact with one another via hydrogen bonding) that enable the small droplets to agglomerate to large patches and be more readily retained by rapid SF, thus providing rapid oil removal without prolonged ozonation treatment necessary for degradation.

4. Conclusions

Results of this work show that ozonation in pressure cycles when sequentially coupled with SF provides an alternate technique for rapid removal of oil from process waters and prevention of oil sheen after discharge. Oil removal is primarily via chemical conversions that alter interfacial properties of the oil droplets, rendering them abatable by conventional SF. A two-stage system appears most effective in which the first stage with fewer ozonation cycles can target removing the bulk of dispersed oil and the second stage with more ozonation cycles can convert remaining dispersed and dissolved hydrocarbons into organic acids, thus lowering residual oil and eliminating sheen. Preliminary biological contact results show that the treated effluent now with soluble organic acids diminish after contact, which suggests the possibility of further biological treatment such as via attached growth processes.

Acknowledgement

This project was funded in part by the US DOE through the Utah Heavy Oil Program at the University of Utah.

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Treatment of oil spill water by ozonation and sand filtration



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HIGHLIGHTS

- ▶ Flotation, ozonation, and sand filtration treated oil spill water for immediate discharge.
- ▶ Crude oil (2.5%) in waters was removed by 100% via the treatment.
- ▶ COD and O&G of 20000 and 11000 mg L⁻¹, respectively, were completely removed.
- ▶ Turbidity was reduced to <1 from 4000 NTU with no sheen formation.
- ▶ BOD/COD ratio of 0.3–0.5 showed biodegradable residuals in the effluent.

ARTICLE INFO

Article history:

Received 24 September 2012
 Received in revised form 8 January 2013
 Accepted 9 January 2013
 Available online 6 February 2013

Keywords:

Oil
 Spill
 Treatment
 Ozone
 Sand
 Pressure

ABSTRACT

Increasing volumes of crude oil being produced and transported throughout the world in recent decades have resulted in increased risks of spill and high-profile spill incidents of significant environmental and ecological impacts over extended periods of time. While immediate *in situ* and *ex situ* responses have been implemented, none are available for onsite treatment of contaminated water for immediate release of the treated water. We demonstrate here a potential treatment scheme involving ozonation and sand filtration intended for immediate treatment and discharge of the impacted water. Waters of tap, Utah Lake, and Great Salt Lake sources were spiked with crude oil of the Great Natural Butte of Utah at 2.5% and 0.025% oil (v/v) and tested for treatment. The results showed near complete removal (100%) of both Chemical Oxygen Demand (COD) and oil and grease (O&G) from initially 20000 and 11000 mg L⁻¹, respectively, via flotation pretreatment, ozonation in pressure cycles, and sand filtration. At lower oil level of 0.025%, complete removal of COD and O&G from waters were achieved without floatation. The treated waters showed reduction of turbidity to <1 from 4000 NTU and high Biochemical Oxygen Demand/COD ratio of 0.3–0.5 that reflected highly biodegradable residual organics. The results showed synergistic oil removal when two well practiced methods, namely ozonation and sand filtration that either alone seems ineffective, are combined sequentially. It indicates a potential onsite treatment response for oil spill incidents where the collection and transport of a large amount of contaminated water may be avoided.

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1. Introduction

Increasing volumes of crude oil production, transportation, and storage have increased risks of spill to marine and freshwater environments (Vandermeulen and Ross, 1995; Fingas, 2011). Between 1974 and 1994, there were 175 major oil spills worldwide, costing US\$ 20–200 L⁻¹ for cleanup depending on the location and type of spill (Abdullah et al., 2010; Fingas, 2011). High-profile spills in recent decades are numerous, causing not only loss of the energy resource but also significant injuries to the environment and

ecosystems (Seymour and Geyer, 1992; González et al., 2006; Firby and Law, 2008; Schnoor, 2010; Allan et al., 2012; Lin and Mendelssohn, 2012). Monthly, thousands of oil spills in smaller scales occurred on land freshwater systems throughout the world from production activities and transports by pipeline, rail, and truck, accounting for 11000 t of pipeline spills annually, 1700 t of refinery spills, 1300 t of tanker truck spills, and 500 t of tanker ship spills yearly in the US (Fingas, 2011). Oil spills release hazardous chemicals such as polycyclic aromatic hydrocarbons that are toxic to aquatic life and human and may require decades to remove (Seymour and Geyer, 1992; Allan et al., 2012).

