



Oil recovery from refinery oily sludge via ultrasound and freeze/thaw

Ju Zhang^a, Jianbing Li^{a,*}, Ronald W. Thring^a, Xuan Hu^b, Xinyuan Song^a

^a Environmental Engineering Program, University of Northern British Columbia, Prince George, British Columbia, Canada V2N 4Z9

^b College of Environmental Sciences and Engineering, Peking University, Beijing 100871, China

ARTICLE INFO

Article history:

Received 23 February 2011
Received in revised form 30 August 2011
Accepted 2 December 2011
Available online 13 December 2011

Keywords:

Freeze/thaw
Oil recovery
Oily sludge
Petroleum hydrocarbons (PHCs)
Ultrasound

ABSTRACT

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

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

The effective disposal of oily sludge wastes generated from petroleum industry during crude oil transportation, storage and refinery process is a worldwide problem. Generally the oily sludge is a complex water-in-oil (W/O) emulsion, typically including 30–50% of oil, 30–50% of water and 10–12% of solids by mass [1,2]. Due to the existence of high concentration of petroleum hydrocarbons (PHCs), oily sludge is considered to be hazardous to environments and human health, thus requiring effective remediation [3]. However, the emulsion and high PHC concentration could make the conventional sludge treatment process (i.e. landfarming, landfilling, incineration) to be time-consuming, ineffective and expensive [4,5]. Given the high oil concentration in oily sludge, oil recovery before disposal would be considered as one feasible method to improve the performance of those conventional treatment processes [6,7]. In fact, the treatment of sludge containing over 10% of oil could result in economic benefit from oil recovery [1]. The oil recovery would significantly reduce the PHC concentration and the volume of sludge for further treatment, thus the efficiency of conventional process such as landfarming could be

improved through significantly reducing soil/sludge mixing ratio in landfarm and providing a PHC concentration non-toxic to micro-organisms [8].

Solvent extraction has been applied to recover oil from waste oily sludge. For example, Zubaidy et al. [7] applied methyl ethyl ketone (MEK) and LPG condensate (LPGC) for oil recovery from sludge generated from the storage of crude petroleum, and found that these two solvents could achieve an oil recovery of 39% and 32%, respectively, when using the optimal 4:1 solvent-to-sludge ratio; Avila-Chavez et al. [9] used the supercritical fluid extraction apparatus to investigate the extraction of hydrocarbons from a crude oil tank bottom sludge with supercritical ethane at varying pressure and temperature conditions, and an extraction yield of up to 58.5% was obtained; Taiwo and Otolurin [10] reported an oil recovery of about 67.5% from the accumulated sludge in oil storage facilities by using hexane and xylene extraction. Although being applied to a number of oil recovery studies, the solvent extraction method is still associated with relatively lower oil recovery efficiency and requires the use of massive volume of solvents which may then restrict its application [7]. In addition to solvent extraction, a number of other studies have been reported to focus on physical approaches for oil recovery, including air flotation, thermal desorption, sonication, electrical and microwave heating [1,11–13]. Among these methods, ultrasonic irradiation has been proved as an effective treatment of removing adsorbed materials

* Corresponding author. Tel.: +1 250 9606397; fax: +1 250 9605845.
E-mail address: li@unbc.ca (J. Li).

from solid particles, solid/liquid separation in high-concentration suspensions (i.e. dewatering of biological sludge), and decreasing the stability of water/oil emulsion [14–17]. The cavitation collapse due to ultrasound can not only affect the surface of solid particles but also penetrate into the soil matrix, and could thus improve the separation of oil from soils and slurries [15,18]. A number of ultrasonic factors such as ultrasonic power and treatment time were found to affect the separation efficiency, while some experiments also indicated that the addition of alkaline reagents or sodium salts could enhance the separation [18,19]. In spite of the successful application to many engineering fields, few studies were reported to apply ultrasound for oil removal or recovery from oily sludge.

In order to effectively recover oil from the sludge, the emulsions need to be broken down. Freeze/thaw (F/T) used for sewage sludge dewatering in cold regions has been reported as one effective and feasible method for demulsification in recent years [20–22]. For example, Lin et al. [23] applied the freeze/thaw treatment method to break the water/oil emulsions with loosely packed droplets that were produced from oils, and the volume expansion of water turning to ice and interfacial tension of oil–water interface were determined as the main driving forces of demulsification. A number of factors such as freezing and thawing temperature as well as freezing time were found to affect the performance of this method [21,23], and some other parameters such as components in aqueous phase (salts, surfactants) were also reported to affect the demulsification process [24]. In general, ultrasonic and freeze/thaw treatment processes represent simple but effective methods for demulsification. It is recognized that the combination of alternative demulsification methods maybe more effective than individual method [22]. However, there have been very few studies into combining ultrasound with freeze/thaw for increasing the water/oil separation of oily sludge.

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

2. Materials and methods

2.1. Materials

The oily sludge used in the experiments was collected from a crude oil tank bottom in an oil refinery plant in western Canada. The sludge was very sticky, and its characteristics are listed in Table 1. The total petroleum hydrocarbon (TPH) concentration in sludge was analyzed based on the sample extraction process which will be described in Section 2.3, the metal elements were measured using Inductively Coupled Plasma (ICP) analysis based on the method given in ASTM D5185 [25], the water content was analyzed based on the ASTM D1744 method [26], and the solid content was calculated based on the measured TPH and water contents. Rhamnolipid (JBR 425) purchased from Jeneil Bio-surfactant Co. (LLC, USA) was used as the bio-surfactant. It is a 25% aqueous solution mixed with two rhamnolipids: $C_{26}H_{48}O_9$ and $C_{32}H_{58}O_{13}$. Dichloromethane (DCM) and cyclohexane (>99%, HPLC) were used as solvents for sample extraction. Silica gel (purchased from Sigma) activated at 105 °C for 12 h was used to clean up extraction solution (see Section 2.3), and anhydrous sodium sulfate dried at 400 °C for 12 h was used to absorb water in the extraction solution.