Major oil spill response methods include skimming, controlled burning, bioremediation, and uses of sorbent and dispersant (Vandermeulen and Ross, 1995; Zhu et al., 2004; Yang et al., 2009; Fingas, 2011; Sueiro et al., 2011; Tamis et al., 2011; Zhu

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et al., 2011). Each method has its own deployment requirements, advantages, along with limitations and concerns. While burning and dispersion create concerns for air, water, and ecosystems (Vandermeulen and Ross, 1995; Fingas, 2011; Tamis et al., 2011); skimming and adsorption collect a large amount of oil-contaminated water that must be transported from sites (Vandermeulen and Ross, 1995; Fingas, 2011; Zhu et al., 2011). Bioremediation requires an extended period subject to the location (Zhu et al., 2004; Yang et al., 2009; Sueiro et al., 2011). We propose a treatment scheme combining ozonation and sand filtration in sequence for potential onsite treatment of contaminated water and immediate discharge of the treated water. Both ozonation and sand filtration have been well practiced for decades in water treatment – the former in destruction of chemical and biological contaminants and the latter in removal of particulate matter. However, neither is known to be effective for oil removal from water. Recently, Cha et al. (2010) demonstrated the removal of hydrocarbons from produced water using ozonation in pressure cycles followed by sand filtration, revealing the synergistic removal of oil from water. Here, we report a treatment train that includes flotation, first-stage sand filtration, ozonation, and second-stage sand filtration for removal of oil from an influent concentration of 25 000 to <2 mg L⁻¹, targeting the oil levels in spill impacted water. The method may provide an onsite treatment and release option in an oil spill event.

2. Materials and methods

2.1. Chemical and analyses

The synthetic spillage simulating oil and water collected from a spill event was prepared by mechanically stirring 2.5% (v/v) of the Great Natural Butte crude oil (UT, USA) in water until homogeneous. Tap water, Utah Lake (UL) water, and Great Salt Lake (GSL) water were chosen to represent oil-contaminated fresh water, groundwater, and seawater. Water characteristics are shown in Table 1. COD (HACH 800, high and low ranges), soluble COD (sCOD, through 1.5- μ m filter), Biochemical Oxygen Demand (BOD) (APHA et al., 2005), pH (APHA et al., 2005), total hardness (TH) (APHA et al., 2005), calcium hardness (CH) (APHA et al., 2005), total solids (TS) (APHA et al., 2005), volatile total solids (VTS) (APHA et al., 2005), volatile dissolved solids (VDS) (APHA et al., 2005), turbidity (HACH 2100N turbidimeter) (APHA et al., 2005), oil and grease (O&G) (USEPA method 1664, 1999), and oil sheen (Lehr et al., 1994) of the samples before and after treatment were analyzed in triplicate. O&G extraction was once with 100 mL of hexane (Sigma–Aldrich, analytical reagent), or three times with 35 mL each; the extract was concentrated by rotary evaporation and further evaporated at 70 °C before gravimetric measurements.

Organic contents in all water samples were extracted by dichloromethane (DCM; Sigma–Aldrich, ACS reagent) (200 mL of water sample by 50 mL of DCM); the extract was concentrated to 1 mL by a gentle N₂ stream and analyzed by GC/MS. The GC/MS system with a GC 6890N (Agilent Technologies) was installed with a capillary column (HP-5 ms, nonpolar column, 30 m \times 0.25 mm \times 0.25 μ m, Agilent Technologies), coupled with a MSD 5973 (Agilent Technologies), and controlled by the MSD Productivity ChemStation software (Agilent Technologies). One microliter of

sample was injected into a splitless inlet at 250 °C. The sample was carried by helium gas at 35 cm s⁻¹ and the mass range from 50 to 550 *m/z* was scanned. The oven temperature was programmed from 50 (initially held for 1 min) to 100 °C at 25 °C min⁻¹, followed by 100–350 °C at 5 °C min⁻¹ and at the end the temperature was maintained for 5 min.

2.2. Treatment train – flotation, sand filtration, ozonation in pressure cycles, and sand filtration

The synthetic spill sample was treated by sequential processes of flotation, sand filtration, ozonation in pressure cycles, and sand filtration, as illustrated in Fig. 1.

2.2.1. Flotation

The flotation column of 7 cm in diameter contained water of 60 cm in depth. An air diffuser at the bottom provided floatation bubbles of 1–2 mm in size at 2.5 L min⁻¹, driven by a small air compressor typically used in aquariums capable of delivering 4.5 L min⁻¹ of air. Installed at 40 cm from the column bottom was a bundle of polypropylene straws of 2 cm in length and 0.6 cm in diameter adhered together by silicone gel. The spike water was introduced at the top into the flotation column at downward flow velocity of 5.2 cm min⁻¹ against the rising air bubbles at 2.5 L min⁻¹. The straw bundle section in the column reduced turbulence in the column and provided more uniform upward airflow through the restricted vertical spaces within and between the straws, which prevented small oil droplets from passing through the bundle barrier to reach the exit at the column bottom. At every 5 L of collected spillage, the floated oil at the water surface of the column was removed by a pipette. The recovery efficiency of crude oil was 60–70%, which was not influenced by the water types. The recovered oil was analyzed by the GC/MS.

2.2.2. First sand filter

After the flotation column, the water was passed through a sand bed (SF1) of 5.5 cm in diameter and 20 cm in depth, packed with sand grains of 0.25–0.42 mm, at a filtration velocity of 8 cm min⁻¹. Prior to use, the sands were sieved, washed with 10 M HCl (EMD, analytical reagent) and 10 M NaOH (Mallinckrodt, analytical reagent) solutions sequentially, rinsed with tap water until stable pH, and finally dried at 550 °C for 30 min. When effluent COD reached 200 mg L⁻¹, the sands were regenerated by heating to boiling in 500 mL of water (sand to water volume ratio of about 1). The oil recovered at the surface during regeneration was returned to the flotation column of the process train, and the regenerated sands were returned to the sand filter.

2.2.3. Ozonation

Ozone (1.5% v/v) was generated at 2 L min⁻¹ by an ozone generator (Model T-816, Polymetrics Corp.) from dry, filtered oxygen at 100 V. Ozonation was carried out by bubbling the ozone stream into a batch reactor for a prescribed period under atmospheric condition or via compression–decompression cycles for a prescribed number of cycles as in Cha et al. (2010). Ozonation via pressure cycles was performed in a 2.2-L pressure-resisting stainless-steel reactor containing 2 L of the water sample (Fig. 1). The pressure

Table 1
Water characteristics before spiking.

Water	pH	Turbidity (NTU)	TH (mg L ⁻¹ as CaCO ₃)	CH (mg L ⁻¹ as CaCO ₃)	Alkalinity (mg L ⁻¹ as CaCO ₃)	TS (mg L ⁻¹)	VTS (mg L ⁻¹)
Tap water	7.7	0.45	130	98	140	290	N/A
Utah Lake	8.5	0.23	180	80	110	760	N/A
Great Salt Lake	8.2	2.7	–	–	460	100,000	20,000

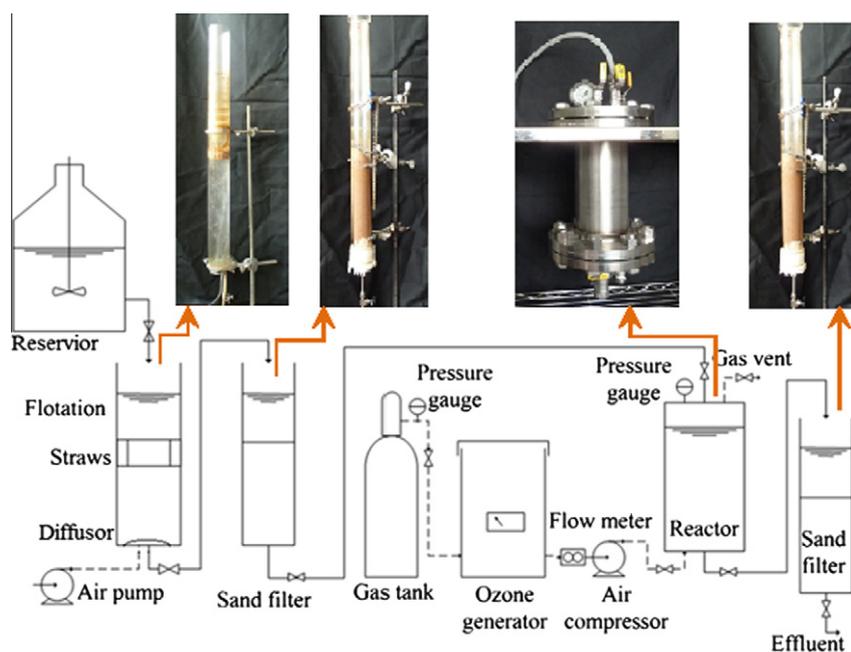


Fig. 1. Treatment train for the oil spill water.

reactor design featured a gas vent, pressure gauge, and water inlet at the top; gas inlet and water outlet were at the bottom. Ozonation treatment began with a compression stage when the top vent was closed and the bottom inlet valve opened to admit the ozone/air stream driven by a gas compressor (GAST). Treatment was conducted at different compression pressures and numbers of pressure cycles. Once the designated pressure was reached (690 kPa in 10 s, 550 kPa in 8 s, or 350 kPa in 5 s for a headspace of 0.2 L; 690 kPa in 18 s, 550 kPa in 15 s, or 350 kPa in 10 s for a headspace of 0.7 L), the inlet valve was closed and the vent valve opened to allow controlled decompression in the next 1 min, thus completing one pressure cycle. The compression–decompression cycle was repeated as prescribed, each cycle requiring about 70 s to complete depending on the selected headspace volume and compression pressure. When carried out at ambient pressure, ozonation was conducted for 20 min with 1.8 L of water in a 2-L beaker. All experiments were at room temperature of 20–23 °C.

2.2.4. Second sand filter

After ozonation, the effluent was passed into a second sand bed (SF2), which was of 7 cm in diameter and 25 cm in depth consisting of sieved sands of 0.25–0.42 mm and 0.12–0.25 mm in equal volumes with the larger sands on top of the smaller. The sand bed was operated at a filtration velocity of 2 cm min⁻¹; when the velocity dropped to 1 cm min⁻¹ the bed was backwashed with tap water of equal volume to the sands. The backwash water was returned to join the influent to the first filter. After repeated backwashings, oil sheen could begin to appear in the effluent; at this point, the sands were removed and regenerated in oven at 550 °C for 30 min and reused afterward.