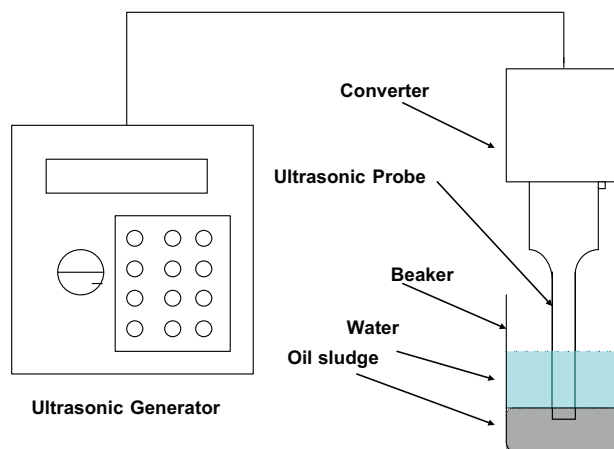


Fig. 1. Ultrasonic treatment system.

2.2. Experimental design

2.2.1. Experiments on oil recovery by using three different processes

The experiments were conducted to compare the efficiencies of oil recovery from refinery sludge by using three different treatment processes, including ultrasonic treatment alone (US), freeze/thaw alone (F/T) as well as the combined ultrasonic and freeze/thaw treatment (US + F/T). In terms of ultrasonic treatment alone, 10 g of oily sludge was placed inside a 120 ml beaker which contained 40 ml of deionized water, and was then treated by placing the 0.5 in. diameter titanium sonic probe into the center of the sample. The sonic probe was operated by a 20 kHz Misonix Sonicator 3000 generator. The treatment was conducted at a working power of 66 W for 10 min. Fig. 1 illustrates the ultrasonic treatment system. After ultrasonic treatment, the treated sample was observed to have a reduced viscosity than the original sludge and was transferred into a 50-ml centrifuge tube. The sample was then centrifuged for 15 min at 5000 rpm. The oil and aqueous phases after centrifugation were then separated using a separation funnel, and the mass of oil layer separated was then measured and considered as the oil recovery. The total petroleum hydrocarbon (TPH) concentrations in the separated oil layer and aqueous phase were also analyzed.

In terms of freeze/thaw treatment alone, 10 g of oily sludge was put into a 50-ml centrifuge tube with 40 ml of DI water and was frozen within a freezer under -20°C for 12 h. The frozen sample was then thawed at an ambient temperature of 24°C . After thawing, the sample in the tube was centrifuged for 15 min at 5000 rpm. The oil and aqueous phases after centrifugation were separated using a separation funnel, and the mass of oil layer separated from the sample as well as the TPH concentrations in oil layer and aqueous phase were then measured. In terms of the combined ultrasonic and freeze/thaw treatment process, 10 g of oily sludge was put into a 120 ml beaker with 40 ml of deionized water, and was then treated by ultrasound at 66 W for 10 min. After ultrasonic treatment, the sample was transferred to a 50-ml centrifuge tube and was centrifuged for 15 min at 5000 rpm. After centrifugation, the sample in the tube went through the freeze/thaw process, and the remaining treatment procedures were the same as those for the freeze/thaw treatment alone.

2.2.2. Experiments on factors affecting the combined treatment process

The individual impacts of five different factors on the oil recovery rate from the combined ultrasonic and freeze/thaw treatment process were further examined to better understand this process and provide useful information for its effective operation.

Table 1
Characteristics of the oily sludge.

Parameter	Concentration (mg/kg)	Parameter	Concentration (mg/kg)
TPH	61% (by mass)	Barium	2136
Water content	24% (by mass)	Iron	6339
Solid content	15% (by mass)	Zinc	209
Sodium	76	Copper	43
Potassium	423	Lead	19
Magnesium	432	Chromium	11
Aluminum	999	Nickel	9
Calcium	1145		

Five factors were selected, including ultrasonic power, ultrasonic treatment duration, sludge/water mixing ratio, bio-surfactant concentration, and salt (NaCl) concentration. Table 2 summarizes the corresponding levels of the experimental factors, while the interaction effects of different factors were not investigated in this study. In terms of ultrasonic power, experiments were conducted at four levels from 21 to 66 W with an ultrasonic treatment duration of 10 min (i.e. the maximum treatment duration level in this study) and a sludge/water ratio of 1:4 (i.e. the medium mixing ratio level selected in this study), without the addition of bio-surfactant and salt. In terms of ultrasonic treatment duration, four levels (0.5, 1, 5 and 10 min) were examined at the ultrasonic power of 66 W (i.e. the maximum power level selected in this study) and sludge/water ratio of 1:4 without the addition of bio-surfactant and salt. In terms of other factors, four different sludge/water mixing ratios from 1:8 to 1:1 as well as five different levels of bio-surfactant concentration (from 0 to 700 mg/L) and salt concentration (from 0 to 5.0% by mass) were investigated at the ultrasonic power of 66 W and 10 min of treatment time. For the examination of sludge/water ratio, no rhamnolipids and salt were added to the sludge slurry system; for the examination of bio-surfactant concentration, a sludge/water ratio of 1:4 was maintained without the addition of salt, and for the examination of salt concentration, a sludge/water ratio of 1:4 was applied without the addition of rhamnolipids. The experimental procedures for each factor's examination were the same as described before.

2.3. Sample extraction and analysis

2.3.1. TPH concentration in the recovered oil layer

1 g of the recovered oil layer sample was dissolved with 20 ml of solvent (cyclohexane) in a 40-ml vial and then the vial was placed on an orbital shaker for mechanical extraction at 150 rpm for 1 h. After shaking, the extraction solution was transferred into a glass column for cleanup to remove moisture, particulate, and unwanted polar organic compounds [27]. The column was packed with silica gel and anhydrous sodium sulfate and rinsed with 20 ml of solvent (1:1 cyclohexane/DCM) before use. After the extraction solution passed through, another 20 ml of solvent (1:1 cyclohexane/DCM) was poured to elute the column. A round flask with mass of M_0 (mg) was put under the column to collect the extraction solution after cleanup, and then the extraction solution in the flask was evaporated using a rotary evaporator to remove the solvent contained in the extraction solution. After evaporation, the round flask with residue was put in the fume hood for 30 min at room

Table 2
Influencing factors and their corresponding levels.

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

temperature and only petroleum hydrocarbons (PHCs) were left in the flask [27]. The mass of the flask containing PHCs was then measured as M_T (mg). Consequently, the concentration of TPH in the recovered oil can be calculated by Eq. (1). Similarly, TPH concentration in the original sludge can also be obtained.

$$C = \frac{M_T - M_0}{M} \quad (1)$$

where M is the mass of oil layer sample or original sludge sample used for extraction analysis (g), and C is the TPH concentration in oil layer or original sludge (mg/g). The oil recovery was defined as the ratio of the mass of PHCs in the recovered oil to the mass of PHCs in the original sludge sample, and can be obtained using Eq. (2):

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

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

2.3.2. TPH concentration in separated aqueous phase

The separated aqueous phase from the sample after oil recovery treatment consists of petroleum hydrocarbons and could be considered as wastewater, and the TPH concentration in such aqueous phase should also be analyzed. This was completed using about 40 ml of aqueous phase water through liquid–liquid extraction with 15 ml of cyclohexane for three times [28]. About 45 ml of extraction solution was collected and then cleaned up through a glass column packed with silica gel and anhydrous sodium sulfate as described above. The remaining procedures were the same with that for measuring TPH in oil layer. As a result, TPH concentration in the aqueous phase C_{water} (mg/L) was obtained using Eq. (3):

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

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

2.3.3. PHC fraction analysis

After evaporation using a rotary evaporator, petroleum hydrocarbons in the round flask were transferred into a 15-ml sample vial by adding with cyclohexane, and 2 ml of solution in the vial was then sent for the analysis of PHCs using a Varian CP-3800 Gas Chromatograph with flame ionization (GC-FID). External standard method was used to calculate PHC concentration in the sample solution, and decane (C10), hexadecane (C16), tetratriacontane (C34), and pentacontane (C50) were used as standard compounds to determine the PHC fractions [29], where fractions F1, F2, F3 and F4 were defined as the group of hydrocarbons from C6 to C10, C10 to C16, C16 to C34, and C34 to C50, respectively. The GC analysis conditions include: ZB-capillary column

(Phenomenex Torrance, CA) with 30 m × 0.25 mm ID (inner diameter) and 0.25- μ m film thickness; inject volume of 1 μ L; injector and detector (FID) temperatures at 320 °C; carrier gas (helium) at a constant flow rate of 1.5 ml/min during analysis. The splitless injection mode was performed on the 1079 PTV injector and after 0.7 min the split mode was activated at split ratio of 10:1. The capillary column temperature program was initially held at 50 °C for 1 min, then ramped at 15.0 °C/min to 110 °C and further increased at 10.0 °C/min to 300 °C and then held for 11 min. The total running time for a sample analysis was 35 min.

3. Results and discussion

3.1. Comparison of methods

The experimental results of using different oil recovery methods are summarized in Table 3, and it was indicated that F/T method alone worked more effectively in terms of the oil recovery rate (with an oil recovery of 65.7%) than the two other methods (Fig. 2). It is recognized that the water/oil emulsion is stabilized by the existence of an emulsifying film consisting of surfactant molecules which could prevent water droplets from contacting each other [21]. During the freezing of water droplets, some surfactant molecules would be expelled from the ice lattices at the oil–water interface and diffuse into the oil phase, and during thawing process more surfactant molecules could be diffused away from the interface, leading to the lack of surfactant molecules on the emulsifying film. Thus the water droplets could coalesce and form larger water droplets which facilitate the water/oil separation, while some surfactants may form micelles inside the water droplets with trace amount of oil [21,22]. It was found from the experiments that ultrasonic treatment alone was associated with the lowest oil recovery (i.e. 58.9%), while the combination of ultrasound and freeze/thaw achieved an oil recovery of 64.2% which was close to that for F/T alone. This may indicate that ultrasound alone could not effectively break the emulsifying film of surfactant molecules.

However, ultrasound alone achieved the highest TPH concentration in the recovered oil layer (i.e. highest purity) (Fig. 3a). The TPH concentration in the recovered oil was 625 mg/g for F/T, 933 mg/g for US and 851 mg/g for US+F/T, while the TPH concentration in the original oily sludge was 610 mg/g. As a result, the recovered oil from ultrasonic treatment alone contained 93.3% of TPH. In fact, for a multiphase system when solid phase exists,

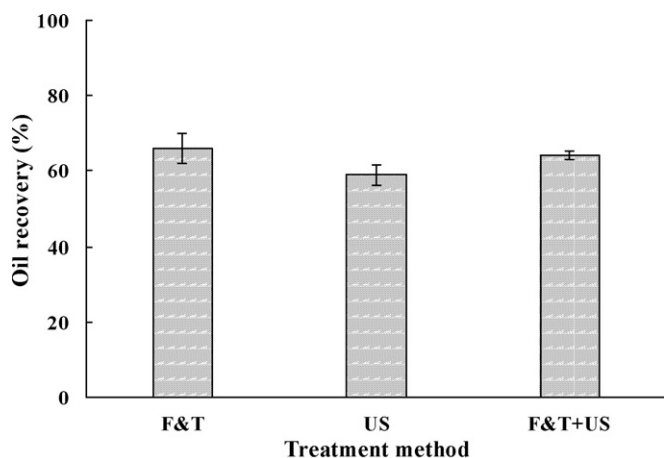


Fig. 2. Oil recoveries for different treatment methods (error bar represents standard deviation).

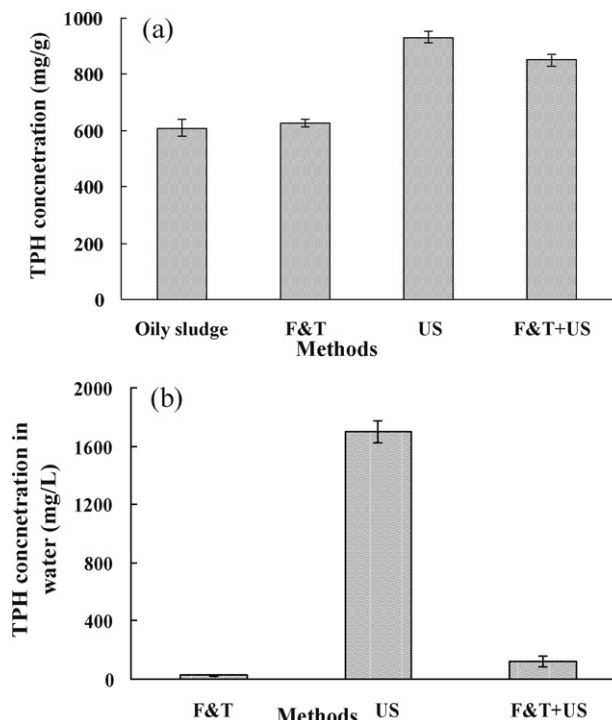


Fig. 3. TPH concentrations in separated oil layer (a) and water (b) (error bar represents standard deviation).