2.3. Evaluation of ozonation treatment and sand filter capacity

To reduce the volume of crude oil needed for experiments during evaluation of ozonation effectiveness under different conditions, a separate series of experiments was conducted with reduced spike concentration (0.025% oil content) that simulated the first filter effluent. For the same reason, a smaller sand filter was constructed by means of a 10-mL syringe body packed with 7 mL of sands of equal portions of sizes 0.25–0.42 and 0.12–

0.25 mm. The diameter and depth ratio was identical to the larger column version, and the filtration velocity was 2 cm min⁻¹ as before. The combined ozonation and sand filtration treatment outcomes as well as the filter capacity were evaluated for different ozonation conditions in terms of pH, turbidity, COD, BOD, and O&G. All measurements including filtration capacity were in triplicate and shown with standard deviations.

3. Results and discussion

3.1. Flotation

Table 2 shows various waters spiked with 2.5% (v/v) crude oil, resulting in 18 g L⁻¹ of COD and 6.7 g L⁻¹ of O&G in the tap water, 20 g L⁻¹ of COD and 9.2 g L⁻¹ of O&G in UL water, and 11 g L⁻¹ of O&G in GSL water (COD in GSL water was not measured because of its high salt content). After the flotation process, removals were 64% of COD and 87% of O&G from tap water, 90% of COD and 98% of O&G from UL water, and 88% of O&G from GSL water. After flotation, the turbidities decreased from between 2800 and 3900 NTU to between 120 and 370 NTU, a decrease of 91–96% in turbidity. VDS also decreased by 80% for tap water and by 85% for UL water. After 5 L of throughput, the coalesced oil on the water surface was removed and analyzed by GC; chromatograms of Fig. 2 confirmed little changes in the collected oil from its parent spike.

3.2. First-stage sand filtration

The water was then passed through the SF1, after which removals were 99% of COD and 98% of O&G from tap water, 100% of COD and 100% of O&G from UL water, and 100% of O&G from GSL water (removals were with respect to influent spike levels). The turbidities decreased further to 8.4, 4.6, and 6.8 NTU for tap, UL, and GSL waters, respectively. VDS remained relatively unchanged after sand filtration, which was expected as filtration was not capable of removing dissolved organics. However, the ratio of sCOD/COD increased significantly from 1.4% to 63% in the tap water, which indicated a significant change in the oil makeup of the water, namely from equal amounts of dissolved and suspended oils to

Table 2
Influent and effluent qualities of oil spill waters as being subjected to sequential treatment processes.

	Process	COD (mg L ⁻¹ , % removal)	sCOD/COD (%)	BOD/COD (%)	pH	Turbidity (NTU)	VDS (mg L ⁻¹ , % removal)	O&G (mg L ⁻¹ , % removal)
Tap water	Influent	18000 ± 4200	–	–	8.1–8.2	2800 ± 82	470 ± 22	6700 ± 1100
	Flotation	6300 ± 1150 (64)	1.4	0.70	8.4–8.5	370 ± 40	92 ± 5 (80)	860 ± 240 (87)
	SF1	170 ± 40 (99)	27	27	8.4–8.5	8.4 ± 2.4	98 ± 18 (79)	110 ± 17 (98)
	Ozonation	91 ± 26 (100)	51	33	8.0–8.2	7.9 ± 1.8	97 ± 21 (79)	5.2 ± 1.0 (100)
	SF2	29 ± 7 (100)	94	33	8.3–8.4	0.57 ± 0.34	N/A	N/A
Utah Lake water	Influent	20000 ± 2400	–	–	8.2–8.3	3900 ± 28	710 ± 94	9200 ± 1300
	Flotation	2100 ± 250 (90)	4.0	3.3	8.3–8.5	120 ± 25	100 ± 2 (85)	159 ± 26 (98)
	SF1	80 ± 6.4 (100)	62	42	8.4–8.5	4.6 ± 0.20	120 ± 14 (83)	42.1 ± 8.7 (100)
	Ozonation	60 ± 0.40 (100)	65	50	8.3–8.3	9.1 ± 0.80	N/A	7.6 ± 2.4 (100)
	SF2	22 ± 2.8 (100)	87	48	8.4–8.5	0.61 ± 0.04	N/A	N/A
Great Salt Lake water	Influent	–	–	–	8.2–8.3	4000 ± 12	–	11,000 ± 900
	Flotation	–	–	55 ^a ± 0.50	8.2–8.2	290 ± 6.0	–	1400 ± 610 (88)
	SF1	–	–	20 ^a ± 0.50	8.1–8.2	6.8 ± 0.10	–	51 ± 9.6 (100)
	Ozonation	–	–	12 ^a ± 2.8	8.1–8.1	15 ± 4.0	–	7.5 ± 2.1 (100)
	SF2	–	–	N/A	7.9–8.1	0.66 ± 0.02	–	N/A

Treatment conditions: influent, 2.5% (v/v) oil; flotation, 5.2 cm min⁻¹ water, 2.5 mL min⁻¹ air; first filtration, 8 cm min⁻¹; ozonation in pressure cycles, 2-L sample in 2.2-L reactor, 690 kPa, 8 cycles, 8 s compression, 60 s vent; second filtration, 2–2.5 cm min⁻¹ flow.