petroleum hydrocarbon molecules are either strongly adsorbed onto the surface of solid particles or trapped inside the sediment matrix, and this would prevent the separation of oil from the multiphase system. Previous studies [30–32] proved that ultrasound could effectively promote the desorption of organic compounds. Due to ultrasonic irradiation in liquid media, micro-bubbles could form and then collapse or implode when they reach some critical size [33], leading to localized high pressure and temperature shockwave. The collapse or implosion occurring in the vicinity of particle surface would release the adsorbed or trapped organic compound molecules from the solid particles or sediment matrix into the solution. Moreover, the collapse can bring high-speed liquid micro-jets with strong shear force which can then break the aggregates of solid particles and result in the detachment of oil and water from the solid particles [30,34]. Consequently, ultrasound could considerably enhance the separation of oil from solid phase and more adsorbed or trapped oil could enter the oil layer after oil/water separation. The experimental results in this study indicated that freeze/thaw alone was not effective for desorption. Although it obtained the highest oil recovery, the concentration of TPH in the recovered oil was the lowest (i.e. 62.5%). Through application of ultrasound, the TPH concentration in the recovered oil for combined US+F/T process increased significantly from 62.5% to 85.1% which was close to that for ultrasonic treatment alone (i.e. 93.3%).

The TPH concentrations in aqueous phase after water/oil separation for different treatment methods are presented in Fig. 3b. It was found that for ultrasonic treatment alone, the separated aqueous phase contained very high concentration of TPH (1550 mg/L). Such high concentration may result in high cost for further treatment of the wastewater after oil recovery. In contrast, freeze/thaw treatment alone was associated with the lowest TPH concentration in wastewater (i.e. less than 25 mg/L). The application of ultrasound could promote the desorption of adsorbed or trapped PHCs and then effectively release them to the solution, while freeze/thaw was not effective in promoting the desorption. In fact, for the samples

Table 3
Summary of oil recovery results using different methods.

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

treated by freeze/thaw alone, it was observed in the experiments that the solid particles were hardly separated and settled in the bottom of the tube. Thus the recovered oil layer also contained high contents of solids, and the TPH concentration in the recovered oil (i.e. 62.5%) was close to that in the original sludge (i.e. 61%). The observed sludge settleability after freeze/thaw treatment in this study was not in agreement with previous study conducted by Jean et al. [20] who used freeze/thaw to treat the oily sludge samples taken from the dissolved air flotation (DAF) unit of a wastewater treatment plant. The crude oil tank bottom sludge used in this study contained more solid content (i.e. 15%) than the DAF sludge (i.e. 7.8%), and this emulsion had an oil/solid ratio of about 4.0 (Table 1). The oil recovery from sludge requires not only the separation of oil from water but also the detachment of oil molecules from solids. It was suggested that the F/T method was effective to drive hydrocarbon molecules away from water to form free oil layer [21]. However, as described before, the F/T method could not provide a strong driving force to remove the adsorbed oil to the aqueous phase from solid particles within the crude oil tank bottom sludge.

For samples treated by ultrasound or combined ultrasound and freeze/thaw, it was observed in the experiments that the solid particles were significantly separated from aqueous phases and settled in the bottom of the tube, and this indicates that ultrasound could enhance the settling of solid particles. As a result, the recovered oil for ultrasound alone and combined ultrasound and freeze/thaw contained much less solids but with much higher TPH (i.e. 93.3% and 85.1%) as compared with that for freeze/thaw alone. Due to ultrasonic irradiation, some desorbed PHCs from solids also entered the aqueous phase, but with the effect of freeze/thaw, some hydrocarbon molecules could be expelled from the expansion of water droplets turning into ice and then enter the oil phase. As a result, it was observed that the TPH concentration in the separated aqueous phase for combined ultrasound and freeze/thaw was much lower (i.e. 200 mg/L) than that for ultrasound alone (i.e. 1550 mg/L) but higher than that for freeze/thaw alone (i.e. <25 mg/L). This was in agreement with previous studies that F/T method was effective for separating oil from the aqueous phase [20,21]. As described above, the combined process brought higher oil recovery than that for the ultrasonic treatment alone, and much higher TPH concentration in the recovered oil layer than that for the F/T method. Consequently, the combined ultrasonic and freeze/thaw treatment was identified in this study as more effective than the other two methods and was further examined for oil recovery from the refinery crude oil tank bottom sludge.

3.2. Effects of different factors on the combined treatment process

3.2.1. Effects of ultrasonic power and treatment duration

In terms of the combined ultrasonic and freeze/thaw treatment process, Figs. 4 and 5 present the oil recovery results under the impacts of ultrasonic power and treatment duration. It was observed from Fig. 4 that the oil recovery of the combined process could be improved by increasing ultrasonic power at low level. For example, the recovery rate was increased from 57.7% at ultrasonic

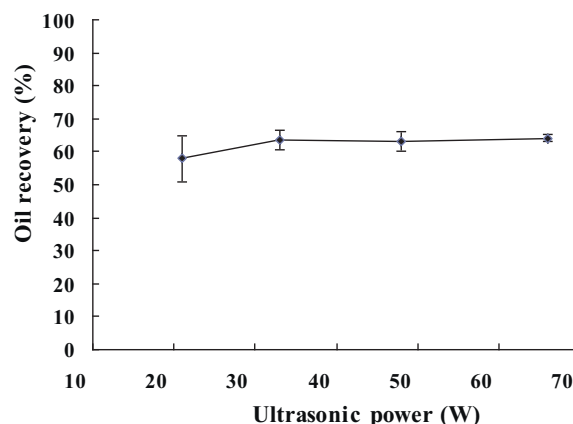


Fig. 4. Oil recovery versus ultrasonic power for the combined process (error bar represents standard deviation) (experimental condition: ultrasonic treatment duration of 10 min, sludge/water ratio of 1:4, without the addition of rhamnolipids and NaCl).

power of 21 W to 63.6% at 33 W. However, further increase in ultrasonic power at level above 33 W was not associated with significant enhancement of oil recovery. The oil recovery was only increased to 64.1% at ultrasonic power of 66 W. Similar results of the limitation of ultrasonic power have also been reported in many studies in other areas [30,35]. It has been reported that the phenomena of ultrasonic cavitation could play a significant role in enhancing the desorption of adsorbed molecules, and the effect of cavitation depends on the size of bubbles while more energy could be stored within the bigger bubbles [31]. In this study, the low frequency of ultrasound (20 kHz) was applied. In order to produce shockwave and high speed microjets, implosion radius of bubbles is around 170 μm at 20 kHz [36]. However, bubbles with radius at a few microns usually become unstable and collapse at such ultrasonic frequency, leading to the rare existence of larger bubbles.

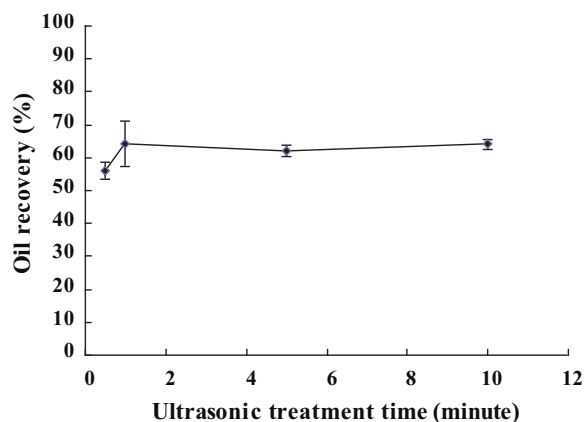


Fig. 5. Oil recovery versus ultrasonic treatment duration for the combined process (error bar represents standard deviation) (experimental condition: ultrasonic treatment power of 66 W, sludge/water ratio of 1:4, without the addition of rhamnolipids and NaCl).

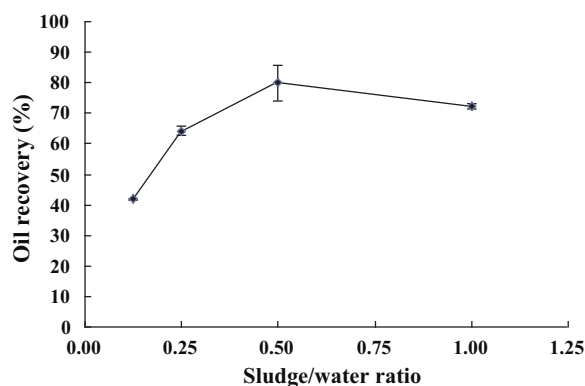


Fig. 6. Oil recovery versus sludge/water ratio for the combined process (error bar represents standard deviation) (experimental condition: ultrasonic power of 66 W, ultrasonic treatment duration of 10 min, without the addition of rhamnolipids and NaCl).

Thus the inhibition on the size of cavitation microbubbles could be attributed to no further significant increase of oil recovery rate even though the ultrasonic power was increased from 33 W to 66 W.

In terms of the impact of ultrasonic treatment duration, it can be found from Fig. 5 that the oil recovery was increased to 64.2% within 1 min of ultrasonic treatment followed by freeze/thaw. No further significant increase of oil recovery was observed when ultrasonic irradiation was increased to 10 min. The oil recovery was 64.1% when the treatment duration was 10 min which was close to that at 1 min of treatment. This may be explained by the fact that when adsorbed organic molecules were desorbed from solid particles into aqueous phase even through long duration of ultrasonic treatment, re-adsorption might happen in the system during freeze/thaw process and would thus compromise the effect of ultrasonic desorption [30].

3.2.2. Effects of sludge/water ratio

Fig. 6 presents the oil recoveries at different sludge/water ratios for the combined treatment process. It can be observed that oil recovery was increased from 41.9% to 80.0% as the slurry content was increased from sludge/water ratio of 1:8 to 1:2 and then slightly dropped to 72.2% at sludge/water ratio of 1:1. The increase of sludge content in the slurry system could result in more oil recovery. However, further increase of sludge content when the sludge/water ratio was above 1:2 could result in increased viscosity of the slurry which then could impede the formation and collapse of cavitation bubbles. As a result, the effect of sonication was weakened and oil recovery rate was decreased when the sludge content was too high in the slurry. Similar phenomena was also reported by Feng et al. [30] who used ultrasonic irradiation to remove diesel from solid in slurry state, and they indicated that the increase of solid concentration above 50% significantly inhibited cavitation process in oily sand–water system. In terms of the TPH concentration in the recovered oil, it was observed to be 658, 846, 851, and 659 mg/g for the sludge/water ratios of 1:1, 1:2, 1:4 and 1:8, respectively. The TPH concentration in the recovered oil for sludge/water ratio of 1:2 was close to that for sludge/water ratio of 1:4. Consequently, by considering oil recovery and the quality of the recovered oil, the effective sludge/water ratio was 1:2 when using the combined treatment process.

3.2.3. Effects of bio-surfactant (rhamnolipids)

The effect of rhamnolipid addition to the oily sludge slurry system on the combined treatment process is shown in Fig. 7. It can be found that the oil recovery was increased from 64.1% to 73.2% as the concentration of rhamnolipids in water was increased from 0 to 100 mg/L. However, the oil recovery dropped to 61.8%

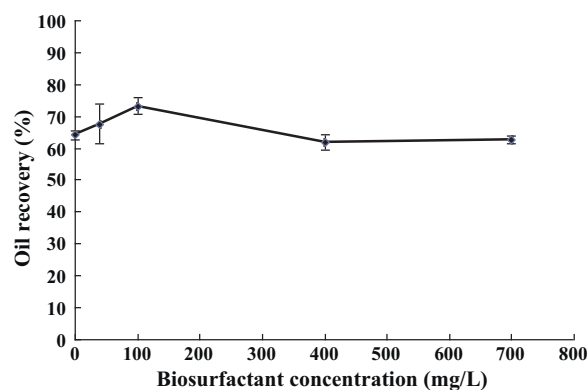


Fig. 7. Oil recovery versus bio-surfactant concentration for the combined process (error bar represents standard deviation) (experimental condition: ultrasonic power of 66 W, ultrasonic treatment duration of 10 min, sludge/water ratio of 1:4, without the addition of NaCl).

and 62.5% at rhamnolipids concentration of 400 and 1000 mg/L, respectively. Rhamnolipids are a class of glycolipid bio-surfactants usually produced by specific bacterial strains [37], and the critical micelle concentration (CMC) has been reported between 10 and 230 mg/L [38]. The addition of rhamnolipids into the oily sludge slurry samples could affect the adsorption energy of petroleum hydrocarbons with solid particles and lower the energy required for desorption, and thus the organic compounds could be easily removed at the same ultrasonic power application. Furthermore, the presence of surfactant could lower the surface tension and affect the formation and collapse of ultrasonic cavitation bubbles. Therefore, an apparent increase of oil recovery was observed with addition of rhamnolipids up to 100 mg/L. However, when the adsorbed hydrocarbon molecules was continuously removed from solid particles by ultrasonic irradiation, the free sites on solid particle surface could allow for the adsorption of bio-surfactants if there were a large amount of rhamnolipids in the oil/solids/water multiphase system. The ultrasonic cavitation would also exert an effect on the adsorption and desorption of rhamnolipids, and thus not all of the ultrasonic energy introduced into the system was used to remove oil from solid particles. As a result, the oil recovery rate dropped when the rhamnolipid concentration was above 100 mg/L.