^a BOD (mg L⁻¹) only; 100% removals indicate ≥99.5% at 2 significant digits.

mostly dissolved oil after sand filtration. This change in oil content resulted in increased ratios of BOD/COD, from 0.7% to 32.7% for tap water and from 3.3% to 42.0% for UL water, which along with increased sCOD/COD ratios suggested quite plausibly that in aqueous environment dissolved oil was more amenable to biodegradation than the suspended counterpart.

3.3. Ozonation in pressure cycles

The effluent from SF1 was to be treated by ozonation. Prior to such, however, effective ozonation conditions (e.g. compression pressure and number of pressure cycles) were first determined in a separate series of experiments using tap water spiked with a reduced oil amount (100 mg L⁻¹ of COD; 0.5 mL L⁻¹ oil) that simulated the oil level in SF1 effluent. Removals of COD and O&G under different pressures and cycle numbers are shown in Fig. 3. As shown, COD removal was about 37%, relatively independent of pressure from 350 to 690 kPa and of the number of pressure cycles from 5 to 10. However, the removal of O&G increased with increasing pressure as well as increasing number of pressure cycles, although a maximum removal of 83% appeared to have been attained at 550 kPa and 5 cycles, the conditions of diminishing benefit beyond which further increases in either parameter yielded little further removal. Thus, ozonation conditions of 690 kPa and 8 cycles were employed for subsequent treatment of SF1 effluent. It should be noted that the outcome of continuous ozonation for 20 min without pressure cycles was included as a point of reference; COD removal by 31% and O&G removal by 55% were achieved by 20 min of continuous ozonation, where the supplied O₃ amount was 1900 mg O₃ in 20 min relative to 190 mg O₃ via 8 cycles and 690 kPa. Ozonation in pressure cycles achieved higher levels of removal with a reduced dose, which agreed with our previous study (Cha et al., 2010).

The SF1 effluent was transferred to the reactor and treated by ozonation in 8 pressure cycles at the compression pressure of 690 kPa. Table 2 shows the treatment outcomes. CODs in both tap and UL waters were further reduced to 91 and 60 mg L⁻¹, respectively, indicating >99.5% removal. The reduction of O&G in all three waters was near complete (99.9%), leaving 5–8 mg L⁻¹ in them. The remaining VDS was 97 mg L⁻¹ in tap water and not detected (i.e. <20 mg L⁻¹ for a 50-mL of sample) in UL water. The ratios of sCOD/COD in both tap and UL waters increased likely due to increased solubility of more polar products from ozonation of the hydrocarbon compounds (Beltran, 2004; Hong et al., 2008; Cha et al., 2010). Cha et al. (2010) found the presence of an

expanding gas bubble interface as created by pressure cycles to be more effective than bubbling ozonation in conversion of hydrophobic compounds into ketones, aldehydes, and acids (Cha et al., 2010).

The ratios of BOD/COD also increased after ozonation, which was attributed to an increased microbial accessibility of the soluble polar products. It should be noted the BOD/COD ratios of 0.33 for tap water and 0.50 for UL water indicated the residual organics were highly biodegradable, which are comparable to ratios of 0.3–0.8 for domestic wastewaters that are routinely treated by biological processes. The high ratios indicated readily biodegradable substances in the effluent.

3.4. Second-stage sand filtration

The ozone-treated effluent was passed through the SF2. Table 2 shows the SF2 effluent qualities. The turbidity of all three waters was below 1.0 NTU. O&G and VDS were below detection limits, which were 20 mg L⁻¹ for VDS based on a 50-mL sample and 2 mg L⁻¹ for O&G based on a 500-mL sample. These results showed effectiveness of SF2 in further reducing particulate contents. When small oil droplets react with ozone at the reactive gas–liquid interface, nonpolar aliphatic compounds are functionalized with keto and carboxylic groups; the surface properties change resulting in larger droplets through H-bonding and bridging, which become easier for the sand filter to capture (Cha et al., 2010).

While, after ozonation, the BOD/COD ratios remained little changed (0.33 for tap water and 0.48 for UL water), the sCOD/COD ratios increased significantly (from 0.51 to 0.94 for tap water and from 0.65 to 0.87 for UL water). These increases now indicated that much of the remaining COD (20–30 mg L⁻¹) was in the form of soluble organics, likely polar ozonation products from their parent hydrocarbon. These products were highly biodegradable as revealed by their high BOD/COD ratios. The SF2 effluent pH was not significantly changed from the influent and variations were within 0.2 of the influent pH values.