3.2.4. Effects of salt addition (sodium chloride)

Fig. 8 presents the effect of sodium chloride (NaCl) concentration on the combined treatment process. It was found that the oil recovery was increased from 64.1% to 74.2% as the addition of

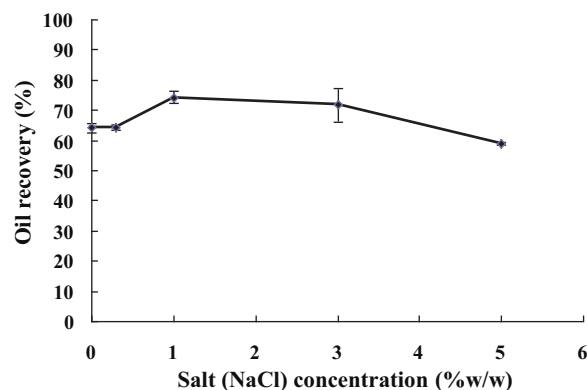


Fig. 8. Oil recovery versus NaCl concentration for the combined process (error bar represents standard deviation) (experimental condition: ultrasonic power of 66 W, ultrasonic treatment duration of 10 min, sludge/water ratio of 1:4, without the addition of rhamnolipids).

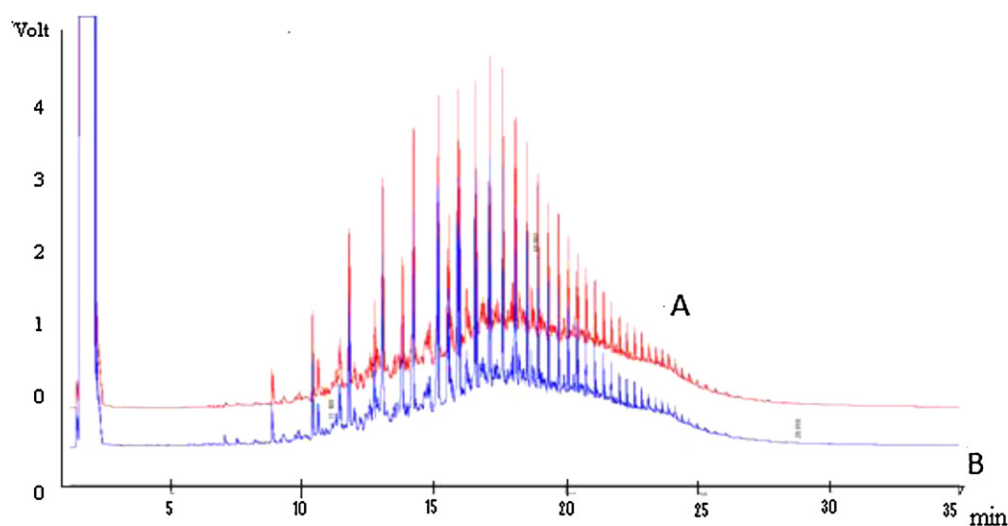


Fig. 9. GC profiles of samples from oil recovery treatment (A represents oil sample after US + F/T treatment and B represents original oily sludge sample).

Table 4
PHC fraction distribution for samples before and after US + F/T treatment.

Samples	PHC fraction distribution (%)		
	F2	F3	F4
Original sludge	22.98%	63.86%	13.17%
Oil recovered at 66 W for 10 min with no salinity and bio-surfactant (with sludge/water ratio of 1:4)	21.77%	64.05%	13.28%
Oil recovered at 66 W for 1 min with no salinity and bio-surfactant (with sludge/water ratio of 1:4)	21.78%	64.92%	13.30%
Oil recovered at 66 W for 10 min with 3% NaCl (with sludge/water ratio of 1:4)	21.90%	64.70%	13.39%
Oil recovered at 66 W for 10 min with 40 mg/L bio-surfactant (with sludge/water ratio of 1:4)	21.63%	64.88%	13.49%

NaCl was increased from 0 to 1%. As the salt concentration was further increasing, the oil recovery started decreasing and dropped to 59.0% when the NaCl concentration was 5%. Thus the low salinity showed a positive impact while the high salinity illustrated a negative impact on oil recovery from oily sludge. Low salinity brine injection has been studied for oil recovery and it has been reported that the presence of ions would affect the adsorption of oil onto clay or mineral layers [39,40]. Abramov et al. [18] indicated that the addition of Na^+ helped to break the bond between oil and sand soils by increasing the negative charges on the soil surfaces. In addition, the presence of NaCl could also enhance cavitation bubble implosion and thus enhance the sonic power intensity [41]. As a result, the addition of salt could introduce a positive effect on oil recovery using the combined treatment process. However, excessive amount of NaCl (i.e. above 1%) in the sludge slurry system could reduce the concentration of PHCs in the aqueous phase and lead to a negative impact on the desorption of PHCs from solid particles by ultrasound [42]. Therefore, the effective salinity was found to be about 1% for oil recovery from oily sludge.

3.3. PHC fraction analysis for recovered oil

Fig. 9 presents the GC profiles of samples from the combined ultrasonic and freeze/thaw treatment, and it can be found that there was no significant difference between PHC fraction distribution in the original sludge sample and the recovered oil sample, indicating that the effect of ultrasonic destruction of petroleum hydrocarbons was not significant (i.e. no significant shift of peaks towards the left of GC profile), and the main mechanism of enhanced oil recovery through the combined process was ultrasonic enhanced desorption.