The spike influent and effluents from each treatment process have been extracted and analyzed by GC, and the results are shown in Fig. 4. The results indicate dramatic decreases in organic contents after flotation and SF1 followed by continual removal of the residual contents through ozonation and SF2. The removal of organics from water was corroborated by other measurements including turbidity, COD, VDS, and O&G through various sequential steps as described above.

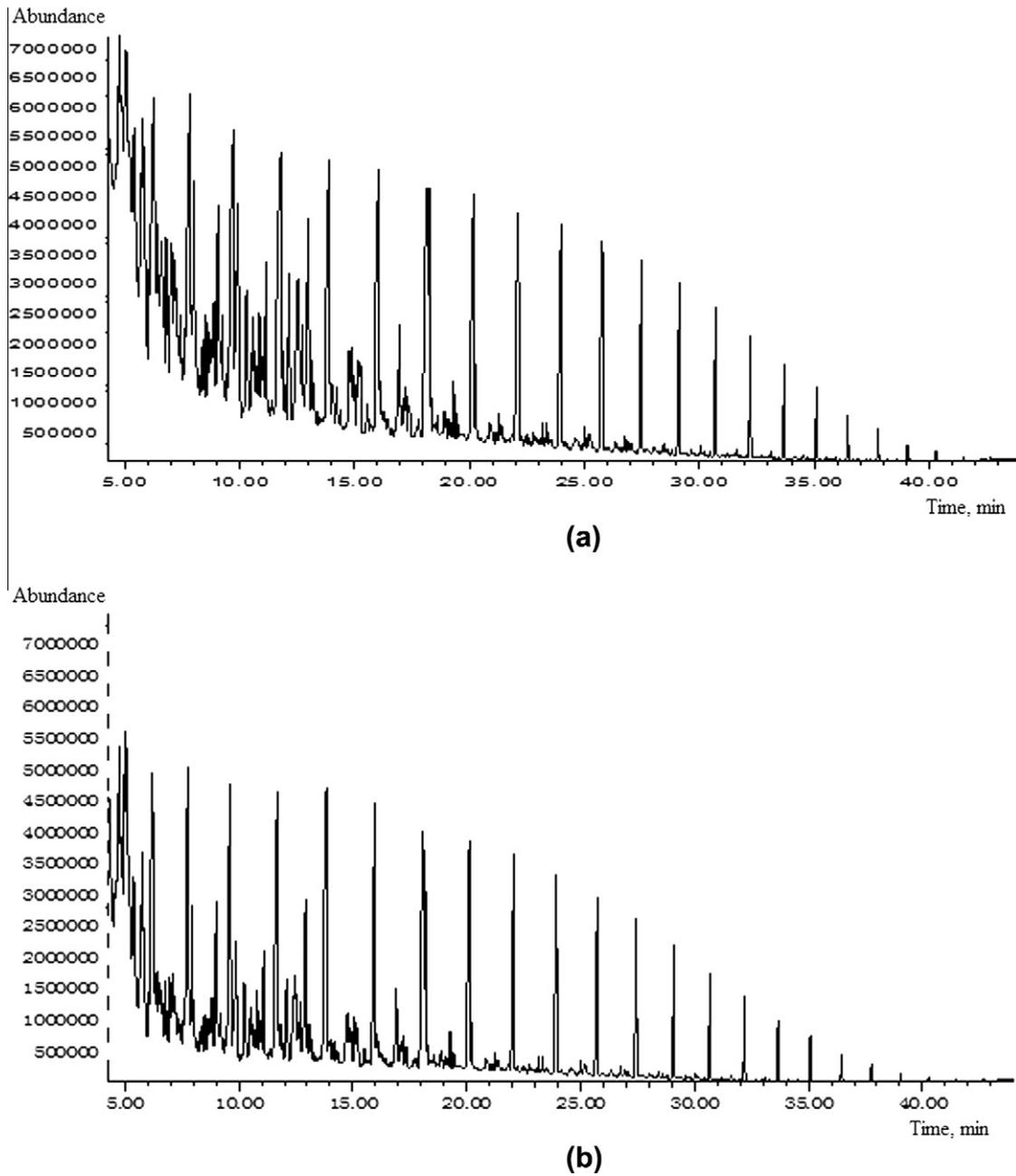


Fig. 2. Chromatograms of (a) crude oil and (b) recovered oil.

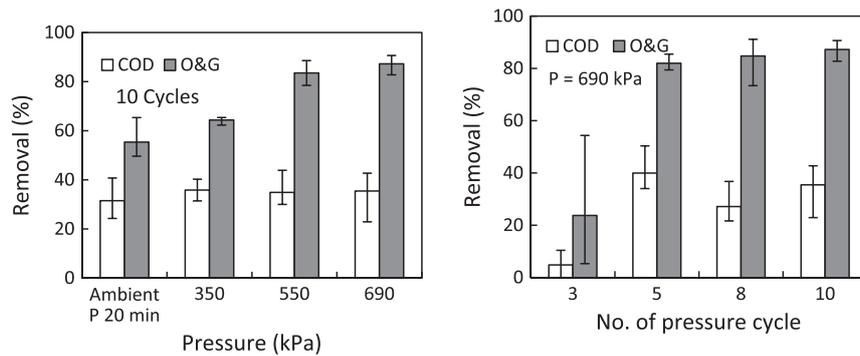


Fig. 3. Removals of COD and O&G from oil spill water according to compression pressure and number of pressure cycles used in ozonation (initial COD = 100 mg L⁻¹; initial O&G = 70 mg L⁻¹).