Table 4 lists the PHC fraction distributions in the original oily sludge sample and several recovered oil samples under different treatment conditions. It can be found that the difference among the proportions of PHC fractions in the recovered oil under different ultrasonic treatment conditions was very small, and the average F2, F3, and F4 fractions in the recovered oil were 21.77%, 64.64%, and 13.37%, respectively. The F2 fraction in the recovered oil was slightly lower (i.e. about 1.2%) than that in the original sludge, while the F3 and F4 fractions in the recovered oil were slightly greater (i.e. about 0.8% and 0.2%) than that in the original sludge. This may indicate that the application of ultrasound could destruct some light oil compounds such as F2, leading to slight increase of the proportion of F3 and F4 fractions in the recovered oil. However, the effect of ultrasonic destruction was not very significant. It has been reported that the destruction of organic compounds such as long-chain hydrocarbons was resulted from the production of hydroxyl radicals [30]. This usually occurs when the ultrasound is in the mid frequency from 200 to 400 kHz [31,43]. In this study, the condition for the production of hydroxyl radicals was not reached at low frequency of 20 kHz, thus there was no significant destruction to change the PHC proportions in the recovered oil. However, the energy released from ultrasonic cavitation under this frequency was enough to overcome the affinity of hydrocarbon molecules with solid particles and to increase oil desorption.

4. Conclusions

Oil recovery from refinery oily sludge was investigated in this study using three different approaches, including ultrasonic treatment alone, freeze/thaw alone, and combined ultrasonic and freeze/thaw treatment. By comprehensively considering oil

recovery efficiency, as well as TPH concentrations in the recovered oil and in the separated wastewater, the combination of ultrasound and freeze/thaw was identified as an effective method with satisfactory performance. Under the experimental conditions, it achieved an oil recovery rate of 64.2%, and TPH concentrations of 85.1% and 200 mg/L in the recovered oil and wastewater, respectively. The experimental results revealed that ultrasound could promote the separation of oil from solids while freeze/thaw could promote the separation of water and oil in the multiphase system. Several different factors were further examined to investigate their individual impacts on the performance of the combined treatment process, and it was observed that under the experimental conditions, the oil recovery was improved with ultrasonic power at low power level, but further increase in ultrasonic power at level above 33 W was not associated with significant enhancement of oil recovery. The oil recovery was increased to its peak within 1 min of ultrasonic treatment, and thereafter no further significant increase of oil recovery was observed. The results of examining the individual impacts of other factors on the combined treatment process indicated an effective sludge/water ratio of 1:2, a rhamnolipid concentration of 100 mg/L, and a NaCl concentration of 1%, respectively. An oil recovery rate of up to 80.0% was observed under the experimental conditions of ultrasonic power of 66 W, ultrasonic treatment duration of 10 min, sludge/water ratio of 1:2, and no addition of bio-surfactant and salt.

The analysis of PHC fraction distributions in the recovered oil samples indicated that the effect of ultrasonic destruction of organic compounds was insignificant, and the major mechanism of oil recovery enhancement was through enhanced ultrasonic desorption of PHCs from solid particles under the low frequency application of 20 kHz. In this study, the individual impacts of different factors on the combined treatment process were examined through a series of laboratory experiments. However, the interaction effects among these factors, the identification of major influencing factors, and the optimal combination of these factors were not examined. This could be investigated through factorial experimental design method in future studies. In addition, the recovered oil from the crude oil tank bottom sludge in this study was not a pure mixture of petroleum hydrocarbons, and may need further treatment. The value of the recovered oil as fuel (such as asphaltene content, ash content, salt content, and heat of combustion) and the detailed cost/benefit of the proposed treatment process were not analyzed, and should be examined in future studies. In summary, the combined ultrasonic and freeze/thaw process could represent an environmentally friendly and economically competitive alternative for the effective treatment of oily sludge waste from the petroleum industry, and is worth of further investigations.

Acknowledgments

This study has been supported by the Natural Sciences and Engineering Research Council of Canada, the British Columbia Innovation Council (ICSD-2007-Li-J), and the University of Northern British Columbia (UNBC Research Project Award). The authors would like to thank the anonymous reviewers for their comments and suggestions that helped in improving the manuscript.