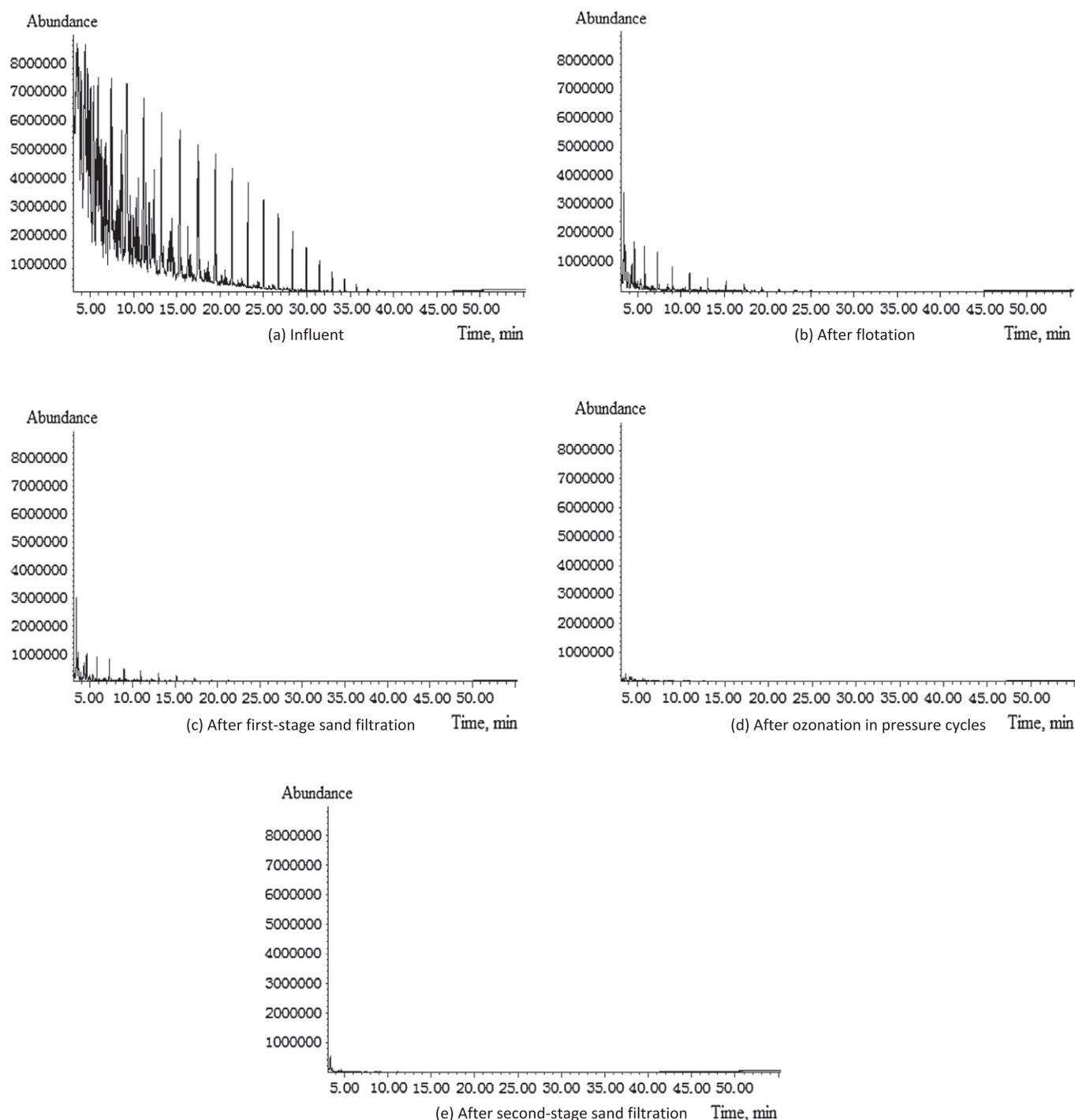


Fig. 4. Chromatograms of extracts from various stages of the sequential treatment process: (a) influent (2.5% v/v oil in tap water); (b) after flotation (HRT = 11 min, velocity = 5.2 cm min⁻¹); (c) after first filtration (HRT = 2.5 min, velocity = 8 cm min⁻¹, grain size = 0.25–0.44 mm); (d) after ozonation (P = 690 kPa, 10 cycles, 1.5% O₃ at 2 L min⁻¹ or 0.02% O₃ in air as compression gas); (e) after second filtration (HRT = 12 min, velocity = 2 cm min⁻¹, grain size = 0.25–0.44 mm and 0.12–0.25 mm at equal portions).

The three waters represented contaminated surface waters spanning a wide range of salinity from freshwater to nearly 10 times of seawater. As revealed by turbidity, COD, VDS, and O&G measurements in the effluents, the gradual removal of oil from water through the treatment train was not affected by the type of waters with very disparate characteristics (Table 1). In the final effluent from SF2, O&G was completely removed from all waters and VDS was removed from tap water and UL water.

3.5. Sand filtration capacity according to ozonation conditions

In addition to measured water quality parameters, the final effluent was visually examined for sheen appearance. No sheen appeared in any of the treated spiked waters (COD₀ = 300 mg L⁻¹) from a properly functioning sand bed (SF2); however, it would eventually appear as the filter capacity exhausted through accumulation of organic matter. It should be noted here that spiked

Table 3Sand filtration capacity according to different ozonation conditions (initial COD = 300 mg L⁻¹ in tap water).

Ozonation (kPa, cycles)	COD (mg L ⁻¹)	BOD/COD (%)	pH	Turbidity (NTU)	Throughput before sheen appearance (bed vol.)	No. of backwash before sheen appearance
No. treatment	11 ± 4.3	–	8.3–8.3	0.69 ± 0.33	10 ± 2.0	0
5 min Bubbling ozonation	39 ± 0.6	22 ± 4.0	8.2–8.3	1.0 ± 0.49	31 ± 1.0	1
690, 8 With air only	15 ± 2.0	26 ± 17	8.1–8.3	1.2 ± 0.20	30 ± 2.9	1
550, 10	34 ± 1.2	35 ± 1.3	7.4–8.8	2.3 ± 0.66	38 ± 4.7	1
690, 5	37 ± 9.2	32 ± 9.3	8.3–8.5	1.1 ± 0.66	58 ± 3.8	2
690, 8	42 ± 3.3	31 ± 4.0	7.8–8.3	0.58 ± 0.37	150 ± 2.8	3
690, 10	43 ± 4.3	32 ± 4.4	8.1–8.3	1.4 ± 0.41	140 ± 2.8	3

COD of 300 mg L⁻¹ was used, which was higher than observed in SF1 effluent (ca. 100 mg L⁻¹), to achieve breakthrough in a manageable period. Apparently, the throughput reaching backwash of the sand filter (defined by 50% reduction in filtration velocity) as well as the total throughput reaching sheen appearance depended on employed ozonation conditions. Therefore, using sheen appearance as a criterion we examined the capacity of the sand filter in terms of the number of backwashing and the total throughput before sheen appeared in the effluent, at which point thermal regeneration of the sands was required. The results are shown in Table 3. Without ozonation treatment, sheen appeared in the effluent very soon at 10 bed volumes (bv). With 5 min of ozonation or with pressure cycles of air, sheen still appeared soon at 30 bv although COD in the former was 2.6 times higher at 39 mg L⁻¹ due to formation of soluble organic acid products during ozonation. When the water had been treated with the optimal ozonation conditions, i.e. 690 kPa and 8 cycles, a total throughput of 150 bv over 3 filtration-backwashing cycles were sustained before sheen appeared in the effluent. Effluent quality parameters as defined by residual COD, BOD/COD ratio, and turbidity were 42 mg L⁻¹, 0.31, and 0.58 NTU, respectively, were maintained during this extended operation. These effluent characteristics were very similar to the final SF2 effluent originated from the heavily spiked water containing 2.5% oil and about 20000 mg L⁻¹ in COD.

Ozonation or sand filtration alone was not known to effectively remove oil and sheen from water. Combining the two in sequence, however, enabled essentially complete removal of oil and grease. Cha et al. (2010) explained the synergistic oil removal in two central steps: (1) during decompression, the heightened interaction of ozone and hydrocarbon at the expanding gas–liquid interface, and (2) the conversion of non-polar hydrocarbon droplets by ozone into ones with polar organic acid groups such as carboxylic groups resulting in agglomerated droplets that were more amenable to filtration. The results of combined ozonation in pressure cycles and sand filtration are consistent with the previous finding (Cha et al. 2010).

4. Conclusions

The removal of oil from an artificial oil spill water with 2.5% (v/v) oil was successfully demonstrated by a treatment train consisting of flotation, sand filtration, ozonation in pressure cycles, and sand filtration. Three spiked waters of varied sources including tap, Utah Lake, and Great Salt Lake sources at influent COD of 18000–20000 mg L⁻¹, VDS of 470–710 mg L⁻¹, and O&G of 6700–11000 mg L⁻¹ were treated to effluent COD of 22–29 mg L⁻¹, VDS of <20 mg L⁻¹, and O&G of <2 mg L⁻¹. The influent turbidity of 2800–3900 NTU was reduced to <0.7 NTU in the effluent, well below EPA's ambient water standards. The effluent showed little

changes in pH (<0.2) and increased BOD/COD ratios (0.33–0.48) that indicated highly biodegradable organic contents of <30 mg L⁻¹ in the effluent. The positive outcomes suggest the scheme's potential for onsite treatment of oil spill.

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