References

- [1] D. Ramaswamy, D.D. Kar, S. De, A study on recovery of oil from sludge containing oil using froth flotation, *J. Environ. Manage.* 85 (2007) 150–154.
- [2] V.R. Reynolds, S.R. Heuer, Process for the recovery of oil from waste oil sludges, U.S. Patent #: 5,269,906, 1993.
- [3] M.D. Ferrari, E. Neirrotti, C. Albornoz, M.R. Mostazo, Biotreatment of hydrocarbons from petroleum tank bottom sludges in soil slurries, *Biotechnol. Lett.* 18 (1996) 1241–1246.
- [4] J. Shie, C. Chang, J. Lin, Resources recovery of oil sludge by pyrolysis: kinetics study, *J. Chem. Technol. Biotechnol.* 75 (2000) 443–450.
- [5] N. Buyukkamaci, E. Kucukselek, Improvement of dewatering capacity of a petrochemical sludge, *J. Hazard. Mater.* 144 (2007) 323–327.
- [6] M. Elektorowicz, S. Habibi, Sustainable waste management: recovery of fuels from petroleum sludge, *Can. J. Civil. Eng.* 32 (2005) 164–169.
- [7] E.A.H. Zubaidy, D.M. Abouelnasr, Fuel recovery from waste oily sludge using solvent extraction, *Process Saf. Environ.* 88 (2010) 318–326.
- [8] W. Liu, Y. Luo, Y. Teng, Z. Li, L.Q. Ma, Bioremediation of oily sludge-contaminated soil by stimulating indigenous microbes, *Environ. Geochem. Health* 32 (2010) 23–29.
- [9] M.A. Avila-Chavez, R. Eustaquio-Rincon, J. Reza, A. Trejo, Extraction of hydrocarbons from crude oil tank bottom sludges using supercritical ethane, *Sep. Sci. Technol.* 42 (2007) 2327–2345.
- [10] E.A. Taiwo, J.A. Otolorin, Oil recovery from petroleum sludge by solvent extraction, *Pet. Sci. Technol.* 27 (2009) 836–844.
- [11] M. Elektorowicz, S. Habibi, R. Chifrina, Effect of electrical potential on the electro-demulsification of oily sludge, *J. Colloid Interface Sci.* 295 (2006) 535–541.
- [12] H.A. Nour, R. Sothilakshmi, H.A. Nour, Microwave heating and separation of water-in-oil emulsions: an experimental study, *Int. J. Chem. Technol.* 2 (2010) 1–11.
- [13] N. Xu, W.X. Wang, P.F. Hang, X.P. Lu, Effects of ultrasound on oily sludge deoiling, *J. Hazard. Mater.* 171 (2009) 914–917.
- [14] A.P. Newman, J.P. Lorimer, T.J. Mason, K.R. Hutt, An investigation into ultrasonic treatment of polluted solids, *Ultrason. Sonochem.* 4 (1997) 153–156.
- [15] Y.U. Kim, M.C. Wang, Effect of ultrasound on oil removal from soils, *Ultrasonics* 41 (2003) 539–542.
- [16] G. Ye, X. Lu, P. Han, F. Peng, Y. Wang, X. Shen, Application of ultrasound on crude oil pretreatment, *Chem. Eng. Process.* 47 (2008) 2346–2350.
- [17] R. Dewil, J. Baeyens, R. Goutvrind, Ultrasonic treatment of waste activated sludge, *Environ. Prog.* 25 (2006) 121–128.
- [18] V.O. Abramov, S.K. Myasnikov, M.S. Mullakaev, Extraction of bitumen, crude oil and its products from tar sand and contaminated sandy soil under effect of ultrasound, *Ultrason. Sonochem.* 16 (2009) 408–416.
- [19] A.F. Collings, A.D. Farmer, P.B. Gwan, Processing contaminated soils and sediments by high power ultrasound, *Miner. Eng.* 19 (2006) 450–453.
- [20] D.S. Jean, D.J. Lee, J.C.S. Wu, Separation of oil from oily sludge by freezing and thawing, *Water Res.* 33 (1999) 1756–1759.
- [21] G.H. Chen, G.H. He, Separation of water and oil from water-in-oil emulsion by freeze/thaw method, *Sep. Purif. Technol.* 31 (2003) 83–89.
- [22] V. Rajakovic, D. Skala, Separation of water-in-oil emulsions by freeze/thaw method and microwave radiation, *Sep. Purif. Technol.* 49 (2006) 192–196.
- [23] C. Lin, G. He, X. Li, L. Peng, C. Dong, S. Gu, G. Xiao, Freeze/thaw induced demulsification of water-in-oil emulsions with loosely packed droplets, *Sep. Purif. Technol.* 56 (2007) 175–183.
- [24] S. Ghosh, J.N. Coupland, Factors affecting the freeze–thaw stability of emulsions, *Food Hydrocolloids* 22 (2008) 105–111.
- [25] Standard test method for determination of additive elements, wear metals, and contaminants in used lubricating oils and determination of selected elements in base oils by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), ASTM D5185, 2009.
- [26] Standard test method for determination of water in liquid petroleum products by Karl Fischer reagent, ASTM D1744, 1992.
- [27] Canadian Council of Ministers of the Environment (CCME), Reference method for the Canada wide standard for petroleum hydrocarbons in soil – tier 1 method, 2001.
- [28] SW-846: test methods for evaluating solid wastes: physical/chemical methods, Publication 955-001-00000-1, United States Environmental Protection Agency (EPA), Office of Solid Waste (OSW), U.S. Government Printing Office, Washington, DC.
- [29] Canadian Council of Ministers of the Environment (CCME), Canada-wide standards for petroleum hydrocarbons (PHC) in soil: scientific rationale, 2000.
- [30] D. Feng, C. Aldrich, Sonochemical treatment of simulated soil contaminated with diesel, *Adv. Environ. Res.* 4 (2000) 103–112.
- [31] M. Breitbach, D. BATHEN, H. Schmidt-Traub, Effect of ultrasound on adsorption and desorption process, *Ind. Eng. Chem. Res.* 42 (2003) 5635–5646.
- [32] O. Hamdaoui, E. Naffrechoux, J. Sptil, C. Fachinger, Ultrasonic desorption of *p*-chlorophenol from granular activated carbon, *Chem. Eng. J.* 106 (2005) 153–161.
- [33] O. Hamdaoui, E. Naffrechoux, An investigation of the mechanisms of ultrasonically enhanced desorption, *AIChE J.* 53 (2007) 363–373.
- [34] T.J. Mason, Developments in ultrasound – non-medical, *Prog. Biophys. Mol. Biol.* 93 (2007) 166–175.
- [35] T.J. Mason, J.P. Lorimer, *Applied Sonochemistry: The Uses of Power Ultrasound in Chemistry and Processing*, Wiley-VCH, Weinheim, 2002.
- [36] B.S. Schueller, R.T. Yang, Ultrasound enhanced adsorption and desorption of phenol on activated carbon and polymeric resin, *Ind. Eng. Chem. Res.* 40 (2001) 4912–4941.
- [37] N.C. Mulligan, Environmental applications for biosurfactants, *Environ. Pollut.* 133 (2005) 183–198.

- [38] M. Nitschke, S.G.V.A.O. Costa, J. Contiero, Rhamnolipid surfactants: an update on the general aspects of these remarkable biomolecules, *Biotechnol. Prog.* 21 (2005) 1593–1600.
- [39] A. Lager, K.J. Webb, C.J. Black, Low salinity oil recovery – an experimental investigation, in: SCA 2006-36, International Symposium of the Society of Core Analysts, Trondheim, Norway, 2006.
- [40] M. Cissokho, S. Boussour, Ph. Cordier, H. Bertin, G. Hamon, Low salinity oil recovery on clayey sandstones: experimental study, in: SCA 2009-05, International Symposium of the Society of Core Analysts, Noordwijk, Norway, 2009.
- [41] R.P.S. Suri, T.S. Singh, S. Aburi, Influence of alkalinity and salinity on the sonochemical degradation of estrogen hormones in aqueous solution, *Environ. Sci. Technol.* 44 (2010) 1373–1379.
- [42] M. Dukkanci, G. Gunduz, Ultrasonic degradation of oxalic acid in aqueous solutions, *Ultrason. Sonochem.* 13 (2006) 517–522.
- [43] C. Petrier, A. Francony, Ultrasonic waste-water treatment: incidence of ultrasonic frequency on the rate of phenol and carbon tetrachloride degradation, *Ultrason. Sonochem.* 4 (1997) 295–300.